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Hygro-Gradient Model for Permeability of Unsaturated Cementitious Composites

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Abstract

A new method for predicting the water absorption process of unsaturated cementitious composites is proposed, and its functionality is experimentally verified. The mechanism of the capillarity on water absorption process is mathematically termed by a slip boundary condition of micro-flow of pore water, and employed to an unsaturated water permeation on the scheme of multi-scale modeling. The rapid sorption just after the exposure to condensed water is fairly simulated owing to the non-local formulation of hygro-gradient, which simply represents the thermodynamics of non-equilibrated states in dry pores. The proposed model of complexity of micro-pore connection is examined in terms of the initial water content, porosity and saturation of micro-pore structure and volume ratio of aggregate. It is further examined in terms of the intrinsic hydraulic profile by using the Boltzmann’s transform.

1. Introduction

Water transport in cement-based materials is an important issue since it significantly affects chemical ion ingress, steel corrosion, freeze-thaw cycles, calcium leaching and other durability related events (Basheer et al. 2001; Tang et al. 2015). Permeability, which is defined as the flow rate of a sole fluid through a solid under the unit pressure gradient, is the property that partly controls the process of water transport, and of great importance in evaluating the durability of such materials (Zhou 2014a). Real structures are rarely saturated (Zhou 2014a), and unsaturated flow is the dominant mechanism of water transport through them in practice. A water absorption test is a convenient and standard one for specify the unsaturated permeability (Hall 1989; ASTM 2004).

Many experimental and analytical studies involving water absorption have been conducted (Hall 1989; van Bellegem et al. 2016), and several unsaturated permeability models have been proposed to predict moisture and water transport. Most of the models use the extended Darcy’s law to describe the unsaturated flow through a porous medium (Maekawa et al. 2003). The permeability in cement-based materials is significantly affected by the water content and its profile expressed by the hygro-gradient of pore water pressure. Udell (1985) fitted the experimental data by Fatt and Klikoff (1959) to obtain a simple relative permeability. Corey (1954) and Maréchal and Beaudoux (1992) also presented a similar expression that assumes a constant initial saturation. Another widely used model is the VGM model (Mualem 1976; van Genuchten 1980), which is also a function of the liquid saturation. Recently, Zhou (2014a,b) derived an expression of the unsaturated water permeability from the hydraulic diffusivity obtained by a sorption test.

Although the unsaturated permeability predictions of these models are reasonably accurate, there is some room of improvement for real-time water absorption. This is probably due to the complex internal porosity of a cement-based material (Gonen and Yazicioglu 2007) and the significant dependence of the absorption rate on the properties of fluid and its interactions with the porous medium (Li and Firoozabadi 2000).

Another method to simply estimate water absorption involves the direct utilization of the hydraulic diffusivity denoted by $D(\theta)$ [m²/s]. An example is the exponential expression in terms of $D(\theta)=D_0 e^{-n\theta}$, where $D_0$ [m²/s] and $n$ are constants (Kutilek and Valentová 1986) which vary with the initial state. In practical applications, $n$ is often set within 6–8, while $D_0$ is calculated based on the experimentally determined sorptivity (Wang and Ueda 2011), which is defined as the slope of the cumulative absorbed water curve expressed by the $\theta^{1/2}$ law (Hall and Hoff 2011). This model has been confirmed to be useful in some cases (Wang and Ueda 2011; Bellegem et al. 2016).

However, utilization of the model requires systematically arranged tests and measurements in order to identify porosity, initial water content and sorptivity of great importance, which facilitate the prediction of the water absorption process. Thus, a useful expression of the water transport coefficient is required to conveniently simulate real-time water absorption.

Considering the availability of just few models for appropriate simulation of water absorption, a model for

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predicting the whole process of water absorption was developed based on the multi-scale concrete model (DuCOM) established by Maekawa et al. (1996, 1999, 2003). The model affords a complete framework of the hydration phenomenon, microstructure formation, and moisture transport through a cement-based material. It produces precise moist vapor transport and its spatial distribution, as determined by their fair agreement with experimental ones (Ishida et al. 1998; Maekawa et al. 2003, 2008), when unsaturated moist boundary conditions would be applied to structural concrete.

However, it has been recognized that when condensed liquid water boundary conditions would be applied on the surfaces, the model’s applicability is comparatively less compared to the case of quasi-vapor transport of high accuracy. In a practical use, the mass transport coefficient on the surface boundaries can be magnified by a factor of about 100-500 times. This may be attributable to the rapid local bulk motion of condensed water into larger micro-pores nearby surfaces where the greater hygro-gradient develops. It means that the moisture state is far from quasi-equilibrium.

Based on the foregoing, and using several physical assumptions of rationale, more versatile permeability model for condensed water on surfaces is proposed for simulating water transport through a cement-based material. It describes the equilibrium condition of the liquid-vapor interface in a cylindrical pore.

\[
\frac{\partial \theta}{\partial t} + \text{div}(J(\theta, \nabla \theta)) + Q = 0
\]

where \( \theta \) [kg/m\(^3\)] is the mass of water in a unit volume of concrete, \( t \) [s] is the time, \( J \) [kg/m\(^2\)-s] is the moisture flux and \( Q \) [kg/m\(^2\)-s] is the sink term related to cement hydration.

