Pergamon

Cement and Concrete Research 31 (2001) 277–282

CEMENT AND CONCRETE RESEARCH

Permeability and pore structure of OPC paste

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Received 7 July 2000; accepted 6 November 2000

Abstract

A model is presented to predict the water permeability of OPC paste from its pore structure. It is based on the General Effective Media (GEM) theory and considers the contributions of capillary pores and gel pores. The pore structure of cement paste was determined by mercury intrusion porosimetry (MIP). The water permeability of cement paste was measured by using the input method. The model is shown to apply to both low- and high-permeability cement paste. The calculated results are in good agreement with experimental results. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cement paste; General Effective Media theory; Microstructure; Permeability

1. Introduction

It is well known that durability of a cementitious material largely depends on the possibilities of penetration of hazardous ions into the porous material with water as medium. Therefore, the water permeability of the cementitious material is very crucial to its durability. There are several methods to measure the water permeability directly [1–3]. However, these methods are time consuming especially for low-permeability concrete, mortar, or cement paste. Therefore, it is necessary to find some other ways to predict the water permeability instead of direct measurement.

Many models have been developed to relate water permeability to pore structure of cementitious material. Hughes [4] used parallel model to relate the water permeability to second intrusion of mercury intrusion porosimetry (MIP) data. Some other researchers, such as Christensen et al. [8], have directly applied the Katz and Thompson permeability theory [Eq. (1)] [5–7] to predict the water permeability of OPC paste.

$$k = \frac{1}{226} l_c^2 \frac{\sigma}{\sigma_o} \tag{1}$$

where l_c is the critical pore diameter of the cementitious material. It can be defined as follows. If the pores were added to the network one by one from largest to smallest, the critical diameter l_c is the diameter of the pore that completes the first connected pore pathway. σ is the electrical conductivity of the sample, and σ_o is the electrical conductivity of pore solution in the sample. Therefore, σ/σ_o is the relative conductivity of the sample, which includes the information of the connectivity of pore network. For OPC paste, this value can be calculated from the MIP data by Eq. (2), which was proposed by Garboczi et al. [9–11].

$$\frac{\sigma}{\sigma_o} = 0.18(\phi - \phi_c)^2 \tag{2}$$

where ϕ_c is the critical value of capillary porosity for percolation. Substituting Eq. (2) into Eq. (1), the Katz and Thompson equation for OPC paste can be obtained as follows:

$$k = \frac{1}{226} l_c^2 \cdot 0.18 \cdot (\phi - \phi_c)^2 \tag{3}$$

Many researchers have tried to apply the Katz and Thompson theory to cementitious material. However, the results are not as good as those in rock and stone. El-Dieb and Hooton [12] measured the water permeability and pore structure of both OPC and blended cement pastes but did not measure their relative conductivity directly. The porosity of the samples was very low. The experimental results were much different from the results obtained by using the Katz and Thompson equation. They concluded that the Katz and

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PII: S0008-8846(00)00474-9

Thompson theory could not be applied to cementitious material. Christensen et al. [8] has used the theory to predict the water permeability of very porous cement paste and measured directly the relative conductivity. They found that predicted permeability was in agreement with measured permeability. Tumidajski and Lin [13] has applied the theory to predict the water permeability of concrete and found that the Katz and Thompson theory cannot be directly used in concrete systems.

The question is whether or not the Katz and Thompson theory can be applied on cementitious material. This question can be answered by examining thoroughly the pore structure of cement paste and compare it with pore structure of stone. The difference in pore structure between stone and cement paste is the existence of gel pores. Powers et al. [14] observed that the permeability of cement paste drops sharply when the capillary porosity of the sample is smaller than a critical value. This is due to the discontinuity of capillary pores by hydration product when its capillary porosity is smaller than a critical value. In this situation, water has to pass through the gel pores whose size are more than one order smaller than capillary pores. Therefore, gel pores control the water permeability. It results to a much lower value. The gel pores do not exist in stone or rock. Thus, the Katz and Thompson theory, which is successfully applied on single pore structure stone and rock, may not be appropriate to bipore structure cementitious material with low porosity since the permeability will be controlled by gel pores. When cement paste is very porous, capillary pores control the water permeability. In this case, Christensen et al. [8] found that the Katz and Thompson theory could be used. However, for low porosity, the model should consider the roles of both capillary pores and gel pores.

