

Predicting Model for Pore Structure of Concrete Including Interface Transition Zone between Aggregate and Cement Paste

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Abstract: This paper proposes a semi analytical model to describe the pore structure of concrete by a set of simple equations. The relationship between the porosity and the microstructure of concrete has been considered when constructing the analytical model. The microstructure includes the interface transition zone (ITZ) between aggregates and cement paste. The predicting model of porosity was developed with considering the ITZ for various mixing of mortar and concrete. The proposed model is validated by the rapid experimental programs. Although the proposed model is semi-analytical and relatively simple, this model could be reasonably utilized for the durability design and adapted for predicting the service life of concrete structures.

Keywords : porosity, microstructure, interface transition zone, durability, service life.

1. Introduction

It has been established for many years in the research community that the presence of chloride ions is the most significant cause for the corrosion of reinforcing bars in concrete structures. A great deal of work has been done to characterize and prevent the ingress of these chlorides into concrete. It is known from research works that the microstructure of concrete is the key to understand chloride diffusivity of concrete. The modeling of concrete material should be conducted considering the microstructure in order to predict the realistic deterioration of structures.

Chloride diffusivity is strongly affected by the pore size distribution and connectivity. There are different types of pores in concrete: the gel pores in the cement gel, the capillary pores between the solids in the cement gel and finally, the pores in the interface between the cement gel and the aggregate. In addition, there can be air voids and cracks.

During recent decades, a number of models have been developed for describing concrete, cement paste and the interfacial zone between cement paste and aggregates. The aim of these models has varied ; Earlier models¹ aimed principally at the understanding of the physical behavior, geometry and shape of the paste, ranging from nano scale to micro scale. On the contrary, later models² are frequently of numerical nature aiming at calculating the time-

dependent specific properties such as porosity and pore geometry, heat of hydration, strength, transport properties, or aiming at developing numerical models regarding long-term properties, such as durability.

This paper proposes a semi analytical model to determine the porosity for the Ordinary Portland Cement. This model has been developed to use the diffusivity analysis of concrete. To this end, the relationship between the porosity and the microstructure of concrete has been established by mathematical equations. The microstructure includes the interface transition zone (ITZ) between aggregate and cement paste. The predicting model of porosity was developed with considering the various mixing of mortar and concrete. The model proposed in the present study has been validated by three types of experimental programs on cement paste, mortar and concrete. The analytical results are discussed and compared to the test results in order to validate the new model.

2. Microstructure of concrete

2.1 Composition of concrete

At the macroscopic level, concrete is made up of two main phases: aggregate and cement paste. The aggregate is fixed within the cement paste by bond between the particles of the aggregate. Concrete is usually composed of approximately 65%~75% with aggregate and 25%~35% with cement paste.

It is obvious at the microscopic level that the two phases, aggregate and paste, are neither homogeneously distributed with respect to each other, nor are themselves homogenous.

At the casting of the concrete, air voids are entrapped due to treatment or compression work, or entrained when frost-entraining agents are added. Such air voids are much larger (0.3 ~ 1 mm) than the other pores in the paste, but are normally assigned to the paste phase. In the presence of aggregate, the structure in the vicinity of large aggregate particles is usually very different from

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that of the bulk paste. There is a third phase, the transition zone, which represents the interfacial region between the large aggregate particles and the cement paste. A schematic picture of the composition of concrete is shown in Fig. 1.

2.2 Microstructure of cement paste

When cement and water are mixed, the cement reacts with the water to form a porous conglomerated mass of fine crystal-like gel particles constituting the cement gel, see Fig. 2. The main volume of the gel consists of calcium-silicate-hydrate (C-S-H) products in which calcium hydroxide (CH) is incorporated, and the gel volume grows as the hydration proceeds. Part of the original volume not occupied by gel consists of capillary pores, which are much coarser than gel pores. Young pastes have a inter-connected capillary-pore system but, as hydration proceeds, the hydration products grow into the capillary pores resulting in the reduction of the capillary pore volume.

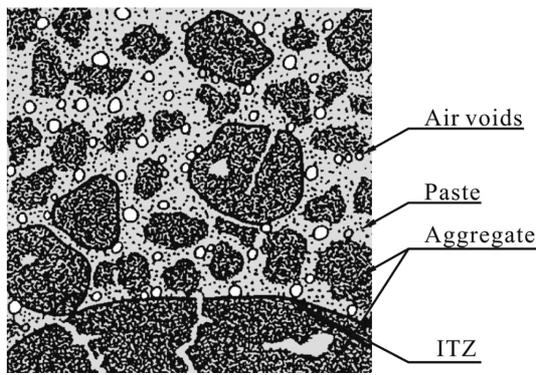


Fig. 1 Schematic picture of the composition of concrete.

Photographs taken by an SEM microscope, one of the specimen tested in the present work are shown in Fig. 3 obtained from the previous research.³ The physical structure of the cement paste can be discerned to some extent there. The fluffy balls consist of hydrated C-S-H gels that have grown into the capillary pores. The internal porosity of the cement paste is high, as can be seen. The CH grows inside the C-S-H, or between the parts of it. It is limited in size by the space available.

The older the cement paste becomes the denser and the more featureless the C-S-H gel appears. Tobermorite and Jennit are natural minerals that resemble C-S-H gel. This has an extraordinarily high internal surface area as measured by water adsorption, in the range of 250 ~ 450 m²/g or 100 ~ 700 m²/g.^{4,5}

2.3 Volume relationship of cement paste

A classification of the porosity of cement paste is given in Table 1.⁴ Table 1 shows there is an enormous range of pore size distribution, from 10 μm to less than 0.5 nm in diameter. It is known that the pore size distributions are mainly affected by the w/c ratio and the degree of hydration. As can be seen in Table 1, porosity over the whole size range of pores has an influence on paste properties. Yet it is difficult to get an exact assessment of pore-size distributions because no one measurement encompasses the whole size range and because it is difficult to interpret experimental data. Thus, comparisons of porosity should be made with care.⁴

Basic volume relationships between cement, cement gel, gel pores, capillary pores and water in cement paste are shown in Figs. 4 and 5. Figure 4 shows that the volume relationship in cement paste varies with increasing hydration. As shown in Fig. 5, increasing w/c ratio results in increasing capillary pore volume, but maintaining the constant level of gel pores.

