論文 A Permeability Model of Concrete Considering Its Microstructural Characteristics

Rajesh P. CHAUBE[1] and Koichi MAEKAWA[2]

ABSTRACT : A brief review of methods concerning the prediction of permeability of concrete is discussed. An analytical model is proposed to predict the permeability of concrete, considering the random geometrical characteristics of micro pore-structure as obtained from mercury intrusion porosimetry. Also a model of viscosity of pore water in cementititous materials is proposed to explain the anomalies concerning water permeability of concrete. The gas and liquid permeability of various samples of usual and deteriorated mortar are reasonably predicted.
KEYWORDS : Permeability, pore-structure, durability, viscosity, mass transport, porous media.

1. INTRODUCTION

The transport phenomenon in porous materials has been extensively studied in the past. These studies cover a wide variety of porous media ranging from soil, stones and cementitious materials to various artificially developed synthetic materials and so on. Numerous mathematical models have been proposed that deal with the prediction and understanding of various transport coefficients like permeability of these materials. Due to the recognition of the fact that transport coefficients and pore structure of the porous media are interrelated, we can find many approaches that build upon this correlation. However, abundant diversity in the geometrical as well as physio-chemical characteristics of porous structures has limited the universal applicability of these methods.

Owing to the durability problems, transport phenomenon in construction materials, especially concrete has also been a subject of thorough investigation and several studies have tried to interrelate the transport coefficients notably permeability to the microstructure. Aim of this paper is to give a brief overview of the existing microstructure based permeability models and then propose a simple micro-structure based mathematical model of permeability of concrete which in part is derived from the works in soil-science. The proposed models are subsystem of a larger durability evaluation system of concrete, combining moisture transport, hydration and micro-structure formation processes [1].

2. REVIEW OF PORE STRUCTURE BASED PERMEABILITY MODELS

Many of the models put forward to interrelate permeability and microstructure include some correction factors that work solely for similar group of materials. Even for a specific material like concrete, different researchers have suggested different microstructure properties and empirical correction factors as the parameters in their models to predict permeability. Mehta[2] suggested a rather empirical formula for the prediction of permeability as

[1] Graduate Student, Department of Civil Engineering, The University of Tokyo
[2] Professor, Department of Civil Engineering, The University of Tokyo

$$K_I = \exp(3.8V_1 + 0.2V_2 + 0.56\times10^{-6}\,TD + 8.09\,MTP - 2.53) \quad (1)$$

where, K_I : permeability coefficient; V_1 and V_2 : pore volumes in the >1320Å and 290-1320Å range, respectively; *TD*: threshold diameter; *MTP*: total pore volume divided by the degree of hydration. It was suggested by Nyame[3] that the maximum continuous pore radius has a close relationship with permeability. Whereas, median or average pore radius of the porosity distribution has been suggested as the controlling factor by others[4,5]. Garboczi [6] reviewed many classical and current pore structure theories and suggested KT theory as a permeability model with universal appeal. This model as such has no adjustable parameters and all the quantities can be measured experimentally.

$$k = (1/226)\left(d_c^2/F\right) \quad (2)$$

where, k: intrinsic permeability; d_c: critical diameter obtained from the threshold pressure in mercury injection experiment; F: formation factor which is the ratio of brine conductivity in the pore space to porous media conductivity (measured experimentally). It appears that KT model gives reasonable estimates of intrinsic permeability. However, criticism of this theory has been directed towards difficulty in measuring accurately the inflection point or threshold pressure in the mercury injection experiment, which due to crack like pore characteristics of concrete may not be even present at all in some cases. Moreover, the theory is not so successful in predicting the permeability values of mortar with *W/C* ratios less than 0.4 [7]. Authors chose a different approach for permeability modeling because, the KT theory itself does not indicates anything about relative permeability or permeability of partially saturated porous media, which implies that it cannot be easily used in a computational scheme which combines the partially-saturated transport, micro-structure formation and hydration in concrete [1]. Theoretically, the model described in next section does not gives very different results compared to the one obtained by KT theory but it is more conducive to a coupled computational scheme of hydration, mass transport and pore-structure formation.

