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Pore Structure Model of Hydrates Comprising Various Cements and SCMs Based on Changes in Particle Size of Constituent Phases

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Abstract

A simulation model to estimate the pore structure of cement hydrates is presented. This paper describes procedures for predicting phase compositions based on the classical hydration model of portland cement, calculating the particle size distribution of constituent phases and evaluating the pore size distribution by stereological and statistical considerations. To evaluate the effectiveness of this model, simulation results were compared with experimental results of the pore size distribution measured by mercury porosimetry. As a result, it was found that the experimental and simulated results were in close agreement, and the simulated results indicated characterization of the pore structure of cement hydrates.

1. Introduction

The ongoing progress of the shift to performance-oriented design has allowed more freedom of material selection and proportioning according to the performance requirements for structures. Also, the use of industrial byproducts as supplementary cementing materials (SCMs) has been increasing for the purpose of reducing CO₂ emissions and waste disposal. Amid such changes in the environment for cementitious materials, contractors are required to select appropriate materials, as well as to grasp the performances of concrete along the time axis, including placeability, strength development, and long-term durability.

Performance requirements for hardened concrete are macroscopic properties, such as structural and durability performances. However, hardened concrete being a porous material, these properties are generally explained with a focus on its microstructures, particularly capillary pores ranging in size from the nm level to 10 μ m. For this reason, the characteristics of pore structures in concrete are evaluated by mercury intrusion porosimetry (MIP), which covers the range of capillary pores.

Various prediction tools for the long-term behavior of concrete have been developed in recent years, including temperature distribution within concrete due to hydration heat, volume change, and durability, with pore structure models being proposed as bases for the evaluation of these physical properties. Various aspects of the microstructure of concrete were considered and illustrated from coherent pictures of mature concrete (Scrivener 1989). Breugel (1991) proposed a hydration model in consideration of the mineral composition of cement, its

particle size distribution (PSD), and the spatial configuration of hydrates. This model expresses changes in the pore structure with the progress of hydration using approximate equations with which the cumulative pore volume exponentially increases with increases in the pore diameter. Bentz and Garboczi (1993) proposed a hydration model (CEMHYD3D). This model uses the cell automaton method and gives the 3-dimensional cement paste structure. Ishida *et al.* (1998) defined three types of pores, calculated the pore volume percentage of each type using the hydration heat model proposed by Kishi and Maekawa (1996), and modeled the pore structure as their sum. These existing pore structure models have been improved for predicting the macroscopic properties of concrete, with good agreement with test results being reported. However, it is necessary to review the parameters of approximate equations to adapt to a wider variety of proportioning conditions. While some of the existing pore structure models do not necessarily emphasize agreement with test results obtained by MIP, this technique has been adopted in many studies to experimentally determine pore structures. Since no other reliable technique has so far been developed for evaluating pore structures, comparison with the results of MIP is also important for pore structure models used for simulating physical properties.

Furthermore, the grading characteristics of cement is a key factor for considering the progress of hydration, because hydration is explained by existing hydration models (Breugel 1991; Kondo and Ueda 1968) as a reaction that progresses from the surfaces of cement particles inward. Nevertheless, existing pore structure models do not explain the pore structure from the aspect of the component substances of hardened cement, and give no consideration to changes in the PSD of unhydrated cement, which contributes to the formation of large voids.

Against this background, this paper attempts to formulate a model that explains the formation process of pore structures in neat cement pastes comprising various cements and SCMs based on hydration and phase com-

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position. It aims to formulate a technique to estimate the pore structure of hardened cement at the proportioning stage from the aspect of its component substances based on the composition of arbitrary materials and their processes of reaction. Evaluation of the macroscopic properties of such cement on a practical level is also aimed for.

To formulate this model, the authors began by taking into account the PSD and chemical composition of the materials to be used as their basic information, calculated their phase compositions based on reaction models and stoichiometric formulas, and calculated the PSD of all constituent phases. Formulation of a model for simulating the pore structure was then attempted from geometrical and stochastic aspects by regarding the component phases as clusters of spherical substances. Furthermore, the pore size distribution was measured by MIP and compared with the pore structure calculated by the proposed model to investigate its applicability.