Based on the extended Darcy’s law, we have the flux term of Eq. (1) as,

\[
J = -(D_{p} \nabla P_{t} + D_{r} \nabla T)
\]

where \( D_{p} \) [kg/Pa-m-s] is the combined moisture conductivity with respect to the pore pressure denoted by \( P_{t} \) [Pa] and \( D_{r} \) [kg/K-m-s] is the moisture conductivity with respect to the temperature \( T \) [K]. During the water absorption process, the variation of temperature (20 ± 2 °C) was controlled to be minimal in this study. Then, the right term of Eq. (2) becomes nil substantially. Here, \( D_{p} \) is composed of two parts as,

\[
D_{p} = k_{i} + k_{v}
\]

where \( k_{i} \) [kg/Pa-m-s] is the unsaturated liquid permeability and \( k_{v} \) [kg/Pa-m-s] is the vapor one.

2.1.2 Vapor permeability

The vapor permeability is dominated by the Knudsen effect (Quenard and Sallee 1992), which is in turn determined by the Knudsen number as,

\[
N_{k} = l_{m} / 2r_{e}
\]

where \( l_{m} \) [m] is the free path length of a water molecule and \( r_{e} \) [m] is the effective pore radius which is given by the actual pore radius \( r \) [m] minus the thickness of the adsorbed water layer [m]. Vapor can be transported just through unsaturated pores. Hence, by taking the tortuosity into consideration and using the modified Fick’s law, the vapor flux \( J_{v} \) [kg/m\(^2\)-s] under isothermal conditions can be expressed as (Maekawa et al. 1999),

\[
J_{v} = \frac{\rho_{v} \phi D_{v} b (1 - S)}{n + N_{k}} \nabla h
\]

where \( \rho_{v} \) [kg/m\(^3\)] is the vapor density under saturated condition, \( \phi \) is the porosity, \( D_{v} \) [m\(^2\)/s] is the vapor diffusivity, \( n \) is the tortuosity factor \((\pi/2)^{2}\) (Maekawa et al. 1999), \( S \) is the water saturation of porosity and \( h \) is the relative humidity. In order to express the vapor permeability in the first term of Eq. (2) together with liquid water permeability, the Eq. (5) is described as,

\[
J_{v} = \frac{\rho_{v} \phi D_{v} b (1 - S) \nabla h}{n + N_{k} \nabla P_{t}}
\]

Then considering the Kelvin’s equation which describes the equilibrium condition of the liquid-vapor interface in a cylindrical pore,

\[
P_{t} = \frac{\rho_{l} RT}{M} \ln h
\]

where \( M \) [kg/mol] is the molecular mass and \( R \) [J/mol-K] is the gas constant and \( \rho_{l} \) [kg/m\(^3\)] is the liquid water
density, the vapor permeability is further obtained as,
\[ K_v = \frac{\rho \phi D_{B}}{n} \frac{1-S}{1+N_x} \frac{Mh}{\rho RT} \]  
(8)

2.1.3 Condensed water permeability
Condensed liquid water flow through a cement-based material can be idealized as a steady laminar flow, which obeys the Hagen-Poiseuille equation (H-P equation), and the pore network can be considered as a bundle of capillary tubes (see Fig. 1). In this figure, a section of porous media (cement-based material) with a finite thickness of \( dx \) is shown and this section is perpendicular to the water flow direction. The water flows through two faces of this section on which the pore radii fitting the same pore size distribution are represented by \( r_a \) and \( r_b \) respectively. The total liquid flux \( J_l \) \([\text{kg/m}^2 \cdot \text{s}]\) through the medium is considered to be composed of the flows between all possible pairs of pores (Quenard and Sallee 1992) and by integrating the flux is obtained as,
\[ J_l = \frac{\rho \phi}{8\eta} \int_0^r r^{-1} a_i dA_i dA_b dV \]  
(9)

where \( A_i \) \([\text{m}^2] \) is the corresponding pore cross-sectional area, \( r_i \) \([\text{m}] \) is the arbitrary pore radius and \( \eta \) \([\text{Pa} \cdot \text{s}] \) is the water viscosity expressed as,
\[ \eta = \eta_i \exp(G_e / RT) \]  
(10)

where \( \eta_i \) \([\text{Pa} \cdot \text{s}] \) is the intrinsic water viscosity under ideal conditions and \( G_e \) \([\text{kcal/mol}] \) is the equivalent free energy, which is the function of the rate of moisture change (Maekawa et al. 1999). Thus, the unsaturated liquid permeability can be expressed in an integral form based on the porosity distribution function and tortuosity \((\pi/2)^2\) as,
\[ K_i = \frac{\rho \phi}{50\eta} \left( \int_0^r r dV \right)^2 \]  
(11)

where \( V \) is the normalized pore volume, \( r \) \([\text{m}] \) is the normalized pore radius, and \( r_c \) \([\text{m}] \) is the critical pore radius at which an equilibrated interface between the liquid and the vapor is created as illustrated in Fig. 2. The liquid permeability \( K_l \) at full saturation is the conventional permeability when \( r_c \) equals to the maximum pore radius, or tends to infinity.