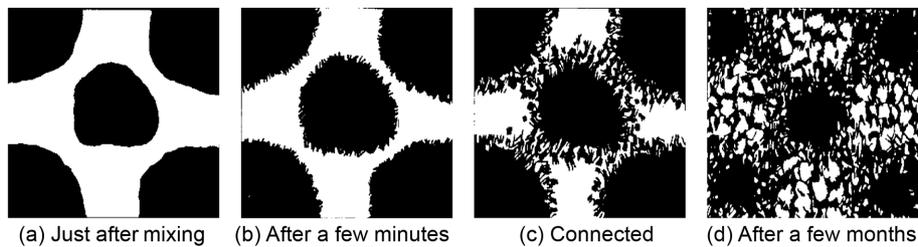
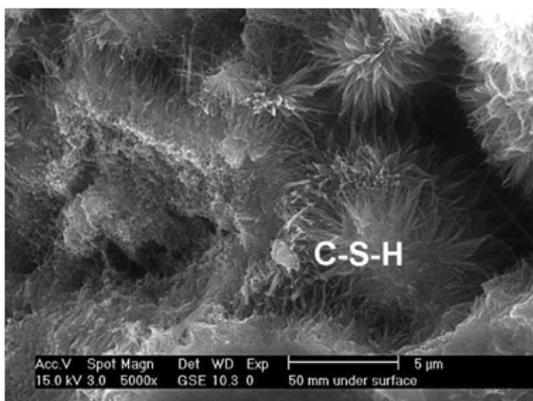
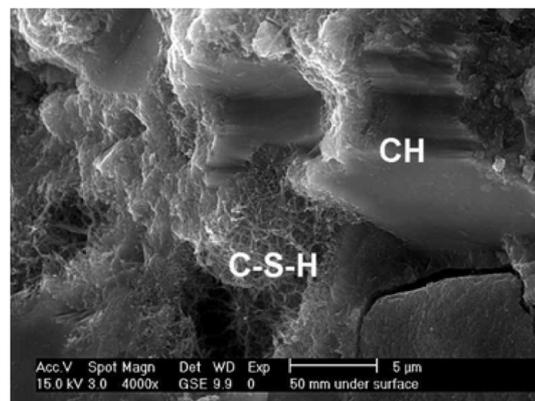


Fig. 2 Development of the structure of cement paste according to Powers.¹



(a) Fluffy C-S-H gel with capillary pores



(b) C-S-H gel into incorporated by CH and capillary pores

Fig. 3 SEM photograph.³

Table 1 Classifications of the pore sizes in hydrated cement.

Type	Diameter (nm)	Description	Role of water	Paste properties affected
Capillary pores	50~10,000	Large capillaries	Behaves as bulk water	Strength, permeability
	10~50	Medium-sized capillaries	Moderate surface tension forces generated	Strength, permeability; shrinkage at high humidity
Gel pores	2.5~10	Small (gel) capillaries	Strong surface tension forces generated	Shrinkage to 50% RH
	0.5~2.5	Micropores	Strongly adsorbed water; no menisci form	Shrinkage, creep
	<~0.5	Micropores "interlayer"	Structural water involved in bonding	Shrinkage, creep

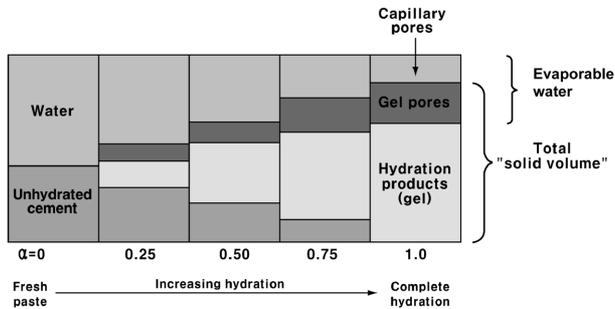


Fig. 4 Volume relationship of hydrated pastes by changing degree of hydration.⁴

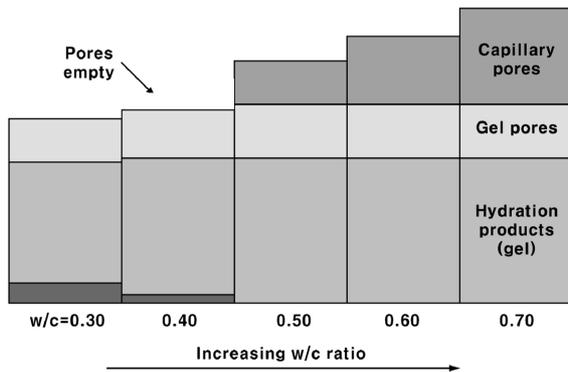


Fig. 5 Volume relationship of hydrated pastes by changing w/c ratios.⁴

3. Analytical model of pore structure of concrete

3.1 Porosity of cement paste

In this study, the structure of the concrete is based on a structural model described in Fagerlund,⁶ which is based on the work of Powers.¹ The model is described mathematically by a set of simple equations, for calculating the volume fraction of the ordinary Portland cement, hydration products (gel) and pores. Powers proposed certain empirically based equations, derived from experimental data. The equations do not distinguish between the various hydration states and different types of the hydration products, all are regarded as cement gel. Besides, a given increase in degree of hydration is assumed to create the same amount and structure of cement gel irrespectively of at what hydration state this additional hydration occurs.

The total pore volume $(V_p)_p$ of the cement paste is as shown in Fig. 6.

$$(V_p)_p = \frac{W - 0.75W_n}{\rho_w} = \frac{W - 0.75k\alpha C}{\rho_w} = \frac{C}{\rho_w} (w/c - 0.75k\alpha) \quad (1)$$

where $(V_p)_p$ = total pore volume of the cement paste (m^3); W =

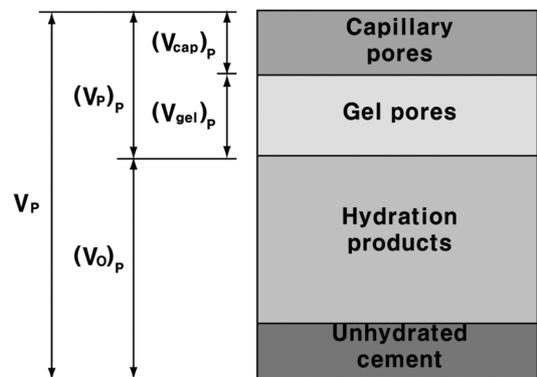


Fig. 6 Volume relationships among constituents of the hydrated paste.

content of water mixed (kg); W_n = chemically bound water (kg); ρ_w = density of water (kg/m^3); and w/c = water to cement ratio.

