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Sensitivity of Capillary Absorption and Sorptivity to Water Retention, Permeability and Other Relevant Characteristics for Cement Mortars

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Abstract. *Concrete materials and structures are neither totally saturated nor dry, making the efficient capillary absorption of water deserve much attention. Basically, absorption of water is a process of unsaturated permeation driven by capillary pressure. This dependence of capillary pressure on water content plays an essential role in predicting capillary absorption and thus calculating sorptivity, which is also affected by inherent permeability, tortuosity coefficient significantly. Considering the evolution of pore structure of cement-based materials (CBMs) upon wetting, the long-term absorption of water into mortars and sorptivity can be predicted. However, a few investigations have been done to understand the precision of measured sorptivity, which is tried numerically in this paper focusing on the influences of varying parameters including water retention characteristics, tortuosity parameter, inherent permeability and swelling time. Based on reported experimental data of two cement mortars, 100 curves of capillary absorption in 10 days are predicted with artificially random parameters. Both the first and secondary sorptivity are further calculated and evaluated with emphases on the coefficient of variation of sorptivity and its sensitivity to varying parameters. Water retention characteristics make certain contribution to the dispersion of both initial and secondary sorptivity. Sorptivity is also sensitive to the variations of porosity and tortuosity representing the heterogeneity of their pore structure. The swelling time brings observable effects on the precision of secondary sorptivity only.*

Keywords: *Capillary absorption; Water retention curve; Sorptivity; Permeability; Water sensitivity*

1 Introduction

Water transport in cement-based materials (CBMs) plays a critical role in the ingress of external aggressive ions and gas (Abdou Ibro et al., 2021), and permeability is closely related to the degradation of concrete (Scherer et al., 2007; Hall & Hoff, 2021). Described by the square root of time (SRT) law, the cumulative water absorption V_w per unit area of inflow surface is theoretically proportional to the square root of absorption time $\sqrt{t}$. The proportionality coefficient is termed as sorptivity S $(\mathrm{mm/min}^{0.5})$ (Hall, 1989). Capillary sorptivity characterizing the absorption rate of water into unsaturated porous medium is helpful to evaluate the durability performance of CBMs.

Anomalous moisture transport in CBMs has been reported that the volume change of water absorption is not linearly related to $\sqrt{t}$ (Hall, 2007). Water absorption into CBMs only obeys the SRT law in first hours then deviates, which can be attributed to the microstructure change caused by chemical interactions of water with calcium silicate hydrate (C-S-H) gels in CBM (Zhang & Angst, 2020). Recent studies have shown that the water absorption into CBMs has two linear stages with different sorptivity and a nonlinear transition stage(Ren et al., 2019).

The precision of sorptivity strongly depends on those of prediction parameters. Generally, the determinations of parameters such as water retention characteristics, tortuosity factor and inherent permeability of CBMs require time-consuming laboratory work. Experimental results of parameters are inadequate for sensitivity analysis of sorptivity. Monte Carlo method with the generations of random variables has been used for sensitivity analysis. By analyzing the sensitivity of sorptivity to relevant parameters, the most important factor affecting the precision of sorptivity can be investigated.

This paper presents numerical simulations of long-term absorption and investigates the sensitivity of sorptivity to parameters. The modeling for water absorption is outlined in Section 2. The random variables for Monte Carlo simulation (MCS) with a one-at-a-time (OAT) approach are introduced in Section 3. The predicted results of water absorption and sorptivity are shown in Section 4. Section 5 analyzed the sensitivity of sorptivity based on simulated results.

2 Modeling for water absorption

With hydraulic diffusivity $D(\theta)$ (m^2/s) and capacity function $C(\theta)$ (m^{-1}), the extended Darcy's law for unsaturated flow can be transformed to classical Richards equation (Hall, 1989).

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[D(\theta)\frac{\partial \theta}{\partial x}\right] \tag{1}$$

where θ (-) is volumetric water content, t (h) is elapsed time, h_c (m) is capillary pressure head, x (m) is the distance from surface of water absorption and $K(\theta)$ (m^2/s) is hydraulic conductivity.