2.1.4 Boundary condition
When solid is exposed to water, the contacting surface is immediately saturated and water absorption occurs simultaneously. Then, we have the initial boundary condition expressed in a simplified one-dimensional form as,
\[
\begin{align*}
&z = 0, \quad t > 0, \quad \theta = \theta_i \\
&z > 0, \quad t = 0, \quad \theta = \theta_s \\
&z \to \infty, \quad t > 0, \quad \theta = \theta_f
\end{align*}
\]  
(12)

where \( Z \) \([\text{m}] \) indicates the position in the employed finite element mesh (Fig. 3), \( \theta_i \) \([\text{kg/m}^3] \) and \( \theta_s \) \([\text{kg/m}^3] \) are the initial and saturated water contents, respectively. One-quarter of the experimental specimen is used for the analysis domain, and the saturated boundary nodes are indicated by red dots in Fig. 3. Since the thermodynamics states vary according to location and time, the sorp-
tion test specimens shall be treated as 3D solid volume with boundary elements on the surface where ambient states are defined according to the curing and exposure conditions.

2.2 Literature and referential models

2.2.1 Model structure

Five permeability models denoted by Eqs. (13) - (17) are focused on for discussion of this study; four literatures referred in Section 1, and the referential one adopted in the multi-scale platform of DuCOM as mentioned in the previous section. All the models are expressed as a function of the water saturation of the medium, and indicate that the relative permeability increases with increasing saturation. This implies that the water sorption gradually increases and finally reaches the maximum.

\[
\text{Fatt & Klikoff model: } k_{rw} = S^3 \quad (13)
\]

\[
\text{VGM model: } k_{rw} = S^m (1 - (1 - S)^{1/m})^2 \quad (14)
\]

\[
\text{Corey model: } k_{rw} = \left(\frac{(S - 0.05)}{(1 - 0.05)}\right)^4 \quad (15)
\]

\[
\text{Zhou model: } k_{rw} = \frac{1}{\alpha} \theta^{-b} (\alpha \theta - \theta + 1) \quad (16)
\]

\[
\text{DuCOM model: } k_{rw} = \left(\int_0^\infty \frac{r}{\cap V} dr\right)^2 \quad (17)
\]

where \(k_{rw}\) is the relative permeability, given by the unsaturated permeability divided by the full saturated permeability \(K_s\) [kg/Pa m s] in Eq. (18), \(q\), \(m\) and \(b\) are fitting parameters and \(\Theta\) is the reduced saturation, given by \((\theta - \theta_i)/(\theta_f - \theta_i)\).

\[
K_s = \frac{\rho g^2}{50 \eta} \left(\int_0^\infty \frac{r}{\cap V} dr\right)^2 \quad (18)
\]

The comparison of these models is illustrated in Fig. 4.

Fig. 4 Water absorption simulation by referential models.

2.2.2 Evaluation

As can be observed in Fig. 4, Fatt & Klikoff model (1959) leads to the most rapid sorption after its commencement. In contrast, the sorption by VGM (1980) and Corey (1954) models exhibits much slow initial absorption followed by intermediate abrupt increases, and approaching to their converging capacity. This is due to the rapid increase in \(k_{rw}\) to its maximum as the saturation approaches to unity in each case. The predictions of these three models are obviously inconsistent with experimental data, with the two latter models particularly having the propensity to cause numerical instability.

Zhou’s model (2014a,b) and the original DuCOM as the reference in this study fairly reflect the actual trend of the water absorption, with their sorption curves both increasing at a nearly constant rate, then, gradually approaching to the capacity. All these models have been examined to be quite reliable for unsaturated moisture (vapor) transport, whereas the trends in Fig. 4 are much divided from the sorption test. This trend underscores the need for the development of improved permeability model for condensed water. The key issue is the rapid initial sorption.

The solid close to the surface is far from quasi-equilibrated states of thermodynamics due to the rapid change of saturation. Then, this is thought to be a source of discrepancy on computed initial sorptivity. Then, the authors will propose the permeation modeling to consider how far the hygro-state would deviate from the quasi-equilibrium. This is the primary objective of the present study.

2.3 Improved modeling

2.3.1 Hydraulic and capillary potentials

H-P formulae is an exact solution of the steady-state Navier-Stokes equations (Zou and He 1997), and useful to describe liquid flow through a porous medium, working particularly well under the external steady pressure (Fig. 5a). Under this condition, the driving force of the liquid flow is the pore pressure gradient, which is

![Fig. 5 Schematic illustration of (a) steady pressure and (b) capillary force of pore water.](image-url)
determined by the external pressure and the pore structure. This condition is the closest to steady flow through a tube.

Another possible state is that of moisture transport through the pore network. This consists of five steps (Maekawa et al. 1996): (a) molecular diffusion and adsorption, (b) moisture flux due to humidity gradient, (c) condensation at pore neck, (d) flow in thin liquid films, and (e) saturated flow (Fig. 6). The moisture transport is driven by the vapor pressure gradient, as expressed by Eqs. (2), (3), and (5), and can be regarded as a steady vapor flow.