In the above model, it is assumed that the chemically bound water "decreases" in volume to 0.75 of the volume it had prior to hydration, and the water bound chemically in the hydration process is $k \cdot \alpha \cdot C$, where α = degree of hydration (-). The typical value of k is 0.23.

For the following expression, the maximum possible degree of hydration, α_{max} equal to $(w/c)/(w/c)^*$, must be substituted for a if $w/c \leq (w/c)^*$. The typical value of $(w/c)^*$ is 0.38.

The compact volume, i.e. the solid volume without any pores, of the cement paste $(V_o)_p$ is;

$$(V_o)_p = \frac{C}{\rho_c} + \frac{0.75W_n}{\rho_w} = \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_c} + 0.75k\alpha \right) \quad (2)$$

where $(V_o)_p$ = compact volume of the cement paste (m^3), ρ_c = density of the cement (kg/m^3)

The total volume of the cement paste V_p is the sum of the pore volume and the compact volume

$$V_p = (V_p)_p + (V_o)_p = \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_c} + w/c \right) \quad (3)$$

The total porosity of the cement paste P_p is

$$P_p = \frac{(V_p)_p}{V_p} = \frac{w/c - 0.75k\alpha}{\frac{\rho_w}{\rho_c} + w/c} \quad (4)$$

The ratio of the volume of hydration product to that of the cement from which it is formed may be calculated by dividing the former quantity by the volume of cement reacted per unit mass of cement, which is α / ρ_c , giving $1 + (w/c)^* \rho_c / \rho_w$. Therefore, the

volume of the cement gel is;

$$V_{gel} = \frac{C\alpha}{\rho_c} \left(1 + (w/c) \frac{\rho_c}{\rho_w} \right) = \frac{C\alpha}{\rho_w} \left(\frac{\rho_w}{\rho_c} + (w/c) \right) \quad (5)$$

It is assumed that the cement gel formed during hydration has a porosity of 28%, therefore the volume of the gel pores ($V_{gel,p}$) is;

$$(V_{gel})_p = 0.28V_{gel} = 0.28 \frac{C\alpha}{\rho_w} \left(\frac{\rho_w}{\rho_c} + (w/c) \right) \quad (6)$$

The gel porosity of the cement paste P_{gel} is

$$P_{gel} = \frac{(V_{gel})_p}{V_p} = 0.28\alpha \left(\frac{\rho_w}{\rho_c} + (w/c) \right) / \left(\frac{\rho_w}{\rho_c} + (w/c) \right) \quad (7)$$

The volume of the capillary pores ($V_{cap,p}$) in the cement paste is

$$(V_{cap})_p = (V_p)_p - (V_{gel})_p = \frac{C}{\rho_w} \left[w/c - \left(0.75k + 0.28 \left(\frac{\rho_w}{\rho_c} + (w/c) \right) \right) \alpha \right] \quad (8)$$

The capillary porosity P_{cap} of the paste is

$$P_{cap} = \frac{w/c - \left[0.75k + 0.28 \left(\frac{\rho_w}{\rho_c} + (w/c) \right) \right] \alpha}{\frac{\rho_w}{\rho_c} + w/c} \quad (9)$$

3.2 Interfacial zones between cement paste and aggregate

The structure of aggregate depends on the types of minerals in the aggregate and on its geological history which differ markedly from one location to another. In Korea, fractions of crushed granite and gneiss are normally used. Such aggregates are hard, tight and not easily dissolved. Although the porosity is low, only about 0~1%, the pores in these types of aggregate are quite coarse and are often so interconnected that the permeability and the diffusivity of for example, granite, are in parity with that of cement paste of a high w/c ratio.^{5,7}

Between the cement paste and the aggregate there is a thin, rather porous inter-facial zone (sometimes called the transition zone, tz), see Fig. 7. It becomes increasingly porous during hydration and normally has a larger content of CH-crystals than the bulk paste located farther from the aggregate does. This zone may also crack due to differences in modulus of elasticity and strength of aggregate and cement paste. Referring to the work of other researchers, Winslow et al.² noted a region of approximately 50 nm thickness which, has quite different properties than the rest of the bulk paste.

Bourdette et al.⁸ estimated from the literature the transition zone (tz) to be 30 μ m thick. Using their models of hydration around the tz, they obtained results for porosity three times as high in tz as in the bulk paste, although it decreased with hydration age, whereas the porosity of the bulk paste remained relatively constant.

3.3 Porosity and density of concrete

For mortar and concrete, additional porosity occurs in pore sizes

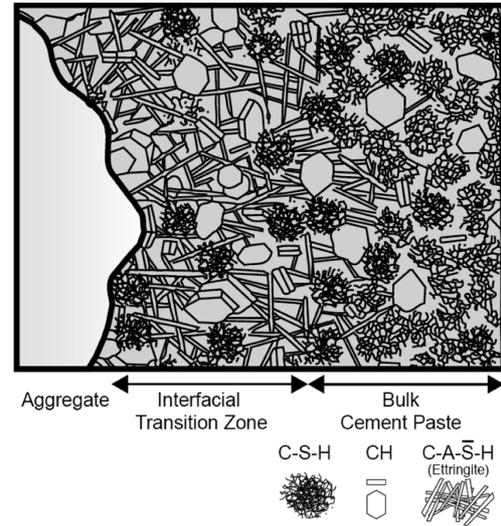


Fig. 7 Schematic representation of the transition zone.⁵

larger than the plain paste's threshold diameter measured by mercury intrusion porosimetry (MIP).² In Winslow et al., mortars with a w/c of 0.4 were made with aggregate of different ratios. The samples were hydrated in lime-saturated water for 28 days and were then oven dried at 105°C. The pore size distributions of the pastes were obtained by MIP. An average thickness of the paste surrounding each aggregate particle was calculated by dividing the volume of paste in the mixture by the surface area of the sand in the mixture. A computer program for random particle placement, percolation assessment and phase fraction estimation was developed. By executing the program for different number of aggregate particles, the volume fraction of aggregate required for interfacial zone percolation for a given aggregate size distribution and interfacial zone thickness was determined and compared to experimental results. An interfacial zone thickness of 15~20 μ m was found to be most consistent with results of the experiments.