3. INTRINSIC PERMEABILITY MODEL

Lets consider a section of the porous media of small but finite thickness dx as shown in Fig. 1. Our goal is to deduce effective intrinsic permeability parameter of the porous media based on the permeation probability through this section. Let Ω_A represent the average *aerial* distribution function of pores exposed on any arbitrary face cut perpendicular to the flow, such that the total aerial porosity ϕ_A is equal to the term $\int \Omega_A\, dr$. Aerial and volumetric porosity are related to each other as,

$$\phi = n\phi_A \quad (3)$$

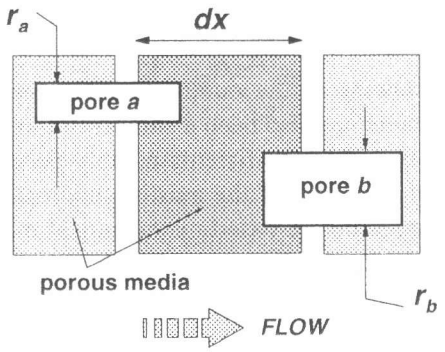

Fig. 1: Probability of permeation across a section of the porous media.

where, n : tortuosity factor = $(\pi/2)^2$ for a uniformly random porous media, ϕ_A : aerial porosity, ϕ : volumetric porosity of the porous media. The fractional area of pores of radius r_a and pores of radius r_b at either face of the section can be obtained as

$$dA_a = \Omega_A dr_a \quad dA_b = \Omega_A dr_b \quad (4)$$

From a statistical viewpoint, the probability of permeation p_{ab} through a and b pores of this section is a product of the normalized areas dA_a and dA_b (or aerial porosity's) of the pores of radius r_a and r_b,

$$p_{ab} = dA_a dA_b \quad (5)$$

It has to be noted that we assume an independent arrangement of pores over the section. For such a case, integrating eq. 3 gives the total penetration probability as ϕ^2. However, if the arrangement of

pores in the porous media were to be constant, the penetration probability p_{ab} as given by eq. 5 would be unity for the same pore radius and zero for others, resulting in a total penetration probability of ϕ which is the classical assumption usually followed. Next we consider a steady state laminar flow through the porous media which is idealized as consisting of a bundle of straight capillary tubes. For such a simple model, total flow through the porous media Q can be obtained as [8],

$$Q = -\left(\frac{1}{8\eta}\int_0^\infty r^2 d\Omega_A\right)\frac{dP}{dx} \tag{6}$$

where, η: fluid viscosity; dP/dx: fluid pressure gradient. In reality however, pores are not a continuous bundle of capillaries. Moreover, a permeation probability is associated for flow across any section and various other geometrical and scale effects can alter the flow behavior significantly. The average flow behavior through a joint of pores of different radii, might be best represented by a pore whose radius is the geometric mean of two pore radii. In other words, we assume that the flow through the system of pores of radii r_a and r_b can be represented by an equivalent pore of radius r_{eq} given by

$$r_{eq}^2 = r_a r_b \tag{7}$$

This assumption appears to give a more balanced weightage to the entire distribution and better estimates of permeability as compared to the conventional methods which give a rather skewed weightage to the distribution[4,5]. Taking these factors into account, we obtain a modified expression for total flow through the porous media by integrating the flow contributions from all the possible pair combinations of pores of the porous media as,

$$Q = -\left(\frac{1}{8\eta}\int_0^\infty\int_0^\infty T\, r_{eq}^2\, dA_a dA_b\right)\frac{dP}{dx} \tag{8}$$

where, T : an unknown parameter which is dependent on the geometrical and scale characteristics of the porous media. We have fixed this parameter as unity for rest of this study. Simplifying eq. 8 and comparing it to the Darcy's law gives intrinsic permeability of the porous media as

$$k = \frac{1}{8}\left(\int_0^\infty r d\Omega_A\right)^2 \approx \frac{\phi^2}{50}\left(\int_0^\infty r dV\right)^2 \tag{9}$$

where, $dV = d\Omega_A/\phi_A$ is the normalized volumetric porosity distribution. The only variable input parameter in above expression is the porosity distribution of the porous media. A note of caution is due when applying eq. 9 to the microstructure of *hcp* as obtained by MIP (Mercury Intrusion Porosimetry) to obtain the intrinsic permeability of *hcp*. From a theoretical viewpoint, all of the conductivity models emphasize the role of larger pores to some extent. That is, larger pores are the one that contribute most to the flow if connected continuously. Due to this reason, it is possible to get erroneous results, if for example MIP data is used without applying any correction for larger pores. For *hcp* samples authors recommend that the pores above first inflection point* in the MIP curve or 1000nm, whichever is greater, should not be used in the analysis, since the test samples are crushed before testing and might contain some inadvertent macroscale defects.