2. Model for calculating pore structure

2.1 Method of calculating hydration and phase composition

This model considers the PSD of cement expressed by the Rosin-Rammler equation as initial information of materials before mixing. It then estimates the pore structure by focusing on changes in the phase composition and PSD in the constituent phases determined from a hydration model, particularly changes in the particle size of unhydrated cement. For cement hydration, an existing hydration model (Breugel 1991; Kondo and Ueda 1968) was simplified, assuming hydration to proceed in a spherical particle from the periphery inward. The phase composition is determined from the volume change of each mineral, which is calculated from its degree of hydration and the chemical hydration formula. **Figure 1**

Fig. 1 Concept of reaction of mineral *i* in a cement particle.

shows the concept of the geometric model expressing the reaction of mineral *i* in a cement particle. A cement particle is assumed to be spherical. This study deals with mixture proportions for normal concrete with a water-cement ratio of 40% to 60%. It is also assumed that there is a sufficient space for cement particles to disperse at the beginning of mixing. Within a cement particle with a radius of *r* (μm), its four mineral components are assumed to be uniformly present depending on their contents independently of the particle size. Hydrates are assumed to be formed inward as water seeps in and reacts with these components, as well as outward as the deposit expands. Assuming that, at an age of *t* (h), the degree of hydration, $\alpha_i(r,t)$, of mineral *i* in a cement particle with a radius of *r* (μm) is the ratio of the volume of the hydrated layer having a hydration thickness of $x_{i,t}$ (μm) to the original volume of the cement particle, this is expressed as follows:

$$\alpha_i(r,t) = 1 - (1 - x_{i,t}/r)^3 \quad (1)$$

Also, the hydration thickness, $x_{i,t}$ (μm), at an age of *t* is expressed as the sum of the products of the reaction rate, k_i (μm/h), of mineral *i* and the time interval between calculation steps, Δt (h), as follows:

$$x_i(t) = \sum_0^t k_i(r,t) \cdot \Delta t \quad (2)$$

In this study, temperature dependence and reductions in the reaction rate due to increases in the degree of hydration are incorporated based on past studies. The reaction rate of mineral *i*, k_i (μm/h), is assumed to change from the initial value, k_{i0} (μm/h), depending on the degree of hydration, $\alpha_i(r,t)$, which varies depending on the size of cement particles as follows:

$$k_i(r,t) = \beta_i(t) \cdot k_{i0} \cdot \log(1/\alpha_i(r,t)) \quad (3)$$

$\beta_i(t)$ was determined as a factor expressing the temperature dependence of the reaction rate of mineral *i*. In this study, this temperature dependence is assumed to follow the Arrhenius equation as given in Eq. (4) at 20 (°C).

$$\beta_i(t) = \exp\left(-\frac{AE_i(t)}{R} \left(\frac{1}{273+T} - \frac{1}{293}\right)\right) \quad (4)$$

where *T*, $AE_i(t)$, and *R* refer to temperature (°C), activation energy of mineral *i*, (J/g), and gas constant (J/gK), respectively.

The method of calculating the phase composition is summarized as follows: Assuming that the rate of volume change, Ex_i , of completely hydrated mineral *i* with respect to the volume before hydration is proportional to the degree of hydration, $\alpha_i(r,t)$, it can be determined from the hydration equation of each clinker mineral. The volume of a hydrate with a radius of *r* formed from mineral *i* at an age of *t*, $v_{Hyd,i}(r,t)$, is defined as the sum of the volume of the internal hydrate formed in the reaction

layer of cement, $v_{in,i}(r,t)$ and the volume of the external hydrate formed out of cement, $v_{out,i}(r,t)$. If the content of mineral i is γ_i , then the volume of its hydrate, $v_{Hyd,i}(r,t)$ is given by Eq. (5). When multiple hydrates are formed, the volume is assumed to be prorated according to their formation ratios.

$$v_{Hyd,i}(r,t) = \gamma_i \cdot \frac{4\pi r^3}{3} (\alpha_i(r,t) \cdot Ex_i + \alpha_i(r,t) - 1) \quad (5)$$

The phase composition was calculated by assuming hydration equations as stated above, while determining the PSD and mineral composition of cement and the initial reaction rate of each clinker mineral.

2.2 Method of calculating a pore structure based on changes in the PSDs of constituent phases

Figure 2 shows changes in phase composition due to hydration and the concept of the PSDs of constituent phases. A PSD is assumed for each of the formed hydrates as shown in Fig. 2 to consider the changes in the PSD of cement with the progress of hydration. Note that unhydrated cement may not retain a spherical shape as hydration proceeds, because the reaction rates vary from one mineral to another. However, the radius of unhydrated cement is calculated by determining an average depth of reaction so that it retains its spherical shape on average depending on the mineral contents.