In this study, the volume of tz is calculated from the concept of equivalent radius of aggregate and thickness of tz. It is assumed that maximum thickness of tz is 30 μ m, which increases by degree of hydration. The equivalent radius of aggregate is calculated from the size distribution of sand and coarse aggregate as follows;

$$(r_e + t_{TZ})^3 - (r_e)^3 = \sum [(r_i + t_{TZ})^3 - (r_i)^3] m_i \quad (10)$$

where r_e = equivalent radius of aggregate, t_{TZ} = thickness of tz, r_i = radius of aggregate used and m_i = mass ratio of aggregate, r_i , in this study, $t_{TZ} = 30$ (μ m).

In this study, the pore volume of aggregate is ignored. The volume of aggregate is

$$V_a = \frac{G}{\rho_G} = \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_G} \beta \right) \quad (11)$$

where $\beta = G/C$

It is assumed that the volume of tz is proportion to degree of hydration. The total volume of tz is calculated as follows;

$$V_{TZ} = \left[\left(1 + \frac{t_{TZ}}{r_e} \right)^3 - 1 \right] \frac{G}{\rho_G} \alpha = \left[\left(1 + \frac{t_{TZ}}{r_e} \right)^3 - 1 \right] \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_G} \beta \right) \alpha \quad (12)$$

where G = aggregate content, ρ_G = density of aggregate.

The porosity of tz is three times as high as in the bulk cement paste,⁸ the pore volume of tz can be calculated;

$$(V_{TZ})_p = 3 \frac{w/c - 0.75k\alpha}{\frac{\rho_w}{\rho_c} + w/c} \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_G} \beta \right) \alpha \quad (13)$$

The total pore volume of the mortar or concrete is as shown in Fig. 8. The Equation (1) is modified since pore volume of tz and air are included.

$$(V_c)_p = (V_p)_p + (V_{TZ})_p + V_{air} = \frac{C}{\rho_w} (w/c - 0.75k\alpha) + 3 \frac{w/c - 0.75k\alpha}{\frac{\rho_w}{\rho_c} + w/c} \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_G} \beta \right) \alpha + V_{air} \quad (14)$$

The total volume of the mortar or concrete is;

$$V_c = V_a + V_p + V_{TZ} + V_{air} = \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_G} \beta \right) + \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_c} + w/c \right) + \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \frac{C}{\rho_w} \left(\frac{\rho_w}{\rho_G} \beta \right) \alpha + V_{air} \quad (15)$$

The total porosity of mortar or concrete is

$$P_c = \frac{(V_c)_p}{V_c} = \frac{(w/c - 0.75k\alpha) + 3 \frac{w/c - 0.75k\alpha}{\frac{\rho_w}{\rho_c} + w/c} \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \left(\frac{\rho_w}{\rho_G} \beta \right) \alpha + \frac{\rho_w}{C} V_{air}}{\left(\frac{\rho_w}{\rho_c} + w/c \right) + \left(1 + \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \alpha \right) \left(\frac{\rho_w}{\rho_G} \beta \right) + \frac{\rho_w}{C} V_{air}} \quad (16)$$

It is assumed that the volume of gel pore is same as the cement paste, so gel porosity of concrete is

$$P_{gel,c} = \frac{(V_{gel})_p}{V_c} = \frac{0.28\alpha \left(\frac{\rho_w}{\rho_c} + (w/c)^* \right)}{\left(\frac{\rho_w}{\rho_c} + w/c \right) + \left(1 + \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \alpha \right) \left(\frac{\rho_w}{\rho_G} \beta \right) + \frac{\rho_w}{C} V_{air}} \quad (17)$$

The pore volume of tz is included in the volume of the capillary pore in the mortar or concrete because pore size of tz belongs to capillary pore. The volume of capillary pore and porosity are;

$$P_{cap,c} = \frac{(V_p)_p - (V_{gel})_p + (V_{TZ})_p}{V_c} = \frac{w/c - \alpha \left(0.75k + 0.28 \left(\frac{\rho_w}{\rho_c} + (w/c)^* \right) + 3 \frac{w/c - 0.75k\alpha}{\frac{\rho_w}{\rho_c} + w/c} \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \left(\frac{\rho_w}{\rho_G} \beta \right) \alpha}{\left(\frac{\rho_w}{\rho_c} + w/c \right) + \left(1 + \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \alpha \right) \left(\frac{\rho_w}{\rho_G} \beta \right) + \frac{\rho_w}{C} V_{air}} \quad (18)$$

The porosity of cement paste in mortar and concrete is;

$$P'_{gel,c} = \frac{(V_{gel})_p}{V_c - V_a} = \frac{0.28\alpha \left(\frac{\rho_w}{\rho_c} + (w/c)^* \right)}{\left(\frac{\rho_w}{\rho_c} + w/c \right) + \left[\left(1 + \frac{t_{TZ}}{r_e}\right)^3 - 1 \right] \alpha \left(\frac{\rho_w}{\rho_G} \beta \right) + \frac{\rho_w}{C} V_{air}} \quad (19)$$