From the definition, intrinsic permeability is a basic micro-structural characteristic and should not be dependent on the fluid used to measure it. However, it has been extensively reported that different values of intrinsic permeability of a porous media are obtained when measured with different fluids, after applying the density and viscosity normalization's. Fig. 2 shows the data of intrinsic permeability of different concrete's as reported by various researchers. For these measurements permeability measurements for different concrete were taken by gas and water, and converted to intrinsic permeability by applying the density and viscosity normalization's. This difference has been

* The point on MIP curve (where cumulative intruded volume V is plotted against log of the pore radius r), which shows a distinct rise in the volume V of intruded mercury.

attributed to various reasons, namely : (**1**) Gas slippage theory [14]; (**2**) Plasticity of water (Visco-plastic nature of pore liquid); (**3**) long-range intra molecular force theory [10]; (**4**) Yield Shear of pore fluid. (A fictitious shearing force acting on pore walls) [11]; (**5**) Swelling of hydrates [9]; (**6**) Resumption of dormant hydration and self-sealing [9]; (**7**) Altered viscosity of pore-water [12]

In addition to above, experimental problems in measuring extremely small values of water permeability [9] has made it practically impossible to trace out the exact cause for the discrepancies in intrinsic permeability's as obtained by gas and water. However, it must be pointed out that the permeability values obtained by using gas, oil or even alcohol as the measuring fluid has traditionally produced more reliable, reproducible and consistent results. It has also been found out and reported that usually it takes more than 20 days to get steady state flow conditions in the case of water permeability. Even, a reduction in water flux or self-sealing behavior of concrete when exposed to water is also reported [9]. For this reason, authors tested each of the above stated cause against a large set of database of water and gas permeability available in the literature but none of the theories could explain the discrepancy completely. Furthermore, some counter-evidence is also available in the literature which negates some of the theories like the delayed hydration of unhydrated CSH in the presence of water [13]. Only altered nature of pore water which probably changes the pore water viscosity in a time-dependent manner seems to be the most likely cause of large difference in intrinsic permeability as measured by gas and water. This aspect is discussed in detail in the next section.

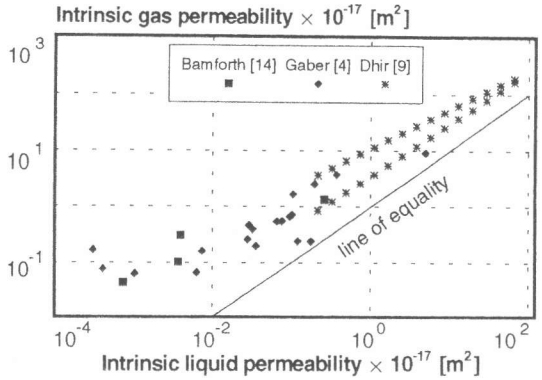

Fig. 2: A non one to one relationship of intrinsic gas and liquid permeability.

4. WATER PERMEABILITY OF CONCRETE

From the theory of viscosity the actual viscosity η of a fluid under non-ideal conditions at absolute temperature T can be obtained as

$$\eta = \eta_i \exp(G_e / RT) \tag{10}$$

where, G_e : free energy of activation of flow in excess of that required for ideal flow conditions, η_i : viscosity under ideal conditions. R : Universal gas constant. The actual permeability of water can be evaluated if the effect of non ideal viscosity of water is taken into account in eq. 8. Past researchers have reported a viscosity about one or two order higher than the ideal viscosity of water under thin quartz plates. The exact physical cause of this phenomenon is currently not known, but authors have considered a phenomenological thermodynamic approach to explain this mechanism. When concrete is exposed to water, a transient phase of apparent reduction in the water permeability is observed until it reaches a *final* value which is quite smaller than the permeability as expected under ideal conditions. One dimensional water sorption experiments in concrete also show a deviation from the square-root law of water absorption after few days [11]. However, drying out the specimens has shown to restore the initial conditions, which indicates that the time-dependent change of water permeability of concrete is indeed a state dependent thermodynamic phenomenon.