Hydrates formed from cement minerals include $\text{Ca}(\text{OH})_2$, C-S-H, AFt, and AFm, which are known to have characteristic shapes and size. For this reason, a PSD is assumed for each hydrate similarly to cement and expressed as $G_j(r)$, where r denotes the radius of hydrate j

similarly to cement. The PSD of total hardened cement is expressed as Eq. (6) by expressing the volume ratio of hydrate j at an age of t determined from the calculated phase composition as $\gamma_j(t)$ and assuming that the solid phase of hardened cement consists of hydrates and unhydrated cement.

$$G(r,t) = \sum \gamma_j(t) \cdot G_j(r) + \gamma_c(t) \cdot G(r_c - x_c(t)) + \gamma_{add}(t) \cdot G(r_{add} - x_{add}(t)) \quad (6)$$

where $\gamma_c(t)$ and $\gamma_{add}(t)$ denote the volume ratios of unhydrated cement and unreacted supplementary cementing material, respectively. $G(r_c - x(t))$ and $G(r_{add} - x(t))$ denote the particle size PSDs of unhydrated cement and unreacted supplementary cementing material, respectively. The unhydrated radius of the supplementary cementing material was calculated assuming that its reaction proceeds by a mechanism similar to that of cement. Cement particles are suspended in water immediately after coming into contact with water, but hydrates are formed by the progress of hydration, during which changes in the PSD of the solid phase can be expressed by Eq. (6).

The pore size distribution of agglomerated particles having a PSD expressed by Eq. (6) is calculated as follows: In this study, packing with particles of constituent phases is assumed to result in a structure composed of four spheres having arbitrary radii as shown in Fig. 3. Two types of pores are conceivable in such a structure: a sphere inscribed in four spheres at their center and a sphere inscribed in three spheres forming one of the four triangles of the tetrahedron ((1) and (2) in Fig. 3, respectively). In regard to the radius of a sphere inscribed in four spheres having arbitrary radii of a , b , c , and d , the radius of a pore, ϕ_r , surrounded by spheres having arbitrary radii

Fig. 2 Change in phase composition due to hydration and particle size distribution (PSD) of constituent phases.

Fig. 3 Packed configurations of spherical particles and concept of pores.

rary radii of a , b , and c (radius of pore (1) in **Fig. 3**), is expressed by Eq. (7). Its relationship with the radius of a pore sphere inscribed in four spheres with radii of a , b , c , and d is approximated by Eq. (8).

$$\phi_r(a,b,c) = \frac{abc}{ab+bc+ca+2\sqrt{abc(a+b+c)}} \quad (7)$$

$$3 \left\{ \sum_{i=a,b,c,d} \left(\frac{1}{r_i^2} \right) + \left(\frac{1}{\phi_r(a,b,c,d)^2} \right) \right\} = \left\{ \sum_{i=a,b,c,d} \left(\frac{1}{r_i} \right) + \left(\frac{1}{\phi_r(a,b,c,d)} \right) \right\}^2 \quad (8)$$

If the volume of spheres with a radius of ϕ_r present in hardened cement is known, then the pore size distribution can be expressed as follows: Determine the number of all particles from the PSD of each constituent phase; arbitrarily select four particles; calculate the pore size in all combinations of the particles to determine the relationship between the pore size and its volume distribution. Putting the total volume of particles with a radius of r and the volume of one particle with a radius of r as $V(r)$ and $v(r)$, respectively, the number of particles, $n(r)$, is expressed by Eq. (9).

$$n(r) = \frac{V(r)}{v(r)} = \left(\frac{dG(r,t)}{dr} \right) / \left(\frac{4\pi r^3}{3} \right) \quad (9)$$

The number of particles of all constituent phases, N , is calculated by Eq. (10).

$$N = N_{total}(r) = \sum n(r) \quad (10)$$

The combination of four particles arbitrarily selected from all of N particles is expressed by Eq. (11).

$$N C_4 = \frac{N P_4}{4!} = \frac{N(N-1)(N-2)(N-3)}{4 \times 3 \times 2 \times 1} \quad (11)$$

The probability, P_{ϕ_r} , of generating pores with a radius

of ϕ_r ($\phi_r(a,b,c,d)$, $\phi_r(a,b,c)$, $\phi_r(b,c,d)$, $\phi_r(c,d,a)$, and $\phi_r(d,a,b)$) surrounded by four spheres with radii of a , b , c , and d is expressed by Eq. (12).