Capillarity is the dominant factor of water absorption when gravity is negligible owing to a very small maximum height of the water frontier (Hall 1989; Bellegem et al. 2016). Conventionally, the extended Darcy’s law is used to describe absorption driven by the capillary force, with the original permeability replaced by an unsaturated permeability, which is dependent on the water content in the case of cement-based material. Here, water absorption process is assumed to be a steady flow although unsaturated, and the difference between saturated and unsaturated flows is dependent on only the permeability.

However, considering that a cement-based material has a pore network of complexity, an unsaturated flow driven by capillary force is hampered by the network structures such as ink-bottle pores, which also affect the capillary force. Thus, the assertion of the perfect unsaturation of micro-spaces might be early, especially when the higher hygro-gradient develops.

2.3.2 Bulk convection at surface boundaries

The capillarity is activated chiefly by the surface tension at the interface between fluid and solid pore walls (Yamamoto et al. 2013) on which the stress points are located. It is reasonable to assume the bulk convection and the local velocity of the condensed water flow at the boundary, as has been specifically reported by Yamamoto et al. (2013). Then, it is not straightforward to apply a no-slip boundary condition under this circumstance, especially in consideration of the adoption of the conventional H-P formulae. Then in this study, a slip boundary condition is tried to describe the velocity profile especially at the surface boundaries where the higher hygro-gradient develops.

The cumulative capillary potential decreases with increasing saturation, and the number of liquid-vapor interfaces also decrease as the water absorption process is in progress (Fig. 5b). This means that a given water content in a unit volume would produce varying numbers of capillary forces under different conditions in regard to the pore radius.

According to a previous study, the number of interfaces in a small pore network is higher than those in a large pore network (Kolias and Georgiou 2005). Hence, the connected pore fraction decreases with increasing capillary water saturation. Owing to the complex pore network, the foregoing phenomenon is not taken into account in existing models of capillary forces, which is calculated by using the Washburn equation (Washburn 1921):

\[ p_j = -\frac{2\gamma \cos \alpha}{r_c} \quad (19) \]

where \( \gamma \) [N/m] is the surface tension of the liquid water, and \( \alpha \) [°] is the contact angle of water on the cement-based material.

The more precise method for describing the effect of the pore network is to calculate the real unsaturated permeability and capillary force. However, this is practically difficult to achieve as the true tortuosity and connectivity can be hardly identified. As an alternative, the authors incorporate the change in the driving pressure, i.e., hygro-gradient, into the unsaturated permeability. In the improved model thus obtained, the unsaturated permeability is not only affected by the water content, but also by the pressure gradient as Yoneda et al. (2015) investigated the nonlocal driving force to cause shrinkage of concrete.

By incorporating three considerations, a new permeability equation is presented. In the new proposed model, a slip length equation is applied to describe the velocity change in the pores. It is assumed that the slip length \( \delta \) [m] occurs at the border, and it is defined as the distance into the pore wall at which the velocity extrapolates to zero (Whitby and Quirke 2007), as shown in Fig. 7.

In the original H-P equation, the velocity profile on a cylindrical cross section is parabolic as no-slip boundary and can be expressed as (Sutera and Skalak 1993),

\[ v = \frac{\Delta P}{4\eta l} \left( r_{\text{max}}^2 + r^2 \right) \quad (20) \]

where \( v \) [m/s] is the velocity of pore water along the pore length \( l \) [m], \( r_{\text{max}} \) [m] is the max pore radius on a cylindrical cross section. Similarly, under the slip boundary condition, Eq. (20) changes into,
\begin{equation}
v = \frac{\Delta P}{4\eta l[(r_{\text{max}} + \delta)^2 - r^2]} \tag{21}
\end{equation}

Thus, the velocity at the border \(v_R\) [m/s] is calculated as,

\begin{equation}
v_R = \frac{\Delta P}{4\eta l} (2r_{\text{max}} \delta + \delta^2) \tag{22}
\end{equation}

In this paper, the velocity profile is assumed linear, equaling \(v_R\) in the pore radius direction for simplicity as shown in Fig. 8. Further, by neglecting the second order small quantity \(\delta^2\), the total flux \(q\) [kg/s] across the cylindrical section is expressed as,

\begin{equation}
q = \frac{\rho \delta r_{\text{max}}}{2\eta} A(r_{\text{max}}) \frac{\Delta P}{l} \tag{23}
\end{equation}

where \(A(r)\) is the cross-sectional area of the single pipe. Then, if we assume the simple bundle of each pore pipes without mutual interaction of pores, we have the overall flux denoted by \(Q\) by integrating the flow of each pipe as,

\begin{equation}
Q = \int_0^\infty \frac{\rho \delta r}{2\eta} d\Omega_A \frac{\Delta P}{l} \tag{24}
\end{equation}

Then, we have the averaged permeation as,

\begin{equation}
K_i = \frac{\rho \delta}{2\eta} \left( \int_0^\infty r d\Omega_A \right) \tag{25}
\end{equation}

where \(\Omega_A\) is the aerial distribution function of the exposed pores on any arbitrary face perpendicular to the flow (Maekawa et al. 1999). The following holds,

\begin{equation}
\delta = 0.06 \cdot (\dot{\gamma})^{0.5} \cdot 10^{-9} \tag{30}
\end{equation}

This equation is based on the experimental results of flow rate in microchannels and Cui et al. (2004) further implemented it in a cylindrical micro tube by using the shear rate as,

\begin{equation}
\dot{\gamma} = \frac{dP}{4\eta L} \tag{31}
\end{equation}

where \(d\) [m] is the diameter of the micro tube, \(P\) [Pa] is the pressure difference between the two ends of the tube with the length \(L\) [m]. Thus, the slip length in a micro tube is expressed as,

\begin{equation}
\delta = 0.06 \cdot \left( \frac{dP}{4\eta L} \right)^{0.5} \cdot 10^{-9} \tag{32}
\end{equation}

Fig. 7 Schematic illustration of slip length.