To account for such time-dependent behavior, we hypothesize that there exists a pore-water and micro-structure interaction which is a time lag phenomenon and roughly depends on the history of pore humidity. That is to say that a change in pore humidity brings about a gradual interaction or altered state of the microstructure and pore water system leading to delayed changes in the liquid

viscosity and hence observed permeability. The additional energy for the activation of flow may be dependent on the altered state of the system and can be imagined to be brought about a fictitious delayed pore humidity H_d. In turn, H_d is dependent on the actual pore humidity H history and micro-structure characteristics. In a mathematical model, this phenomenon is represented by a simple *Kelvin chain* model where, the dash-pot viscosity η_d represents the responsiveness of the microstructure to changes in the actual pore humidity H (stress analogy) that brings about a change in H_d (strain analogy). Our goal through this model is to get the extra energy G_e required for the activation of flow at any point and time such that effective non-ideal viscosity of the pore fluid (η) and therefore permeability can be computed. The computational model is mathematically described below

$$G_e = G_{\max} H_d \quad ; \ddot{H}_d + \left(\frac{1+\ddot{\eta}}{\eta}\right) H_d = \frac{H}{\eta}$$

$$\eta = a\left(1 + bH_d^c\right) \quad ; a = \left[1.59\left(\frac{\phi - \phi_m}{\phi_m}\right) + 0.7\right]^5 \quad ; b = 2.5a \; ; c = 2.0 \tag{11}$$

where, G_{max}: Maximum additional Gibbs energy for the activation of flow = 3500Kcal/mol (assumed constant for all cases), ϕ: total suction porosity, ϕ_m: porosity accessible by mercury intrusion.

5. VERIFICATIONS

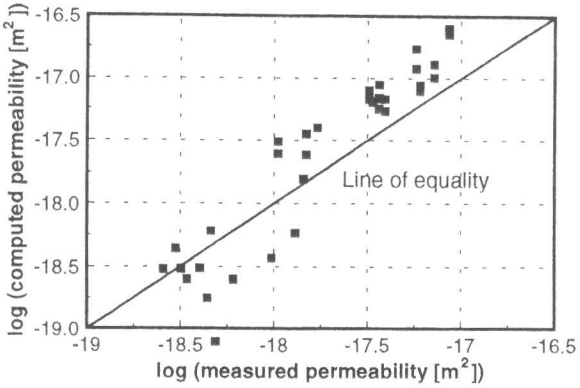

Fig 3 : A comparison of measured and computed intrinsic gas permeability data based upon pore distribution obtained by MIP.

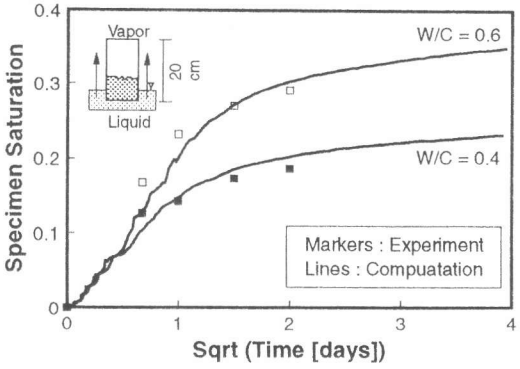

Fig 4 : Prediction of absorption behavior in mortar samples based upon history dependent viscosity model of pore water.

The permeability models discussed above were installed as a part of the generic hydration, mass transport and pore-structure development FEA program DuCOM, which was used for most of the computations [1]. The intrinsic permeability model was verified by comparing the computed permeability value to those obtained from experiments. The experiments were a part of the research project on long-term durability of concrete in which several kinds of mortars were tested. The water to powder ratio by volume ranged from 78% to 190%. The sand volume fractions by compaction ratio (S/S_{lim}) ranged from 0.2 to 0.8. Some mortar mixes with high lime volume fractions of upto 17% of the mix volume were also prepared. After sufficient curing, one pair of specimens was exposed to accelerated calcium leaching tests. Gas permeability measurements and porestructure measurements using MIP of both the exposed and non-exposed group of specimens were done. Fig. 3 shows a comparison of the measured and predicted intrinsic permeability values for many specimens. In the analysis, the porosity distribution lying above 1.1μm pore radius was neglected for all the specimens due to experimental errors usually associated with large pore radii data in MIP method. The modified water permeability model has been verified as a part of the coupled computational system of moisture-transport, hydration and structure formation. It appears that this model works well for