$$P_{\phi_r} = \frac{n(a) C_1 \times n(b) C_1 \times n(c) C_1 \times n(d) C_1}{N C_4} = \frac{n(a) \times n(b) \times n(c) \times n(d)}{N C_4} \quad (12)$$

The volume fraction of pore size ϕ_r in the total constituent phases is expressed by Eq. (13), as pores are treated as spheres.

$$V_{\phi_r} = P_{\phi_r} \times \frac{4\pi \cdot \phi_r^3}{3} \quad (13)$$

As Sakai *et al.* (1998) have presented, the pore amount is regarded as the sum of hydration shrinkage and the volume of unreacted water, and the value obtained by dividing this by the as-mixed volume of water and cement is defined as the pore content (ml/ml). **Figure 4** shows the concept of pore content. The as-mixed volume per unit mass, V_0 (ml/g) is therefore expressed as Eq. (14) by putting the water-cement ratio (W/C) and cement density as w_0 and ρ_c (ml/g). The pore size distribution is expressed as Eq. (15) by putting the pore content at an age of t calculated according to **Fig. 4** as $V_p(t)$ (ml/g). In this equation, $V_{\leq \phi_r}$ denotes the volume fraction of pores with a radius of ϕ_r or less, which is determined from the volume fraction, V_{ϕ_r} , of pore size ϕ_r determined by Eq. (13).

Fig. 4 Concept of pore content at age t .

$$V_0 = \frac{1 + \rho_c \cdot w_0}{\rho_c(1 + w_0)} \quad (14)$$

$$V(\phi_r) = \frac{V_p(t)}{V_0} \cdot V_{\leq \phi_r} \quad (15)$$

3. Conditions for pore structure calculation in this study

3.1 Physical properties of cement

In this study, high-early-strength ortland cement (H), normal ortland cement (N), and low-heat ortland cement (L) available on the market, as well as supplementary cementing materials were used for investigation. **Table 1** gives the mineral compositions of cements under study calculated based on the results of chemical analysis in accordance with JIS R 5202 (Methods for chemical analysis of cements).

Figures 5 and 6 show the PSDs of cements and supplementary cementing materials measured using a laser diffraction particle size analyzer. Prior to measurement, samples are sufficiently dispersed using the built-in ultrasonic vibrator until the PSD is stabilized. The coefficients of each curve approximated by the Rosin-Rammler equation are given in these figures. As given in **Fig. 6**, the supplementary cementing materials include fly ash (FA) and silica fume (SF) with respective density and SiO₂ content of 2.35 g/cm³ and 55%, and 2.20 g/cm³ and 96%.

3.2 Chemical equations

While different chemical equations are adopted by different researchers, the authors adopted Eqs. (16) and (17), which are generally adopted as hydration equations for C₃S and C₂S. In these equations, C₃S, C₂S, H, CSH, and CH denote 3CaO·SiO₂, 2CaO·SiO₂, H₂O, CaO·SiO₂·H₂O, and Ca(OH)₂, respectively. The authors also adopted $m = 1.75$ and $n = 4.0$ as described in a JCI Committee Report (1995).

For C₃A and C₄AF, the authors assumed the following: These form AFt (ettringite) in the presence of gypsum and are then converted to AFm (monosulfate hydrates).

Table 1 Mineral composition of cement (in %).

	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaSO ₄
H	65.6	9.2	8.3	8.1	5.0
N	58.5	16.4	8.9	8.5	5.0
L	30.7	52.3	2.7	7.8	3.9

Fig. 5 Particle size distribution of cement.

Fig. 6 Particle size distribution of cement and supplementary cementing materials.

After the conversion of AFt, residual C₃A and C₄AF are assumed to form C₄AH₁₃ (calcium aluminate hydrates). In regard to the ferrite phase, it forms hydrates having a partial solid solution with Fe₂O₃. Within the range of this study, however, it is assumed to react similarly to the aluminate phase, forming similar hydrates. In the equations below, C₃A and C₄AF denote 3CaO·Al₂O₃ and 4CaO·Al₂O₃·Fe₂O₃, respectively. For each hydrate, AFt represents 3CaO·[xAl₂O₃·(1-x)Fe₂O₃]·3CaSO₄·32H₂O; AFm represents 3CaO·[xAl₂O₃·(1-x)Fe₂O₃]·CaSO₄·12H₂O; and C₄AH₁₃ represents 3CaO·[xAl₂O₃·(1-x)Fe₂O₃]·Ca(OH)₂·12H₂O, in which x denotes 1 and 0.5 in the reaction of C₃A and C₄AF, respectively. Also, CH denotes Ca(OH)₂. The reaction of C₃A and C₄AF are thus written as Eqs. (18) to (23).