The $K_w(\theta)$ for unsaturated flow depends on density ρ_w ($\mathrm{kg/m}^3$) and dynamic viscosity η_w (Pa ·s) of water, as well as water permeability $k_w(\theta)$ (m^2)(Ren et al., 2023).

$$K_w(\theta) = \rho_\mathrm{w} g k_\mathrm{w}(\theta)/\eta_\mathrm{w} = \rho_\mathrm{w} g k_\mathrm{sw} k_\mathrm{rw}(\theta)/\eta_\mathrm{w} \tag{2}$$

where g (m^2/s) is the gravitational acceleration. k_sw (m^2) is saturated water permeability and k_rw (-) is relative water permeability. The relationship between saturation degree Θ (-) and capillary pressure head $h_\mathrm{c}(\theta)$ can be described by van Genuchten (VG) model (van Genuchten, 1980).

$$\Theta = \left[1 + \left(\alpha_\mathrm{vg} h_\mathrm{c}\right)^{1/(1-\gamma_\mathrm{vg})}\right]^{-\gamma_\mathrm{vg}} \tag{3}$$

where θ_sat (-) is the saturated volumetric water content, α_vg (m^{-1}) and γ_vg (-) are fitting parameters of VG model. From VG model and Mualem theory (Mualem, 1976), relative water permeability $k_\mathrm{rw}(\theta)$ can be expressed as VG-Mualem (VGM) model with tortuosity factor ζ(-).

$$k_\mathrm{rw}(\Theta) = \Theta^{\zeta}\left[1 - \left(1 - \Theta^{1/\gamma_\mathrm{vg}}\right)^{\gamma_\mathrm{vg}}\right]^2 \tag{4}$$

The chemical interaction between water and C-S-H gel changes microstructure of CBMs (Zhang & Angst, 2020) and k_sw upon water content. Instantaneous permeability k_iw has been proposed (Hall, 2019; Ren et al., 2021) with time-variation to conveniently characterize the effect of C-S-H gel swelling.

$$k_\mathrm{iw}\left(t_\mathrm{w}\right) = k_\mathrm{final}\left(\frac{k_\mathrm{init}}{k_\mathrm{final}}\right)^{\exp(-t_\mathrm{w}/\tau)} \tag{5}$$

where t_w (h) is the wetting time of CBMs, k_init (m^2) is permeability at initial dry state, k_final (m^2) is permeability at final wet state and τ (h) is the characteristic time constant for time-varying permeability. Then Eq.(1) can be rewritten as modified Richards equation.

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x}\left[D(\theta, t_\mathrm{w})\frac{\partial\theta}{\partial x}\right] \tag{6}$$

The partial differential Eq.(1) with modified parameter $D(\theta, t_\mathrm{w})$ can be transformed by introducing the Boltzmann variable $\lambda(\theta) = x/\sqrt{t}$ (m/s$^{0.5}$) (Hall, 1989).

$$V_\mathrm{w}(t) = \int_{\theta_\mathrm{init}}^{\theta_\mathrm{cap}} x\,\mathrm{d}\theta = \theta_\mathrm{sat}\sqrt{t}\int_{\Theta_\mathrm{init}}^{\Theta_\mathrm{cap}} \lambda(\Theta)\mathrm{d}\Theta = S\sqrt{t} \tag{7}$$

where V_w (m) is the cumulative volume of absorbed water per unit area of the inflow surface, S (mm/min$^{0.5}$) is capillary sorptivity. V_w is proportional to the square-root of t (Hanumanthu & Sarkar, 2022), and the rate is capillary sorptivity S (Martys & Ferraris, 1997). SRT law has been experimentally proven for capillary absorption of organic liquids into CBMs (Hall & Hoff, 2021). But water absorption only obeys SRT law at the first linear stage (with initial sorptivity S_1) for hours and transfers to another linear stage with a smaller secondary sorptivity S_2.

The modeling for V_w into CBMs is a multivariable function considering the properties of water, boundary conditions of saturation degree, microstructure, coefficients of WRC and dynamic permeability. Then S_1 and S_2 can be mathematically fitted with periods of elapsed time.

$$\left.\begin{aligned} V_\mathrm{w} &= S_1\sqrt{t} + a \\ V_\mathrm{w} &= S_2\sqrt{t} + b \end{aligned}\right\} \tag{8}$$

where a (mm) and b (mm) are fitting coefficients.

3 Numerical simulation

The reference values of main parameters are based on physical properties of long-term capillary absorption experiment of a typical cement mortar (Ren et al., 2021), as shown in Table 1.