2. Theory

2.1. General Effective Media (GEM) theory for permeability

In this model, cement paste is considered as a bicomposite material (Fig. 1). It consists of two phases. One phase is the high-permeability capillary pores. The other is the low-permeability phase consists of C-S-H gel, CH, and unhydrated cement particles. The volume fraction and the permeability of each phase will determine the overall permeability of the OPC paste.

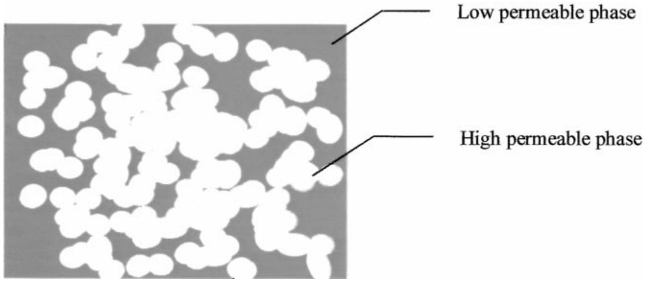

Fig. 1. Bicomposite model of cement.

To calculate the overall permeability, the GEM theory can be used. This theory was developed by McLachlan et al. [15–18] to calculate the overall conductivity of bicomposite material. Based on Bruggeman's symmetric theory and the percolation theory, he proposed the following equation:

$$\frac{(1-V)\left(\sigma_l^{1/t}-\sigma_m^{1/t}\right)}{\sigma_l^{1/t}+A\sigma_m^{1/t}}+\frac{V\left(\sigma_h^{1/t}-\sigma_m^{1/t}\right)}{\sigma_h^{1/t}+A\sigma_m^{1/t}}=0 \qquad (4)$$

$$A=\frac{1-V_c}{V_c}$$

where V is the volume fraction of the high-conductivity phase. σ_h is the conductivity of the high-conductivity phase. σ_l is the conductivity of the low-conductivity phase. σ_m is the overall conductivity of bicomposite material. V_c is the critical volume fraction of the high-conductivity phase, lower than which the high-conductivity phase is isolated by the other phase.

Though water transportation in the porous material is a different physical process compared to electron transportation in the conductor, Darcy's law (Eq. (5)), which governs the water transportation, has the same mathematical expression as the Ohm's law (Eq. (6)), which governs the electron transportation.

$$q=\frac{k}{\mu}\cdot\nabla P \qquad (5)$$

$$i=\sigma\cdot\nabla E \qquad (6)$$

The rate of water flow, q, can be analogous to current density, i. In the same way, the water pressure, P, can be analogous to the electron field, E, and permeability, k, to the conductivity, σ, while the viscosity of the water, μ, is a constant. By replacing the conductivity, σ_i in Eq. (4) with the corresponding permeability, k_i, the GEM equation for permeability can be obtained as follows:

$$\frac{(1-\phi)\left(k_l^{1/t}-k^{1/t}\right)}{k_l^{1/t}+Ak^{1/t}}+\frac{\phi\left(k_h^{1/t}-k^{1/t}\right)}{k_h^{1/t}+Ak^{1/t}}=0 \qquad (7)$$

$$A=\frac{1-\phi_c}{\phi_c}$$

where ϕ is the capillary porosity, ϕ_c is the critical capillary porosity, k_h is the permeability of the high-permeability phase, k_l is the permeability of the low-permeability phase, and k is the permeability of the bicomposite material. The value of k is always between k_h and k_l. In order to obtain k, the values of k_h and k_l have to be determined first. It should be noted that Eq. (7) is based on the analogy of the theory that was designed for conductivity.

2.2. Calculation for k_h

If the cement paste is very porous, water mainly flows through the capillary pores. Comparing with the contribution of capillary pores, the contribution of the low-permeability phase gel pores to overall permeability can be neglected. By substituting $k_l = 0$ into Eq. (7), the following equation can be obtained.

$$k = \frac{k_h}{(1-\phi_c)^t}(\phi - \phi_c)^t \tag{8}$$

As having been said, the Katz and Thompson equation (Eq. (3)) can also be used to predict the permeability of very porous cement paste. Comparing Eq. (3) and Eq. (8), k_h should yield Eq. (9)

$$k_h = \frac{1}{226} l_c^2 (1.8)(1-\phi_c)^2 \tag{9}$$

$$\phi_c = 0.18$$

Therefore, the permeability of high-permeability phase only depends on the critical pore diameter and the critical capillary porosity.