Fig. 8 Difference between the water flow velocities in the classic H-P equation and the newly established permeability equation.
For the unsaturated pore channels in the mortar, Eq. (32) is adopted in the form as,
\[
\delta = 0.06 \left( \frac{r_c}{\eta I} \right)^{0.3} \cdot 10^{-9}
\]
(33)
where \( \frac{\Delta P_l}{l} \) is the hygro-pressure gradient, which decreases with increasing saturation and water dispersion, indicative of the effect of the decreasing number of liquid-gas interfaces.

Here, the critical pore radius \( r_c \) is used rather than the individual pore radius in the integral formula and this is attributed to the assumption that the velocity of the liquid water in the pore channel is determined by the velocity of the liquid-vapor interfaces which is decided by the critical radius. Thus, the unsaturated liquid permeability (Eq. 27, Eq. 29) reflects the effect of decreasing interfaces, the slip velocity, and the retarding effect of the pore network on the pressure. All these effects owe to the slip length by Eq. (30), which is the key point, because it bridges the permeability and the hygro-pressure gradient, and unveils the essential mechanism of the new model and the core reason why the newly proposed model is expected to be effective.

In brief, in the conventional use of H-P equation to describe water absorption, the unsaturated liquid permeability \( K_l \) is a function of the water content \( \theta \). However, with the present assumptions of a slip boundary, and considering the effect of the decreasing liquid-vapor interfaces, \( K_l \) is expressed as a function of both the water content and the capillary force gradient, namely, \( K_l(\theta, VP_l) \), by adopting the slip length equation.

The theoretical permeations of both the simple bundle and the mutual complexity of interlinkage do not encompass the effects of the possible bleeding channels (Ji et al. 2015), the interfacial transition zones around aggregates and the deviation of calculated and real pore connection and distribution system, but mere perfect randomness of micro-pores in space is assumed. Then, the authors tentatively define the index “\( \varepsilon \)” to indicate the impacts of non-ideal factors,
\[
K_i = \varepsilon \frac{\rho \delta \phi S}{2\eta n} \left( \int_0^\infty \nu r dV \right), \quad K_i' = \varepsilon \frac{\rho \delta \phi S}{2\eta n} \left( \int_0^\infty \nu r dV \right)
\]
(34)

The feasibility of this expression in practice is to be examined by simulating the water absorption process in the following chapters.

3. Experiments

3.1 Materials
All the specimens utilized in this study were cast using ordinary Portland cement (OPC) PO 42.5R, tap water, and ISO679:2009 sand. The detailed chemical composition of the cement is given in Table 1.

3.2 Experiment method
Mortar specimens for water absorption experiment were produced by using various combinations of two different water-to-cement ratios and three different sand volume fractions. The employed mix proportions are listed in Table 2, where the specimens are labelled Nos. 1-6. Nine 70×70×70 mm cubic specimens were produced for each mix proportion. After 1 day of sealed curing, the specimens were further cured in a curing room at a temperature of 22±2 °C and relative humidity (RH) of >95% for 13 days. All the specimens were then oven-dried at 70 °C for 7-10 days, at which time the change in weight of each specimen was less than 0.1 g. After drying, the mass of each specimen was measured by using a scale of accuracy within 0.01 g.

The specimens were placed in two environment chambers with RHs of 70% and 90%, respectively. Three specimens of each mix proportion were placed in each chamber, and the other three were stored under sealed conditions. The curing of the specimens under these differing humidity conditions was set up at 22 °C for 14 days. Thereafter, the specimens were sealed for 16 days to allow for relatively uniform distribution of the internal moisture, as an initial experimental condition.

The water absorption experiment was based on the gravimetric method, and performed according to ASTM C1585 (ASTM 2004). Total of 54 specimens were used. The experimental results for each type of specimen were obtained as the average of three samples for all the case of Nos. 1-6.

Table 1 Chemical composition of OPC.