arbitrary drying-wetting cases of the porous media and weight change curves of mortar specimens due to moisture gain or loss can be traced quite satisfactorily with time. Fig. 4 shows the moisture gain curves for different mortar specimens which were exposed to one dimensional water sorption experiments. A clear deviation from the square-root law of water sorption can be observed here which is also reasonably predicted because of a history dependent water permeability model.

6. CONCLUSION

The focus of this paper has been to propose a simple and workable intrinsic permeability model based on micro pore distributions after a review of porestructure based prediction models. Attention has been drawn to the widely reported but rarely investigated anomaly observed in the comparison of intrinsic permeability data as obtained from water and gas permeability measurements. To this end, authors have suggested that a higher viscosity of pore water may be the cause of observed anomalies. Based upon thermodynamic concepts, a history dependent viscosity model of pore-water is proposed which can explain lower water permeability results and the *sealing phenomenon of concrete*. The proposed models can satisfactorily predict the experimental observations.

ACKNOWLEDGMENTS

The authors sincerely acknowledge the cooperation of Mr. Yuji SAITO of Obayashi Research Institute for kindly providing the MIP and gas permeability data of various samples.

REFERENCES

1. Chaube, R.P. and Maekawa, K. (1995), Coupled moisture transport, structure formation and hydration in cementitious materials, *Proceedings of the JCI*, Vol. 17, No. 1, pp.639-644.
2. Mehta, P.K. and Manmohan C. (1980), Pore size distribution and permeability of hardened cement paste, *7th. Intl. Congr. Chem. Cem.*, Paris, Vol.III, VII-1/5.
3. Nyame, B.K. and Illston, J.M. (1981), Relationships between permeability and pore structure of hardened cement paste, *Magazine of Concrete Research*, Vol. 33, No. 116, pp.139-146.
4. Reinhardt, H.W. and Gaber, K. (1990), From pore size distribution to an equivalent pore size of cement mortar, *Materials and Structures*, Vol. 23, No. 133, pp.3-15.
5. Hughes, D.C (1985), Pore structure and permeability of hardened cement paste, *Magazine of Concrete Research*, Vol. 37, No. 133, pp.227-233.
6. Garboczi, E.J. (1990), Permeability, diffusivity and microstructural parameters: a critical review, *Cem. and Concr. Res.*, Vol. 20, pp.591-601.
7. Halamickova, P. etal. (1995), Water permeability and chloride ion diffusion in portland cement mortars: relationship to sand content and critical pore diameter, *Cem. and Concr. Res.*, Vol. 25, 4, pp.790-802.
8. Quenard, D. and Salle, H., Water vapor adsorption and transfer in cement based materials: a network simulation, *Materials and Structures*, Vol. 25, 1992, pp.515-522.
9. Dhir, R.K., Hewlett P.C. and Chan Y.N. (1989), Near surface characteristics of concrete: intrinsic permeability, *Magazine of Concrete Research*, Vol. 41, No. 147, pp.87-97.
10. Luping, T. and Nilsson, L.O. (1992), A study of the quantitative relationship between permeability and pore size distribution of hardened cement pastes, *Cem. and Concr. Res.*, Vol. 22, pp.541-550.
11. Pokharel, A.P. (1992), Idealization of water sorption in concrete, M.Eng. Thesis No. ST-92-18, Asian Institute of Technology.
12. Volkwein, A. (1993), The capillary suction of water into concrete and the abnormal viscosity of the pore water, *Cem. and Concr. Res.*, Vol. 23, pp.843-852.
13. Hearn, N., Detwiler, R.J. and Sframeli, C. (1994), Water permeability and microstructure of three old concrete, *Cem. and Concr. Res.*, Vol. 24, No. 4, pp.633-640.
14. Bamforth P.B. (1987), The relationship between permeability coefficients of concrete using liquid and gas. *Magazine of Concrete Research.*, Vol. 39, pp.3-11.