2.3. Calculation for k_l

In the second limit case, the capillary porosity is assumed to be zero. The permeability of cement paste depends on gel pores in C-S-H. In this situation, the cement paste consists of three components: C-S-H gel, CH, and unhydrated cement particles. Among them, only C-S-H gel is permeable. Therefore, the overall permeability is due to the presence of gel pores. Such kind of material can be considered as a bicomposite material where C-S-H gel is considered as high-permeability phase, and CH and unhydrated cement particles are considered as low-permeability or impermeable phase. Once again, the GEM theory can be applied to calculate the overall permeability. In this case, k_h is the permeability of C-S-H gel. According to Power [19], the permeability of C-S-H gel, $k_{\text{C-S-H}}$ is equal to 7×10^{-23} m^2. The permeability of low or impermeable phase is zero, $k_l = 0$. Thus, the overall permeability is equal to

$$k_{\phi=0} = k_{\text{C-S-H}} \left[1 - \frac{1 - \phi_{\text{C-S-H}}}{1 - \phi_c'} \right]^2 \tag{10}$$

where ϕ_c' is the critical volume fraction of C-S-H, which is chosen to be 0.17 [9], and $\phi_{\text{C-S-H}}$ is the volume fraction of C-S-H in the solid phase, which can be calculated by using Eq. (11):

$$\phi_{\text{C-S-H}} = \frac{V_{\text{C-S-H}}}{V_{\text{unhyd.}} + V_{\text{CH}} + V_{\text{C-S-H}}} \tag{11}$$

The volume fraction of hydration products (C-S-H and CH) and unhydrated cement particles can be calculated by using Power's model [20] for Ordinary Portland Cement paste (Eqs (12) and (13)).

$$\text{Volume fraction of hydration products}: V_{\text{hyd.}} = \frac{0.68\alpha}{(\text{W/C}) + 0.32} \tag{12}$$

$$\text{Volume fraction of unhydrated cement particles}: V_{\text{unhyd.}} = \frac{0.32(1-\alpha)}{(\text{W/C}) + 0.32} \tag{13}$$

where W/C is the water–cement ratio and α is the hydration degree.

The hydration degree can also be calculated from Power's model if the capillary porosity of cement paste, ϕ, is known (Eq. (14)).

$$\alpha = \frac{(1-\phi)(\text{W/C}) - 0.32\phi}{0.36} \tag{14}$$

The ratio of volume fraction of C-S-H and CH can be calculated from stoichiometry. In this study, $V_{\text{C-S-H}}/V_{\text{CH}} = 1.66{:}0.63$ is chosen for OPC paste [10]. Substituting the information into Eq. (12), the volume fraction of C-S-H can be obtained. Then the overall permeability for this limit case can be calculated by using Eq. (10).

2.4. Model of permeability of OPC paste

The general condition for OPC paste exists in-between the two limits. The overall permeability depends on how the capillary pores and gel pores play off each other. Mathe-

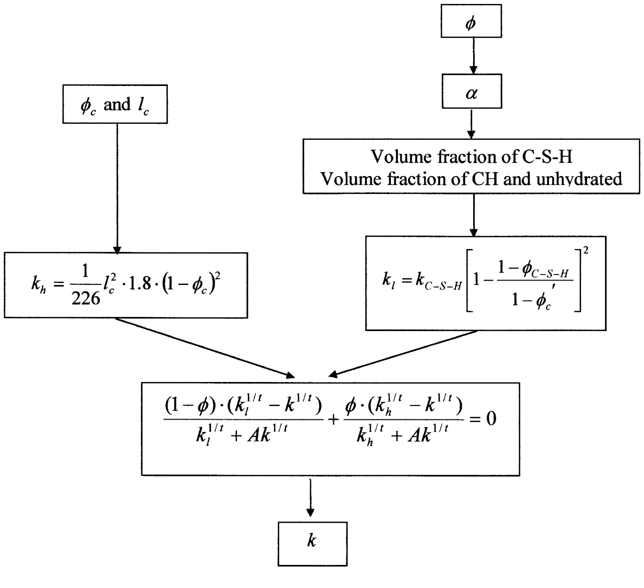

Fig. 2. The flow chart of the calculation of permeability of cement paste.