<table>
<thead>
<tr>
<th>Component</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>MgO</th>
<th>SO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Percent (%)</td>
<td>55.47</td>
<td>22.84</td>
<td>6.36</td>
<td>5.77</td>
<td>3.90</td>
<td>3.04</td>
</tr>
</tbody>
</table>

Table 2 Mix proportions of mortars.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Water/ Cement</th>
<th>Cement (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Volume fraction of sand (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.35</td>
<td>1015</td>
<td>355</td>
<td>832</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>0.35</td>
<td>899</td>
<td>315</td>
<td>1032</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>0.35</td>
<td>749</td>
<td>262</td>
<td>1290</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>944</td>
<td>378</td>
<td>832</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>836</td>
<td>334</td>
<td>1032</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>0.40</td>
<td>697</td>
<td>279</td>
<td>1290</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 9 illustrates the experimental set-up. The specimen was placed in a plastic container with two glass rods used to lift its bottom surface off the container bot-
tom. Water was poured into the container, with its level controlled to 3 mm above the bottom surface of the specimen. The sides of the specimen were sealed with sealant, and the upper surface covered with a plastic film to avoid evaporation. Water was thus absorbed through only the bottom surface. The mass of the specimen was measured at intervals to calculate the cumulative amount of absorbed water with respect to time. The measurement intervals were gradually increased as 0-60 (min), 2-6 (hr), 1-9 (day). Thereafter, the specimen was immersed in water with all the sides exposed until saturation, and the final weight was measured.

4. Verifications and Discussions

4.1 Applicability of hygro-gradient formulation

The thermo-hygral simulation coded by DuCOM (section 2.2.1) first simulates the cement hydration and associated micro pore structure formation in each finite element as shown in Fig. 3. The initial wet curing and flowing ambient exposure conditions applied in experiments are set forth at the boundary temperature and relative humidity, and the moisture-equilibrated states are computed in each micro-pores. Up to this stage before the sorption test, permeability model of condensed water does not influence on the computation because the liquid water is hardly in convective motion.

Figure 10 shows the comparison of computationally obtained saturation degree and the porosity of specimens with the experimentally observed ones for six cases. The concrete thermo-hygral states of the real specimens are precisely predicted by the DuCOM platform. Then, the authors use the computed porosity and the saturation of each specimen as the initial states of the subsequent sorption tests.

Figure 11 shows the sorption simulation by the reference model by Eq. (17) and the proposal by simple bundle permeation (quasi-single) and the interlinked complexity (quasi-network) expressed by Eq. (34). The mere pore-bundle modeling brings about overestimation for all the cases of RH = 70%. If we try to fit the sorption curves to the reality, we need the deviation factor \( \varepsilon \) in Eq. (34) which must be less than unity. But, from a logical point of view, it is not acceptable no matter how fair fitting would be brought about.

On the other hand, the complexity model of pore linkage is the lower boundary of sorption. In this case, the logical soundness is confirmed and the deviation of experiment from the complexity permeation can be explained in view of the bleeding and interface transition zones.

Here, the attention shall be paid to the very beginning of sorption. The proposed permeation successfully leads to the rapid sorptivity at the initial wetting. This attributes to the pore pressure gradient built in the permeation modeling based upon the knowledge of nanochannels. Compared to the reference model as well as others (see Fig. 4), the sorption curve trend gets closer to the reality. The applicability at the latter stage of sorption should be considered with regard to the deviation factor, because the applicability at the beginning stages is less influenced by the deviation factor as shown in Fig. 13 and investigated in section 4.2.

Figure 12 shows the quasi-final sorption expressed by absorbed water at 10,000 min and the comparison with analysis using the interlinked complexity permeation model with \( \varepsilon = 2.0 \). Generally, the analysis is acceptable as a whole, showing a smaller sorptivity with a higher wetted condition of RH. But the authors want to point out that several experimental cases show a bit greater quasi-final sorption of 70% wet specimens rather than the dry case of 0%. Of course, the total saturation of the case of 70% is larger than the case of 0% in both experiment and simulation (see Fig. 10).
Then, this trend seems to be also associated with the driving force of sorption. In a word, initially dried or lower wetted specimens may dynamically absorb less water by the air-trapping effect (Naar and Henderson 1961) which indicates that part of the non-wetting phase is trapped during the process of imbibition in the nano-scale pore channels. The detailed discussion on the dynamics equilibrium of water in micro-pores is required as a future study.

4.2 Deviation factor

4.2.1 Constant form of deviation factor

The practicability of the deviation factor is further investigated as shown in Fig. 13. The interlinked complexity model of permeation is adopted here with the variation of ϵ-deviation factor which is equal to 1.0, 2.0 and 10, respectively. In an overall view, the case of lower wet condition requires a smaller deviation factor and the absorption behavior becomes less sensitive to the deviation factor as the initial saturation of specimens increases. This makes sense to a certain extent because more possible bleeding channels and interfacial transition zones are initially filled by water under higher RH conditions, resulting less random transport through them in absorption process.

Moreover, varying the deviation factor mainly controls the absolute difference between the simulated and experimental results. This tendency becomes more prominent in the second stage (slowing rate of absorption) than the first stage (rapid absorption, 500-1000 min) of the absorption, as the ϵ equaling 1.0 and 2.0 in the case of RH=0% and the ϵ equaling 1.0, 2.0 and 10 in both 70% and 90% cases indicates.

The validity of sorption analysis has much to do with the simulation of structures under wetting and drying cycles of natural environment. In fact, the seasonal rainfall and associated rapid sorption are great influence on the long-term moisture states in concrete (Kunieda et al. 2013). Therefore, the model is required to show somewhat higher applicability around the annual relative humidity, which is 60~70% in East Asia. Then, in practical usage for wetting and drying analysis of concrete structures, the deviation factor can be set as 2.0 for most normal cases in evaluating the first stage of rapid absorption in mortars and concrete, which can also roughly cover the entire behavior of absorption process in natural environments.