For pozzolanic reaction of a mixture containing FA and SF, a reaction equation in which $\text{Ca}(\text{OH})_2$ is consumed to form C-S-H with a Ca/Si molar ratio of 1.0 is assumed as given in Eq. (24) by referring to the known reaction ratio of each component at the age of 28 days. The results are added to the phase composition of cement.

In regard to the density data of clinker minerals and hydrates, the values written in the JCI Committee Report (1995) were referred to. The values used for the calculation of phase composition are given in **Table 2**.

3.3 Rate of hydration

The activation energy in coefficient β_i for the temperature dependence of hydration rate given in Eq. (4) was determined for each clinker mineral by referring to the relationship between the hydration rate and temperature activity proposed by Kishi and Maekawa (1996).

The initial value, k_{i0} ($\mu\text{m}/\text{h}$), of the hydration rate of each clinker mineral at 20°C was calculated by applying the PSD of normal portland cement (N) shown in **Fig. 5** to this model, so that the value would be the average of the results of past studies on the hydration ratio of each clinker mineral in normal portland cement at specified ages presented in a report by the Japan Cement Association (2001).

The reaction ratios of FA and SF were assumed to be 15% and 50%, respectively, at 28 days (Japan Cement Association, 2001), and the initial value, k_{i0} ($\mu\text{m}/\text{h}$), at 20°C was determined by applying the PSD of each supplementary cementing material shown in **Fig. 6** similarly to cement.

Table 3 gives the calculated hydration ratio at different ages and the initial value of hydration rate, k_{i0} ($\mu\text{m}/\text{h}$), of clinker minerals adopted in this study. Note that the initial hydration rate of each clinker mineral was assumed to be constant up to the age of 1 day, and 6 (h) was adopted as the subsequent calculation step, Δt (h).

3.4 Hydration products

For expressing the PSD that changes as hydration proceeds, it is necessary to define the size of hydration products, but direct measurement of their PSD is difficult. For this reason, the PSD of each hydrate was assumed in this study, using lognormal distribution function formulas based on the existing observation results regarding hydrates. These are expressed as Eqs. (25) and (26) by putting the cumulative PSD function and density distribution function as $G_j(r)$ and $g_j(r)$, respectively.

$$g_j(r) = \frac{1}{\ln \sigma \sqrt{2\pi}} \exp \left\{ -\frac{(\ln r - \ln r_{50})^2}{2 \ln \sigma^2} \right\} \quad (25)$$

$$G_j(r) = \int_0^r \frac{1}{\ln \sigma \sqrt{2\pi}} \exp \left\{ -\frac{(\ln r - \ln r_{50})^2}{2 \ln \sigma^2} \right\} d \quad (26)$$

where σ denotes the standard deviation, which is expressed as Eq. (27), with r_i denoting $i\%$ radius.

$$\begin{aligned} \sigma &= r_{84.13} - r_{50} = r_{50} - r_{15.87} \\ \ln \sigma &= \ln r_{84.13} - \ln r_{50} = \ln r_{50} - \ln r_{15.87} \\ &= \ln \frac{r_{84.13}}{r_{50}} = \ln \frac{r_{50}}{r_{15.87}} \end{aligned} \quad (27)$$

$\sigma_g = r_{84.13}/r_{50} = r_{50}/r_{15.87}$, which is referred to as geometric standard deviation, is a value representing the range of a lognormal distribution.

Table 2 Physical quantities of substances used for calculation (JCI, 1996).

	Moll volume (cm^3/mol)	Molecular weight (g/mol)	Density (g/cm^3)
C_3S	72.0284	228.33	3.17
C_2S	52.5152	172.25	3.28
C_3A	89.1749	270.2	3.03
C_4AF	130.29	485.98	3.73
Gypsum dihydrate	74.2155	172.18	2.32
Water	18.02	18.02	1.00
C-S-H	121.216	230.31	1.90
CH	33.08	74.1	2.24
AFt	713.2159	1255.26	1.76
AFm	319.272	622.58	1.95
C_4AH_{13}	277.495	560.54	2.02

Table 3 Initial values of hydration ratio and hydration rate of clinker minerals.