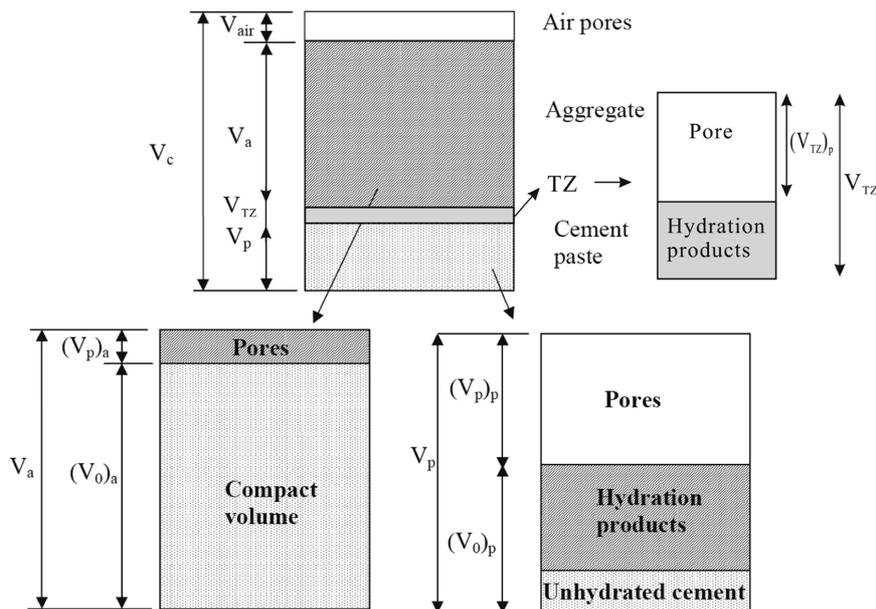


Fig. 8 Schematic volume fractions of pores and solid materials.

$$w/c - \alpha \left(0.75k + 0.28 \left(\frac{\rho_w}{\rho_c} + (w/c)^* \right) \right) + 3 \frac{w/c - 0.75k}{\rho_c + w/c} \alpha \left[\left(1 + \frac{t_{TZ}}{r_e} \right)^3 - 1 \right] \left(\frac{\rho_w}{\rho_G} \beta \right) \alpha$$

$$P'_{cap,c} = \frac{\left(\frac{\rho_w}{\rho_c} + w/c \right) + \left[\left(1 + \frac{t_{TZ}}{r_e} \right)^3 - 1 \right] \alpha \left(\frac{\rho_w}{\rho_G} \beta \right)}{\quad} \quad (20)$$

4. Experiments

4.1 Materials and mixture proportions

The three types of experiments (cement paste, mortar, and concrete) were conducted for the evaluation of porosity. The materials used and mixture properties are summarized in Table 2, Tables 3 and 4. The Ordinary Portland Cement was used for all experiments and porosities are tested at various times, such as 1, 3, 7, 14, 28 and 91 days.

The water-binder ratios of cement pastes are 0.3, 0.35, 0.4, 0.5, 0.6 and 0.7 in cement paste. For evaluating the effects of aggregate, mortar were manufactured. The main variables are w/c (0.4, 0.5, 0.55, 0.6 and 0.65) and the mass ratio of sand and cement (S/c = 1, 1.5 and 2). The maximum sizes of fine and coarse aggregate are 5 mm, 13 mm respectively and various w/c ratios (0.4, 0.5 and 0.6) are used.

4.2 Test methods

Mercury Intrusion Porosimetry (MIP) is a technique used to measure pore size distribution, and has an advantage in that it is able to span the measurement of pore sizes ranging from a few nanometres, to several hundred micrometers. As concrete has a distribution of pore sizes ranging from sub-nanometer to many millimeters, MIP has formed an important tool in the characterization of pore size distribution and total volume of porosity.

The specimens are dried to remove all moisture from the pore structure. They are then placed into sealed "penetrometers" which are weighed both before and after being loaded with the specimen. The penetrometers are placed into the machine where they are evacuated and then filled with mercury. The pressurized testing then commences and the machine calculates and records how much mercury is being forced into the pore structure.

The degree of hydration, α , is defined as the fraction of cement that has fully hydrated. For the present experiments, α was determined experimentally by comparing the amount of non-evaporable water in a sample to the amount needed for complete hydration. To determine the non-evaporable water content, four dried specimens from each paste group were subjected to ignition

Table 2 Mixture proportions for cement pastes.

ID	w/c (-)	Cement (kg)	Type of cement
CP	0.3, 0.35, 0.4, 0.5, 0.6, 0.7	300	OPC

Table 3 Mixture proportions for concrete specimens.

Specimen	w/b (-)	Water (kg m ⁻³)	Binder (kg m ⁻³)	Sand (kg m ⁻³)	Gravel (kg m ⁻³)	Type of cement
C40	0.4	140	350	742	1,135	OPC
C50	0.5	158	350	724	1,107	OPC
C60	0.6	175	350	707	1,080	OPC

Table 4 Mixture proportions for mortar specimens.

Specimen	w/c (-)	Water (kg)	Cement (kg)	Sand (kg)	Type of cement
M1-1	0.4	120	300	300	OPC
M1-1.5	0.4	120	300	450	OPC
M1-2	0.4	120	300	600	OPC
M2-1	0.5	150	300	300	OPC
M2-1.5	0.5	150	300	450	OPC
M2-2	0.5	150	300	600	OPC
M3	0.55	165	300	600	OPC
M4	0.6	180	300	600	OPC
M5	0.65	195	300	600	OPC

at 800°C for 2h, cooled in vacuum desiccators at less than 20 Pa for 1 h, and then weighed. The water in the paste that was not removed by the drying process, W_m (also known as the non-evaporable water) is then estimated as shown in Eq. (21).

$$W_n = \frac{w_1 - w_2}{w_2} C \quad (21)$$

where, w_1 and w_2 are the weights of the dry specimen before and after ignition, respectively.

The degree of hydration can then be calculated as shown in Eq. (22)

$$\alpha = \frac{W_n}{(W_n/C)^* C} = \frac{W_n}{0.25C} \quad (22)$$

where $(W_n/C)^*$ is the non-evaporable water corresponding to a completely hydrated paste. The typical value of it is 0.25.

The total porosity of specimen is calculated by Eq. (23).

$$P_t = \frac{W_3 - W_1}{W_3 - W_2} \quad (23)$$

where, W_1 , W_2 , and W_3 are weight after 105°C oven dry, weight in water and weight in surface dry condition.