4.2.2 Dynamic form of deviation factor

Although the constant deviation factor has shown its
capability for the gradient-dependent model based on quasi-static equilibrium in the analysis of water absorption, the dynamic moisture equilibrium during the water absorption is also considered. When water saturation $S$ is zero, all the pore channels are empty and it probably happens that some water are charged into bigger pores just after the assembly of bundles of micro-pore channels are exposed to water.

However, this quantity of water will be redistributed into much smaller pores because the water in larger pores are unstable due to the unbalanced capillary force. The redistribution rate, which can be calculated according to Washburn (1921), is quickly because it happens locally with a tiny characteristic length. This process is so unsteady and quickly that it prominently accelerates the rate of water transport in pore channels at the start time of water sorption locally. As $S$ is large, many smaller pores are already filled by water, and the accelerating effect will decrease to zero when all the pore channels are filled by water.

Thus, the constant deviation factor in the last section can also be roughly regarded as a kind of constant rate of dynamic equilibrium effect. Then, a simple formula of thermodynamics is further presented that the accelerating effect is assumed to be proportional to the porosity density expressed by a Rayleigh-Ritz distribution (Ishida et al. 1997; Maekawa et al. 1999) as,

$$\frac{dV}{dlnr} = B r e^{-\nu}$$  \hspace{1cm} (35)

where $V$ is the fractional pore volume of the distribution and $B$ [m⁻¹] is pore structure parameter. The saturation can be also expressed in a similar form as,

$$S = 1 - e^{-\nu}$$ \hspace{1cm} (36)

Thus, the porosity density can be expressed by the saturation as,

$$\frac{dV}{d(lnr)} = (S - 1)ln(1 - S)$$ \hspace{1cm} (37)

Here, let us examine how the nonlinear factor works in terms of the saturation degree as,

$$\nu = 1.0 + 4.0 \cdot \frac{dV}{d(lnr)}$$ \hspace{1cm} (38)

Fig. 12 Transient sorptivity of mortar and comparison with analysis: experiment by dotted markers, interlinked complexity model in red with $\nu = 2.0$. 
where the deviation factor reaches to unity at both the completely dried and saturated conditions, and it dynamically changes with the proceeding of water intrusion into pores. Here, the common logarithmic function is used with the trial of constant coefficient 4.0 according to the simulation. The dynamic equilibrium is represented by the multiplication part of Eq. (38), which means the efficiency of water transfer from bigger to smaller pore channels. As can be seen in Fig. 14, the dynamic form of deviation factor fairly works especially for the wetted cases of mortars close to the average relative humidity of the East Asia.

4.3 Comparison in terms of Boltzmann’s scale

As for the model of water absorption, Goual et al. (2000) assumed a type of unsaturated flow through a porous medium and simply expressed as,

\[ u = -K(\theta_w) \nabla P \]  

(39)

where \( u \) [m/s] is the vector of the water flow through the pores, \( K(\theta_w) \) is the unsaturated permeability [m²/Pa·s], \( \theta_o \) is the normalized water content [m³/m³], and \( P \) [Pa] is the capillary potential.

By combining Eq. (39) with the mass conservation equation, we have the flow equation which is reduced to one-dimension as,

\[ \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( K(\theta_w) \frac{\partial P}{\partial x} - \frac{\partial \theta}{\partial x} \right) \]  

(40)

where \( x \) [m] is the space coordinate. By substituting \( D = K(\theta_w) \frac{\partial P}{\partial x} \) into Eq. (40). Then, we have,

\[ \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial \theta}{\partial x} \right) \]  

(41)

where \( D \) [m²/s] is the hydraulic diffusivity. Boltzmann’s transform variable denoted by \( b = x / \sqrt{t} \) is given by Goual et al. (2000) as \( b = x / \sqrt{t} \), based on which Eq. (41) can be reduced to,

\[ \frac{1}{2} \frac{d}{db} \left( D \frac{d \theta}{db} \right) = \frac{d}{db} \left( D \frac{d \theta}{db} \right) \]  

(42)

By integrating Eq. (34), we have,

\[ D = -\frac{1}{2} \frac{d}{db} \left( D \frac{d \theta}{db} \right) \int_0^b \theta \]  

(43)
This means that the hydraulic diffusivity can be calculated based on the water content $\theta_w$ and Boltzmann transform variable $b$ (Boltzmann’s scale). As illustrated in Fig. 15, the last term of the integral in Eq. (43) is the area delimited by the curve $\theta_w = \theta(b)$ and the $\theta_w$-axis from 0 to $\theta$.

The analytical results of the referential and the present enhanced models expressed on Boltzmann’s scale are indicated for different specimen heights in terms of the hydraulic profile $\theta_w = \theta(b)$. The cylindrical specimen 0.5-60% is first referred for the simulation. For computation, the specimen is discretized into five elements along its height (gravity direction), i.e., 0-11, 11-22, 22-33, 33-44, and 44-55 mm. The central height of each part is denoted by $x$. The hydraulic profiles are shown in Fig. 16.