	Hydration ratio (%)					k_{i0} ($\mu\text{m}/\text{h}$)
	1 day	3 days	7 days	28 days	91 days	
C_3S	49	63	74	83	89	0.0104
C_2S	10	18	27	45	72	0.00042
C_3A	56	75	80	87	92	0.01462
C_4AF	25	39	47	56	69	0.00208
FA	2	-	-	15	18	0.0002
SF	30	40	45	50	-	0.0004

Calcium hydroxide (CH) is found to be agglomerates of hexagonal plate crystals with equal crystal orientations by electron microscopy observation and known to be a large hydrate measuring several μm to over $10\ \mu\text{m}$ (JCI Committee Report, 2005).

Specific surface values measured by nitrogen adsorption of 3 to 4 (m^2/g) have been presented for CH (Kim, 1995), which can be converted to radii of 0.5 to 1 μm . Its PSD is therefore assumed to range from 0.5 to 5 μm , with the peak at 2 μm .

C-S-H is known to be 10 to 100 nm in size, though with different types depending on the conditions of formation, while electron microscopy observation has given a size range of 20 to 30 nm. A radius of 5 nm is calculated from the specific surface measured by nitrogen adsorption (JCI Committee Report, 2005). A mean of 20 nm was therefore adopted for C-S-H, while setting coefficients to make the range between several nm to 50 nm. The sizes of ettringite, monosulfates, and calcium aluminate hydrates are known to be several μm or less by observation, though their shapes differ from one another. These hydrates are therefore assumed to have a size of several μm or less, with the mean being 0.5 μm , and coefficients were selected for a maximum radius of around 1 μm (JCI Committee Report, 2005). Thus the PSD of each hydrate was assumed by values given in Table 4. Figure 7 shows the PSD of each hydrate.

4. Verification of the proposed model by comparison with test results

4.1 Experiment overview

An experiment was conducted to confirm the applicability of the phase composition and pore size distribution calculated based on the proposed model. The mineral compositions (calculated by JIS R 5210) of three cements (H, N, and L) given in Table 1 are proportioned with a W/C of 50%. When using a supplementary cementing material, they are used in place of 20% of normal portland cement to obtain a water-binder ratio of 50%. These are mixed using a mortar mixer and fabricated into cylindrical cement paste specimens 50 mm in diameter and 100 mm in height. Mixtures made using N are also prepared with W/Cs of 40% and 60%. After being demolded at the age of 1 day, specimens are wrapped with plastic films, placed in plastic bags, and sealed for seal curing in a thermostatic chamber at 20°C until test ages. There are other N specimens similarly seal-cured in thermostatic chambers at 10°C and 30°C to examine the effect of curing temperatures. At the test ages, specimens are crushed to take samples from near the centers. These samples are immersed in acetone to terminate hydration, dried to the specified degree of vacuum in vacuum freeze-dry equipment, and pulverized further in a mortar for the experiment.

In the experiment, calcium hydroxide (CH) in each specimen is quantified using a differential thermogravimetric analyzer. Measurement is carried out in a ni-

Table 4 Coefficients for hydrates assumed in this study.

Hydrate	r_{50} (μm)	$r_{84.13}$ (μm)
C-S-H	0.02	0.05
CH	2	5
AFm, CAH	0.5	1

Fig. 7 Particle size distribution characteristics of hydrates.

trogen flow environment at a temperature rise rate of 10°C/min. The amount of CH formation is determined by assuming that the reduction in the range of 515°C is due to the dehydration of CH (Sakai *et al.* 1998).

For the determination of pore size distribution, samples are crushed to a size of 5 mm cubes immediately after drying, and several lumps are used for measurement. Calculation is carried out by assuming a cylindrical model with a surface tension and contact angle of mercury of 485×10^{-3} N/m and 130°, respectively. The measurement range is approximately 3 nm to 327 μm (413 MPa to 0.038 MPa by intrusion pressure).

4.2 Calculation of phase composition and comparison with test results

Figure 8 shows the CH content and pore volume in cement mixtures in percentages of the total volume calculated by the model in comparison with those determined by testing. Figure 9 shows the results of mixtures containing supplementary cementing materials. The test results shown in the figure are the volume fractions of hydrates converted from densities with respect to the density of as-mixed cement paste by referring to their density data (JCI Committee Report 1996). The tested pore volumes are the test results obtained from MIP. Figure 8 reveals that calculated and measured changes in the CH content and pore percentage show similar tendencies over time for different cement types. The calculations and porosimetry measurements of pore percentages are particularly close, proving the applicability of the proposed model.

Fig. 8 Content of a constituent phase in different cements by experiment and calculation.

Fig. 9 Content of a constituent phase in different cements with supplementary cementing materials by experiment and calculation.