4.3 Measurements

The results obtained from the instrument are;

- 1) pore size distribution (macro/meso range of porosity spectrum)
- 2) hysteresis curve, specific surface, bulk density
- 3) total porosity (%), particle size distribution

The non-evaporable water contents by degree of hydration, the measured results are summarized in Table 5. The porosities of capillary pore volume were obtained by MIP. The effects of water/cement ratios and sand contents on porosity are estimated by MIP. For various degree of hydration, porosities of specimens are measured and the results are summarized in Table 6.

Table 5 Measured properties of cement paste.

Type		Time (days)					
		1	3	7	14	28	91
w/c = 0.3	W_n (kg m ⁻³)	23.82	27.91	30.06	30.92	33.02	35.10
	α (-)	0.345	0.404	0.436	0.448	0.479	0.509
	P_p (-)	0.269	0.225	0.201	0.178	0.170	0.159
w/c = 0.35	W_n (kg m ⁻³)	-	26.91	29.95	-	-	-
	α (-)	-	0.390	0.434	-	-	-
	P_p (-)	-	0.315	0.285	-	-	-
w/c = 0.4	W_n (kg m ⁻³)	24.34	31.93	35.45	38.64	42.69	41.78
	α (-)	0.353	0.463	0.514	0.560	0.619	0.605
	P_p (-)	0.376	0.315	0.271	0.257	0.227	0.226
w/c = 0.5	W_n (kg m ⁻³)	24.60	30.89	36.68	44.74	46.26	51.97
	α (-)	0.356	0.448	0.532	0.648	0.670	0.753
	P_p (-)	0.439	0.399	0.355	0.327	0.299	0.287
w/c = 0.6	W_n (kg m ⁻³)	24.08	30.18	38.49	45.65	48.79	53.27
	α (-)	0.349	0.437	0.558	0.662	0.707	0.772
	P_p (-)	0.496	0.475	0.421	0.394	0.382	0.340
w/c = 0.7	W_n (kg m ⁻³)	23.82	30.96	38.04	48.18	51.06	56.45
	α (-)	0.345	0.449	0.551	0.698	0.740	0.818
	P_p (-)	0.548	0.522	0.494	0.455	0.425	0.395

Table 6 Measured properties of mortar.

Specimen	w/c	W_n (kg m ⁻³)	α (-)	P_{cap} (-)	Sand/cement
M1-1	0.4	36.018	0.522	0.213	1
	0.4	44.505	0.645	0.177	1
M1-1.5	0.4	35.466	0.514	0.188	1.5
	0.4	43.470	0.630	0.166	1.5
M1-2	0.4	25.530	0.370	0.217	2
	0.4	35.445	0.514	0.169	2
	0.4	44.712	0.648	0.149	2
M2-1	0.4	52.026	0.754	0.123	2
	0.5	40.158	0.582	0.268	1
	0.5	50.094	0.726	0.227	1
M2-1.5	0.5	38.364	0.556	0.248	1.5
	0.5	45.264	0.656	0.220	1.5
M2-2	0.5	28.911	0.419	0.254	2
	0.5	37.398	0.542	0.230	2
	0.5	48.231	0.699	0.196	2
M2-3	0.5	56.580	0.820	0.176	2
	0.55	29.514	0.428	0.276	2
	0.55	40.779	0.591	0.255	2
M2-4	0.55	50.057	0.725	0.214	2
	0.55	59.340	0.860	0.195	2
	0.6	34.500	0.500	0.280	2
M2-5	0.6	43.539	0.631	0.263	2
	0.6	56.580	0.820	0.223	2
	0.6	63.480	0.920	0.208	2
M2-5	0.65	34.500	0.500	0.308	2
	0.65	44.850	0.650	0.288	2
	0.65	58.650	0.850	0.238	2
	0.65	64.860	0.940	0.225	2

5. Validation of analytical model

5.1 Model for cement paste

For validating of the proposed model, the predicted values by Eq. (4) are comprised with data of other researchers as shown in Fig. 9. Figure 9 includes porosities derived from calculated phase compositions, the degree of hydration is assumed to be the value of maximum and a specific volume of cement is $3.17 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$.

As expected, the capillary porosities decreased with the increase of the degree of hydration and the water/cement ratio for all specimens as shown in Fig. 10; capillary pore space is filled with cement hydrates by hydration reaction (pore volume of gel increases by degree of hydration). From the Fig. 10, the predicted values by Eq. (9) are very similar with the measurements.

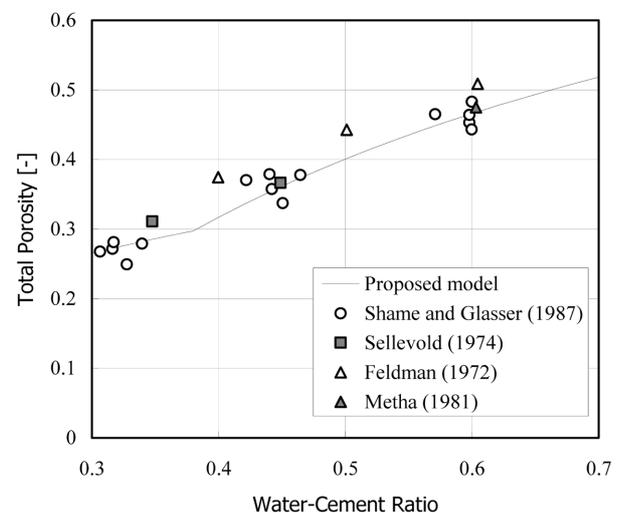


Fig. 9 Relation between total porosity and water/cement ratio.

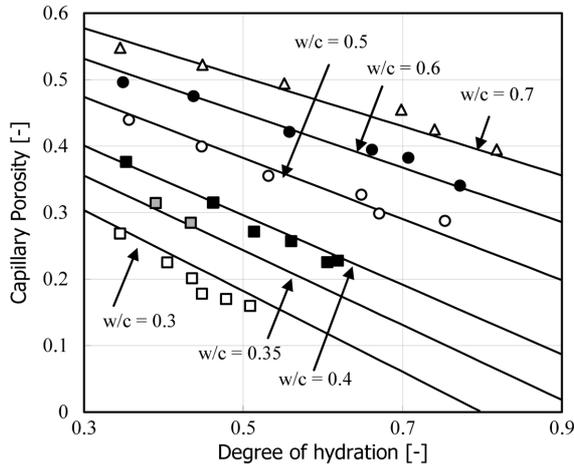


Fig. 10 Comparison of the calculated and measured capillary porosities.