Table 1
Compressive strength and pore structure for samples

	W/C ratio				
	0.3		0.4		
Curing time (days)	7	210	7	35	210
Compressive strength (MPa)	53.2	96.6	50.3	65.4	79.1
Capillary porosity (%)	17.4	5.9	20.69	12.9	9.1
Critical pore diameter (μm)	0.0686	0.0101	0.0453	0.0363	0.0101

For cement paste with W/C = 0.3, the pore size distribution of the sample at 35 days was not obtained.

matically, this interplay can be expressed as GEM equation (Eq. (7)).

$$\frac{(1-\phi)\left(k_{\mathrm{l}}^{1/t}-k^{1/t}\right)}{k_{\mathrm{l}}^{1/t}+Ak^{1/t}}+\frac{\phi\left(k_{\mathrm{h}}^{1/t}-k^{1/t}\right)}{k_{\mathrm{h}}^{1/t}+Ak^{1/t}}=0$$

where

$$k_{\mathrm{h}}=\frac{1}{226}l_{\mathrm{c}}^{2}(1.8)(1-\phi_{\mathrm{c}})^{2}$$

$$k_{\mathrm{l}}=k_{\mathrm{C-S-H}}\left[1-\frac{1-\phi_{\mathrm{C-S-H}}}{1-\phi_{\mathrm{c}}'}\right]^{2}$$

Fig. 2 describes the process to calculate the permeability of cement paste. All the symbols used inside are consistent with other part in this paper.

3. Experimental results

Ordinary Portland Cement pastes were mixed with water at water/cement ratios 0.3 and 0.4. Cement pastes were mixed in pan mixer for 5 min before casting into 10 × 10 × 10 cm mould for compression test and 15 × 15 × 15 cm mould for permeability test. Then they were cured in the moist condition for 7, 35, and 210 days.

Input method was used to measure the permeability [21]. The testing surface of the specimen was carefully polished with a steel brush to remove the surface skin. All samples were tested under a constant pressure, 7 bar, for 3 days. Some samples (210th day) with very low permeability were tested for 4 days. After tests, the three specimens were split to measure the water penetration depth, $x_{\max}$. The coefficient of water permeability was calculated by Eq. (15) [22].

$$k=\eta\left(\frac{x_{\max}}{ht}\right)^{2} \tag{15}$$

Here, η is the air content which was measured by ASTM C231. h is the hydraulic head (m) and t is the testing time (s).

The pore size distribution was determined by 5-mm-thick samples cutting from identically produced and cured cubes. The fragments were dipped into the acetone for 5 min, then dried in the vacuum desiccator for 2 days.

The pressure of mercury intrusion porosimeter ranges from 0 to 60,000 psi (414 MPa). The surface tension of 480 ergs/cm^2 and a contact angle of 130° were used in the Washburn equation to convert applied pressure to pore diameter.

4. Results and discussion

4.1. Compressive strength and pore structure

Compressive strength, capillary porosity, and critical pore diameter of cement pastes cured at 7, 35, and 210 days are shown in Table 1. The capillary porosity and critical pore diameter of pastes decrease sharply from 7 to 210 days curing time. This means that the pore structure of cement pastes become finer with the curing time. The capillary porosity defined here is the porosity of pores