According to Eq. (43), the intrinsic hydraulic diffusivity $D$ mathematically becomes a unique function of the water content $\theta_w$ regardless of the location. Here, it should be first noted that both the referential and the newly proposed models indicate different hydraulic profiles on the Boltzmann’s scale no matter how large the gap of location is. This attributes to the fact that both models commonly take into account the rate of varying thermodynamic states in estimating the Gibbs free energy in Eq. (10) (Maekawa et al. 1999), which is analogous to the effect of inertia of structural dynamics. As we have the highest rate of moisture change at the surface, the hydraulic profile close to surfaces is comparatively apart from the average, and the same trend can be seen in clayey aerated concrete as well (Fig. 17).

However, the group of hydraulic profiles computed by the proposed model at each location is much converged on the Boltzmann’s scale rather than the referential. It means that the proposed model is macroscopically closer to the intrinsic permeability in terms of the moisture. Thus, the proposed model is not full-intrinsic but “quasi-intrinsic” one. Figure 18 shows the comparison of experiments by Park et al. (2012) and the analysis results. In this case as well as the author’s experiment, the applicability of the proposed model is elevated. Similar trend was also found through further verification (Wang and Ueda 2011; Benazzouk et al. 2004; Madjoudj et al. 2002).
Fig. 16 Water content versus Boltzmann transform variable relation (0.5-60% of the authors’ experiment) (a) enhanced model and (b) the referential one.

Fig. 17 Experimentally determined water content as a function of the Boltzmann transform variable (Goual et al. 2000).

Material and mix proportion:
- Water/Cement = 0.50
- Cement/Sand = 1/3
- Air entrained: 6.2%

Preparation:
- 1 day: sealed
- 2 days: T=20 °C, RH=85%
- 5 days: T=20 °C, under water
- 21 days: T=20 °C, RH=60%

Fig. 18 Water content versus Boltzmann transform variable relation: water absorption test by Park et al. (2012).
Gibbs free energy (Maekawa curve of the referential model with different additional sorption, especially the most normal condition the 70%; model. Boltzmann transform method further validates the fraction. Additional comparison with the results of the moisture, porosity, relative humidity and sand volume reveals acceptable agreement in practice in terms of sorption performed on mortar specimens. The comparison involves a new unsaturated liquid permeability. The rapid imbibition of this model was found to study’s point derives from the characteristic of gradients showing a relatively better outcome than by varying retardation in water absorption of cement-based materials. The model simulations performed in the present study exhibit a little large overvaluation.

What has to be pointed out is that the new model performs reasonably well for the normal environmental conditions (like RH = 70%) during the whole water absorption process, which is practically enough for the engineering purpose in that neither the very dried nor wetted mortars are common or necessary to be evaluated for water absorption.

The water absorption simulation method proposed in this paper affords a feasible approach to solving the physical problem constituted by the capillary potential of a porous medium. The method can be used to predict water and ion transport processes in a concrete structure under the effects of rainfall, tide and wave splash, thus enabling better evaluation of the structural durability.

The effectiveness of the model is verified under the condition of relatively uniform distribution of the initial water content. It is the authors’ plan to conduct a more detailed and comprehensive studies of condensed water absorption under arbitrary moisture distribution to cover the whole process of absorption for all conditions to address the limitations of the proposed method.

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References


Fig. 19 Sensitivity of Gibbs energy on the water absorption.

As discussed previously, the magnitude how solely the permeability depends on water content is rooted in the thermodynamic inertia. Then, the sensitivity of the free energy on water absorption is to be examined for fair discussion. Figure 19 shows the computed absorption curve of the referential model with different additional Gibbs free energy (Maekawa et al. 1999). As the standard value (3550 kcal/mol) is specified by normal concrete composites, it might not perfectly fit mortar used in this study, because the absence of coarse aggregates may lead to shorter tortuosity which may cause averaged viscosity in micro-pores. In fact, the smaller energy may bring about the better prediction absolutely as an average, but there is still deviation at the very beginning of absorption. Thus, in considering these series of verification as a whole, the authors came up to the proposal of this quasi-intrinsic model of condensed water permeation for the case of suction.

5. Conclusions
An updated numerical method for simulating the condensed water absorption process in mortars is presented by using a durability concrete model (DuCOM), and involves a new unsaturated liquid permeability. The quasi-intrinsic model is carefully verified by comparison of its prediction with the experimental facts of the water sorption performed on mortar specimens. The comparison reveals acceptable agreement in practice in terms of moisture, porosity, relative humidity and sand volume fraction. Additional comparison with the results of the Boltzmann transform method further validates the model.

The enhanced model may fairly simulate the rapid imbibition just after the exposure of water and its final retardation in water absorption of cement-based materials, showing a relatively better outcome than by varying the Gibbs free energy. The rapid imbibition of this study’s point derives from the characteristic of gradient-dependent permeability. The model was found to work well for the rapid imbibition stage of water absorption, especially the most normal condition the 70%;
wettability on multiphase flow through porous media.” *Journal of Petroleum Technology*, 11(10), 71-76.