For various degree of hydration, Figs. 11 and 12 show the relation between porosity and water cement ratio by the proposed model. The porosity of gel increases with the increase of the degree of hydration and decreases with water/cement ratio, but reverse tendency occurs to the critical water/cement ratio at full hydration because water is insufficient for full hydration.

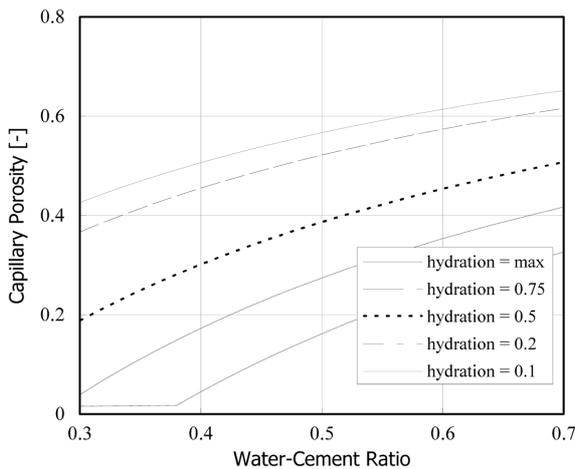


Fig. 11 Relation between capillary porosity and water/cement ratio.

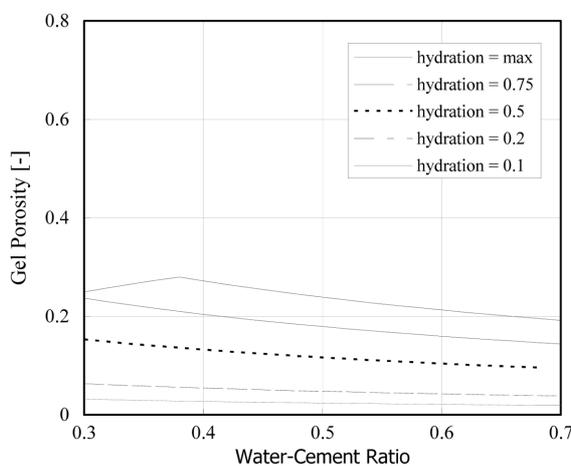


Fig. 12 Relation between gel porosity and water/cement ratio.

5.2 Model for mortar

Fig. 13 shows the experimental results and comparisons between measured and predicted data by Eq. (19). It is thought that predicted values are very close to the measured ones like the cement paste, the capillary porosity of mortar decreases with increasing hydration. As shown in Fig. 13, high water/cement ratio increases the pore volume of mortar.

Mortar and concrete can not properly be described as the composites of coarse and fine aggregates in a matrix of cement paste otherwise identical with the aggregate-free material. The microstructure of the paste close to the aggregate differs from that of cement paste in bulk, and much of the paste in concrete or mortar places or lies in this category.

Interface transition zone (ITZ) between aggregate and cement paste has more pore space than bulk cement paste because the surfaces of aggregates were closely covered with poorly crystalline material as $\text{CH}(\text{Ca}(\text{OH})_2)$. In this zone, it is up to about $30 \mu\text{m}$ wide; the paste is of increased porosity and presumably low in strength.

The porosity of cement paste in mortar and concrete differs from the aggregate-free cement paste. Therefore, property of interface transition zone on porosity must be considered for more accuracy. Figs. 14 and 15 show the relation between sand content and capillary porosity. The capillary porosity of mortar with

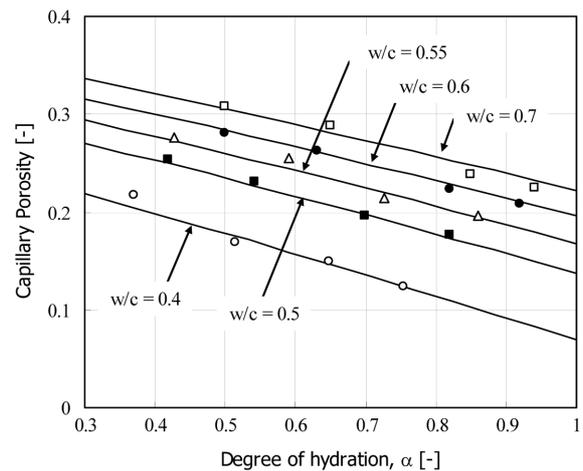


Fig. 13 Relation between water/cement ratio and capillary porosity.

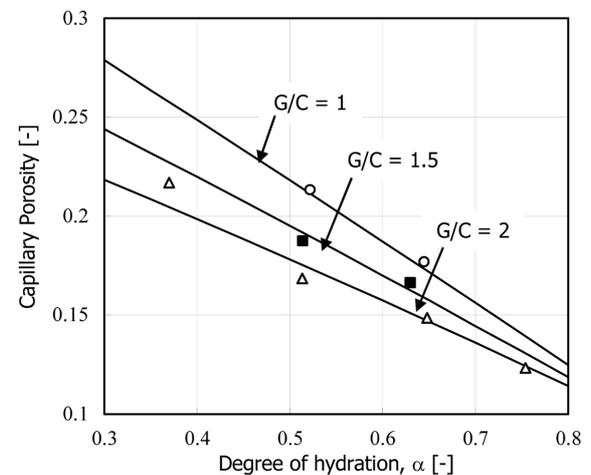


Fig. 14 Relation between G/C ratios and capillary porosity ($w/c = 0.4$).