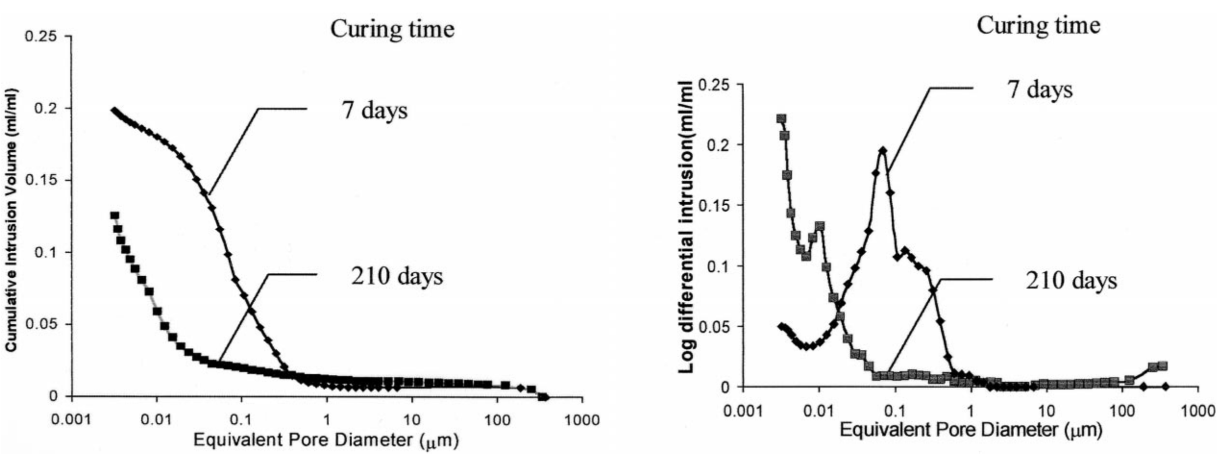

Fig. 3. Pore size distribution of cement paste with W/C = 0.3 at 7 and 210 days of curing time.

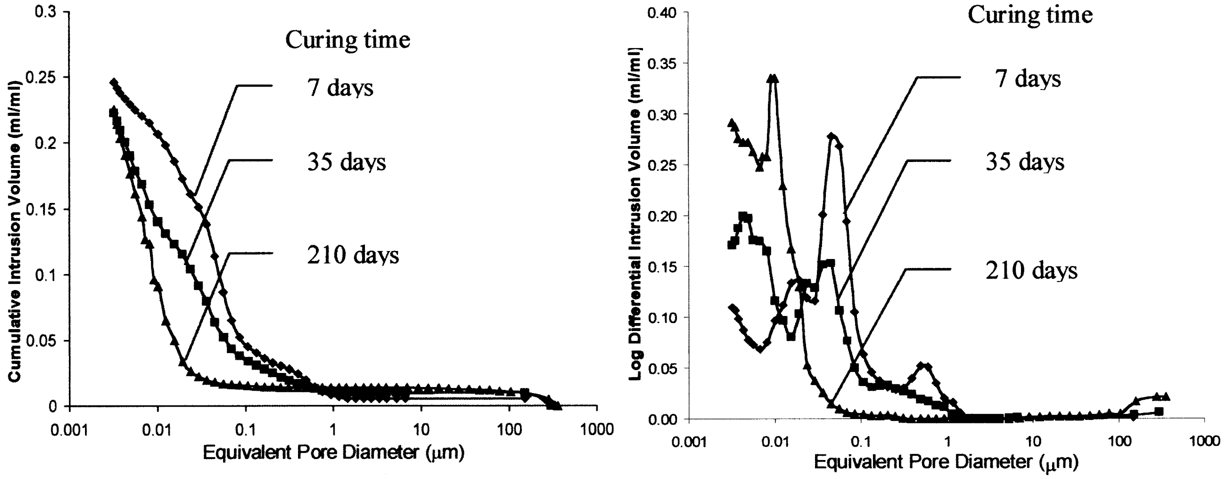

Fig. 4. Pore size distribution of cement paste with W/C at 0.4 at 7, 35, and 210 days of curing time.

whose diameter ≥ 0.01 μm. The pores whose diameter < 0.01 μm are considered as gel pores whose effects on permeability should be counted differently. This assumption is made based on the findings of Mehta and Manmohan [23] that the pores whose diameter < 0.029 μm do not affect much of the permeability.

The pore size distribution of cement pastes cured at 7, 35, and 210 days are shown in Fig. 3 and Fig. 4. From the figures, it is clearly seen that the average size and total intrusion volume of mercury decrease with the increase of curing time. The critical pore diameter has been determined at the point $dV/d \log r = 0$. It is the pore diameter corresponding to the peak of curves in the log differential intrusion volume vs. equivalent pore diameter. The physical meaning of critical pore diameter is the pore diameter above which no connected path could form throughout the sample. It is generally accepted that the smaller the critical pore diameter, the finer the pore structure. In 35th and 210th day, the curves in the log differential intrusion volume vs. equivalent pore diameter sometime show the two peaks. The first peak is larger than 0.01 μm and the second peak is always smaller than 0.01 μm, and, sometimes, it is below the MIP measurement range. This phenomenon is due to the presence of C-S-H gel. The C-S-H gel is produced more with curing time. This hydration product gradually blocks the percolated capillary pores. Therefore, in the cement paste, there are two different pore systems. First, is the capillary pore system with diameter larger than 0.01 μm. The second is the gel pore system with diameter smaller than 0.01 μm. In the log differential intrusion volume curves, the right peak is corresponding to the capillary pore structure and the left peak is related to the gel pore structure.