4.3 Calculation of pore size distribution and test results

Figure 10 shows the results of calculation by the proposed model and the measurements by MIP by cement type. The test results are those of specimens fabricated with a W/C of 50% and seal-cured at 20°C, while the calculations cover pores not smaller than 3 nm, which are measurable with a mercury intrusion porosimeter. The test results show a tendency in which pores become smaller over time, with the cumulative pore volume also decreasing. The pore size distribution varies depending on the cement type and age similarly to test results, but the measured and calculated results significantly differ from each other at 3 days, particularly for low-heat portland cement. This should be investigated further in the future.

Figure 11 compares the calculated and measured pore size distribution at 3, 7, and 28 days in the form of logarithmically differentiated pore volumes related to pore size. This figure reveals that the pore sizes indicating the

peaks (around 0.1 μm and 0.007 μm) and the log differential volumes at peaks by calculation and experiment relatively agree well with each other. The measurements and calculations also agree in that the log differential volume of over 0.1 μm tends to decrease with age, whereas that around 0.007 μm tends to increase with age. Such changes in the tendencies of distribution over time depend on the increases in the amounts of hydrates and reductions in the amount of unhydrated cement, suggesting that pore structures are practically estimable from the aspects of hydration and phase composition.

Figure 12 compares the calculated and measured pore structures of normal portland cement specimens cured at different temperatures. Figure 13 compares the results at 28 days of normal portland cements proportioned with W/Cs of 40%, 50%, and 60%. These figures reveal similar distribution tendencies and cumulative pore volumes by experiment and calculation. The effects of temperature and proportioning conditions on the pore structure formation are thus found evaluable by the

Fig. 10 Calculated and measured pore size distribution in different cements.

proposed model within the range of this study.

Figures 14 and 15 show comparisons between the calculated and measured pore size distributions of specimens containing supplementary cementing materials. **Figure 14** reveals that N+SF leads to the finest pore distribution, followed by N, and N+SF in this order. In

Fig. 15, peaks are found at around $0.1 \mu\text{m}$ and $0.01 \mu\text{m}$, with similar differences among the materials being shown by calculation and test results.

Accordingly, the results obtained from the proposed model agree with the test results, though not strictly coincident, reproducing the differences in pore size dis-

Fig. 11 Relationship between pore size and log differential intrusion in different cements.

tributions due to differences of age and cement type, as well as the pore sizes and volumes at peaks. This model is therefore applicable to the evaluation of physical properties that highly correlate with the characteristics of

pore structures obtained from MIP.

4.4 Discussion of ink bottle-shaped pores

As a problem related to MIP, there have been discussions

Fig. 12 Calculated and measured pore size distribution with different curing temperatures.

Fig. 13 Comparison among pore size distributions by different proportioning conditions (28 days).

regarding the difference between the measurement results by assuming cylindrical pores and the actual pore structure (Diamond 2000). In a cylindrical pore model, mercury is assumed to intrude into larger pores first and

then progressively into smaller pores. For this reason, when a large pore exists ahead of a small pore, only the small pore size is counted, while the large pore is left uncounted. This has been pointed out for some time as a

Fig. 14 Calculated and measured pore size distributions in N, N+SF, N+FA (28 days).

Fig. 15 Calculated and measured pore size distributions in N, N+SF, N+FA (28 days).

problem of ink bottle-shaped pores. It has also been known that the curve measured during an extrusion phase does not coincide with the intrusion curve (Lowell 1980). The hysteresis loop, which is open, suggests that a certain amount of mercury is left trapped in pores after extrusion. This hysteretic behavior can be attributed not only to the difference between the advancing and receding angles of wetting during intrusion and extrusion, but also to the characteristics of ink bottle-shaped pores.

Figure 16 shows two cycles of intrusion-extrusion hysteresis loops together with the concept of ink bottle-shaped pores. Note that the same wetting angle is adopted for both intrusion and extrusion phases in the calculation of pore volume. In the literature, the intrusion-extrusion hysteresis in MIP is attributed to ink bottle-shaped pores, and the difference between the first and second intrusions is regarded as the volume of ink bottle pores to discuss the pore structure (Lowell and Shields

1981). These characteristics of intrusion-extrusion hysteresis loops provide an important clue to the understanding of the characteristics of the ink bottle pore structure of hardened cement. This section discusses the reproducibility of the intrusion-extrusion hysteresis of mercury by introducing the theoretical assumptions of ink bottle pores and the different wetting angles during intrusion and extrusion to the presently proposed model.