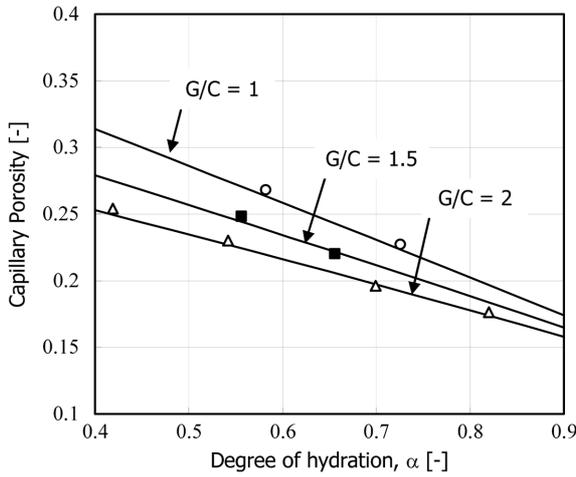


Fig. 15 Relation between G/C ratios and capillary porosity ($w/c = 0.5$).

aggregate was measured by MIP. The measurement of porosity of mortar without aggregate is very difficult because the removal of aggregate is so complicated and needs too much time. Therefore the porosity of cement paste without aggregate in mortar is usually calculated by proposed model.

The porosity of mortar with aggregate decreases with increasing of aggregate contents because component ratio of aggregate is usually high as shown in Figs. 14 and 15. Figures 16 and 17 shows that high content of aggregate increases the capillary porosity of cement paste in mortar (thickness of ITZ: $30 \mu\text{m}$, density of cement: $3,100 \text{ kg/m}^3$)

5.3 Model for concrete

Porosity of concrete can be calculated by same method in mortar if coarse aggregate is included. The influence of water/cement ratios and sand contents on porosity are estimated by MIP. For various degree of hydration, porosities of specimens are measured. The capillary porosities are obtained by cement paste with fine aggregate in concrete because the operation of removing aggregate is impossible.

As expected, the results are very similar with mortar (see Fig. 18). The correlations of porosity by measured data and the proposed model are very good in all types of specimen (cement paste,

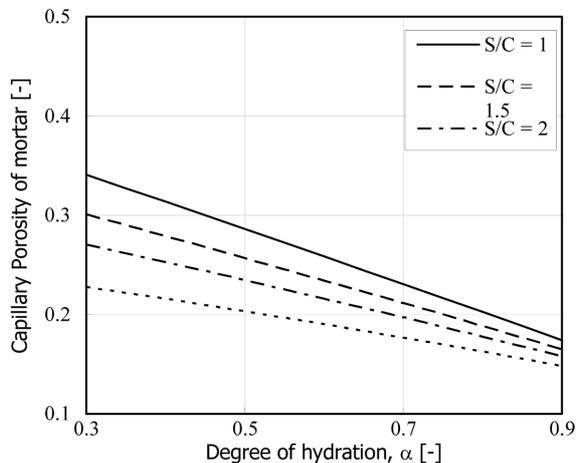


Fig. 16 Capillary porosity of mortar.

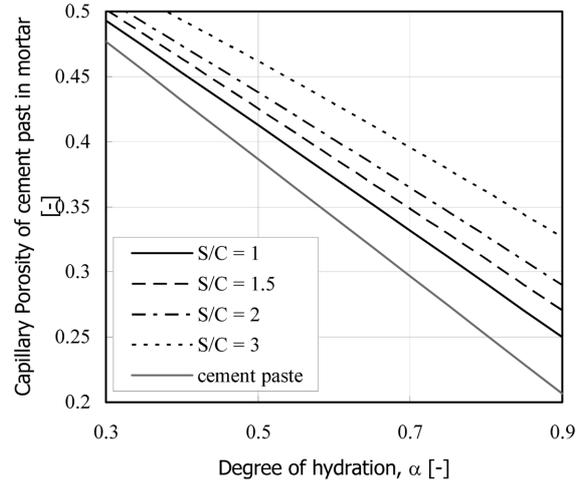


Fig. 17 Capillary porosity of cement paste in mortar.

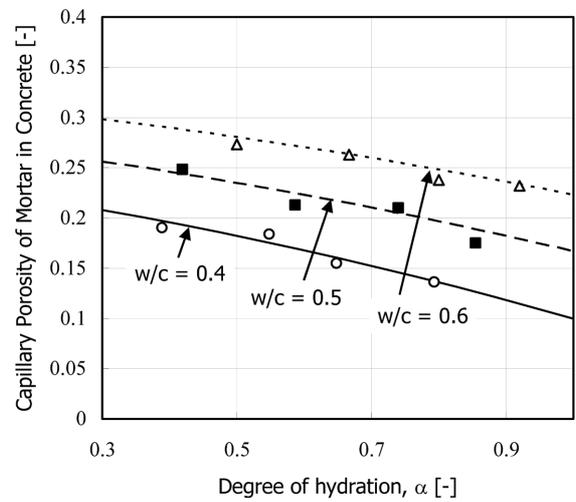


Fig. 18 Total porosity of concrete.

mortar and concrete). The capillary porosities of paste in cement, mortar and concrete are very different due to the existence and quantity of pore volume in interfacial transition zone (see Fig. 19).

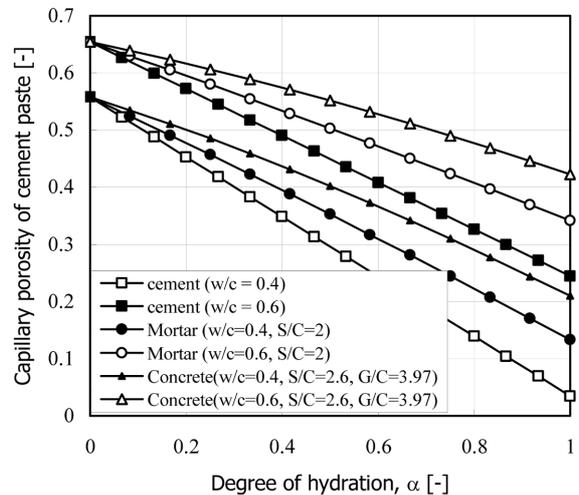


Fig. 19 Capillary porosity of paste in cement, mortar and concrete.

6. Conclusions

The purpose of this study is to propose a semi analytical model to determine the porosity for the Ordinary Portland Cement to use for the diffusivity analysis of concrete. To validate the model proposed in the present study, the measurements of the porosities have been carried out on the three types of experimental programs on cement paste, mortar and concrete. The correlations of calculated and test data show good agreement.

The proposed model is semi-analytical and simple, but it can be used for reasonable durability design and predicting service life of concrete structures.

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