4.2. Water permeability

It should be noted that the water permeability results are notoriously variable. The data in Table 2 are the means of three specimens, the variation of these three specimens is about 70–100%. The permeability of cement paste with W/C ratio 0.3, and curing time 210 days is too small to be measured as the water penetration depth is smaller than 1 mm.

Table 2 shows the details of calculation of water permeability based on the proposed model. The calculated permeability is compared to measured permeability.

Table 2
Permeability from calculation and measurement

	W/C = 0.3		W/C = 0.4		
	7th day	210th day	7th day	35th day	210th day
$\phi_{\text{capillary}}$	0.174	0.059	0.2069	0.129	0.091
l_c (μm)	0.0686	0.0101	0.0453	0.0363	0.0101
α	0.53	0.732	0.69	0.85	0.93
C-S-H volume fraction in solid phase	0.51	0.618	0.602	0.81	0.70
k_l (m^2)	1.201×10^{-23}	2.04×10^{-23}	1.90×10^{-23}	2.55×10^{-23}	2.85×10^{-23}
k_h (m^2)	2.52×10^{-17}	5.46×10^{-19}	1.1×10^{-17}	1.68×10^{-17}	5.46×10^{-19}
k_{cal} (m^2)	2.22×10^{-21}	4.33×10^{-23}	1.83×10^{-20}	2.86×10^{-22}	1.02×10^{-22}
k_{meas} (m^2)	2.66×10^{-21}	$< 2.69 \times 10^{-23}$	8.11×10^{-21}	3.47×10^{-22}	1.22×10^{-22}

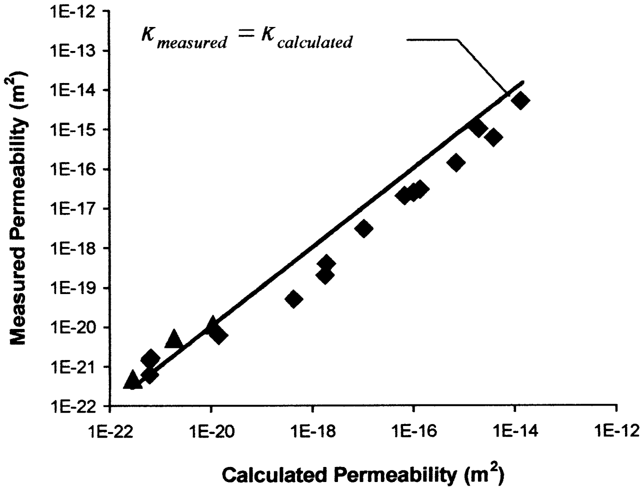

Fig. 5. Correlation between the calculated and experimental permeability.

This model can also be verified by the experimental results obtained by other researchers. Fig. 5 includes the experimental data from Hughes' [4], Christensen's [8], and our work. It covers the most possible range of OPC paste permeability from as low as 10^{-22} m^2 to as high as $\times 10^{-13}$ m^2. It proves that permeability GEM model can be used to predict the permeability of both porous and dense OPC paste.

5. Conclusion

Permeability of cement paste relates to the both capillary pores and gel pores. This bicomposite microstructure distinguishes cement paste from stone and rock in water transport mechanism. It is also the reason why the Katz and Thompson theory cannot directly apply to predict the permeability of cementitious material.

(1) When the cement paste is very porous, capillary pores form a continuous network to cover the whole material. Water mainly flows inside this capillary pore network. The contribution from gel can be ignored. In this case, the Katz and Thompson theory can predict the permeability quite well.

(2) When the cement paste is less porous, part of the capillary pores are blocked by the hydration product. Water flows inside both capillary pores and gel pores to penetrate the material. Permeability of the material depends on how the two phases play off each other. Mathematically, this interplay can be expressed by GEM theory.

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