The cumulative pore volume curve during extrusion and the ink bottle pore volume are calculated using the concept shown in **Fig. 17**, as follows: Determine the cumulative pore volume curve by the present model ((a) in the legend); Assuming that the determined curve is equal to the cumulative pore volume curve by MIP during intrusion, determine the intrusion pressure with a wetting angle of 130°C using Washburn's equation; Re-calculate the cumulative pore volume curve with a wetting angle of 103° by Washburn's equation ((b) in the

Fig. 16 Hysteresis behavior during mercury intrusion.

Fig. 17 Concept of calculation for extrusion.

legend); Translate this calculation result (b) so that it begins from the end point (the maximum cumulative pore volume) of calculation by the present model (a). The curve after translation is (c) in the legend. Note that this concept corresponds to the case where the intrusion-extrusion hysteresis is affected only by the difference between the wetting angles.

In the present model, the pore configurations are assumed to consist of small pores inscribed by four particles and large pores as shown in Fig. 3. If the pores shown in Fig. 3 (1) are assumed to be small pores, then the pores shown in Fig. 3 (2) can be regarded as corresponding to ink bottle pores. Pores in a configuration shown in Fig. 3 (2) extracted from the calculation results

are shown in Fig. 17 ((d) in the legend). The extrusion curve was calculated in this manner by considering the hysteresis due to the difference between the wetting angles (c) and ink bottle pores (d).

Figure 18 shows measured and calculated hysteresis curves of pores in normal Portland cement at the age of 28 days as an example of the calculation of an extrusion curve. The results of MIP include two intrusion-extrusion cycles, in which a wetting angle of 103° is adopted during extrusion as reported by Lowell (1980). Whereas the intrusion and extrusion curves in the second cycle do not coincide in Fig. 16, the curves are found to agree in Fig. 18 by setting the wetting angle during extrusion at 103° . This demonstrates that the hysteretic MIP results can be

Fig. 18 Comparison between measured and calculated hysteresis behavior.

explained by assuming an ink bottle-shaped pore structure and the difference between the wetting angles of mercury during intrusion and extrusion. Also, calculation by the proposed model reproduces tendencies similar to the MIP results both during extrusion and intrusion. The pore volume corresponding to ink bottle pores agrees particularly well with MIP.

Pore structures in actual hardened cement are more complicated than the proposed model, and much room is left for examination regarding the problem of ink bottle-shaped pores. However, the intrusion-extrusion hysteresis in MIP can be reproduced by the proposed model by incorporating the assumption of an ink bottle pore structure and the difference between the mercury wetting angles during intrusion and extrusion.

5. Conclusions

Using phase compositions of cements determined from a hydration model for cement particles, the authors formulated a model for estimating pore structures of hardened cement based on changes in the pore size distribution of constituent phases. The results are summarized as follows:

- (1) A hydration model was defined for an age of 1 day and later in consideration of the particle size distribution and four clinker minerals of cement. The phase composition of cement was calculated on this basis and compared with the contents of hydrates quantified using differential thermogravimetric equipment. The results determined by the model agreed with the tendencies of the measurements.
- (2) The particle size distributions of unhydrated cement and unreacted supplementary cementing materials (SCMs) were determined using the hydration model to define the particle size distribution of each hy-

drate, thereby determining the particle size distribution of the whole component phases. Also, a model was proposed assuming that each component particle is spherical. By this model, the pore size distribution is calculated based on the concept of the probability of particles coming into contact with one another in consideration of the number of particles for different particle sizes. The calculations by the model were then compared with the pore size distributions obtained from mercury intrusion porosimetry (MIP). As a result, this model was found to express the differences in pore size distribution due to age and cement type in agreement with the test results. Agreement was also found in the pore size and volume at peaks.

- (3) This model simulates the characteristics of the pore structures of hardened cement from the aspects of hydration processes and component substances. For this reason, it can be developed into universal models applicable to arbitrary combinations of materials without limitations in proportioning conditions, while being capable of estimating changes in pore structures related to durability including changes in component substances due to external factors. Also, pore structures calculated by this model show tendencies very similar to results obtained from MIP. Therefore, this model has the potential to evaluate other performances such as mass transfer, which are closely related to pore structures expressed by MIP.
- (4) Calculation of the cumulative pore volume curve of ink bottle-shaped pores by the proposed model agreed well with the measurements by mercury porosimetry. The intrusion-extrusion hysteresis in mercury porosimetry was found reproducible by incorporating the assumption of an ink bottle-shaped pore structure and different mercury wetting angles during intrusion and extrusion.

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