Table 1. Basic properties and parameters for absorption modeling of reference material

Symbol	Property	Units	Reference value
Θ_cap	Capillary saturation degree	—	0.808
Θ_init	Initial saturation degree	—	0.084
ϕ	Porosity	—	0.139
α_vg	WRC coefficient in VG model	m^{-1}	8.11×10^{-4}
γ_vg	WRC coefficient in VG model	—	0.38
ζ	Tortuosity factor	—	5.5
k_init	Initial permeability	m^2	5.80×10^{-18}
k_final	Final permeability	m^2	2.03×10^{-19}
τ	Characteristic time of permeability	h	77.53

Modeling parameters were artificially set as random variables (with superscript *) in MCS. Their random distributions and statistical properties are listed in Table 2. Random samples were automatically generated with a sample size of 100, except those of α^*_{vg} and γ^*_{vg}. $\overline{X}$, σ and C_{v} in Table 2 are the mean value, standard deviation and coefficient of variation, respectively.

Table 2. Random distributions and statistical characteristics of variables

Symbol	Units	Distribution	$\overline{X}$	σ	C_{v} (%)
ϕ^*	—	U(0.10, 0.30)	0.193	0.058	29.942
α^*_{vg}	m^{-1}	Shown in Fig. 6 (a)	8.00×10^{-4}	6.459×10^{-5}	8.070
γ^*_{vg}	—	Shown in Fig. 6 (a)	0.381	0.011	2.884
ζ^*	—	N(5.5, 1)	5.539	1.016	18.343
k^*_{init}	m^2	$\mathrm{U}(1 \times 10^{-18}, 1 \times 10^{-17})$	5.363×10^{-18}	2.493×10^{-18}	46.485
k^*_{final}	m^2	$\mathrm{U}(1 \times 10^{-19}, 1 \times 10^{-18})$	5.350×10^{-19}	2.529×10^{-19}	47.280
τ^*	h	N(77.53, 15)	77.617	15.646	20.158

α^*_{vg} and γ^*_{vg} were not directly simulated with random distributions. From Eq. (3), α_{vg} and γ_{vg} can be fitted by a data group of ($\Theta(h_{\mathrm{c,RH}})$, $h_{\mathrm{c,RH}}$). Based on WRC of reference mortar (Ren et al., 2021), $\Theta(h_{\mathrm{c,RH}})$ at each RH was simulated as a random variable, except an outlier $\Theta(h_{\mathrm{c,59\%}})$.

$$\Theta(h_{\mathrm{c,RH}})^* \sim \mathrm{U}(0.9\Theta(h_{\mathrm{c,RH}}), 1.1\Theta(h_{\mathrm{c,RH}})) \tag{9}$$

With 100 simulated samples of each $\Theta(h_{\mathrm{c,RH}})^*$, 100 $(\Theta(h_{\mathrm{c,RH}})^*, (h_{\mathrm{c,RH}}))$ were generated and then 100 WRCs were fitted with 100 sets of WRC parameters (α_{vg}, γ_{vg}). Calculated statistical characteristics of α^*_{vg} and γ^*_{vg} are listed in Table 2.

4 Results of numerical simulation

4.1 Time-dependent transport properties

Predictions of capillary absorption with 100 samples of variable k^*_{init} are numerically predicted, as shown in Figure1 (a). S_1 and S_2 are fitted from the two stages of absorption, respectively. Figure1 (b) shows the calculated sample sets of S_1 and S_2. Figures 2 (a) and (b) present the predictions of capillary absorption and the distributions of two sorptivity, with variable k^*_{final}. And the influences of random τ^* on capillary absorption and sorptivity are shown in Figure 3.

4.2 Pore structure properties

100 samples of capillary absorbed volume V_{w} predicted with variable ϕ^* are illustrated against square root of elapsed time $\sqrt{t}$ in Figure 4. Capillary absorption becomes more rapid with the increase of ϕ. From 4 (b), both S_1 and S_2 increase with ϕ, while the influence on S_1 is greater.

Tortuosity factor ζ is an important parameter in VGM model. Capillary absorption and sorptivity are predicted and calculated with random variable ζ^* and reference values, respectively, as shown in Figure 5.

4.3 Water retention characteristics

WRC parameters used for predictions are determined by saturation degrees $\Theta(h_{\mathrm{c,RH}})^*$ with uniform distributions. Figure 6 (a) illustrates the distribution of fitted WRC parameters. Predictions of capillary water absorption with 100 random samples of fitted WRC parameters are shown in Figure 6 (b). The related variations of S_1 and S_2 are shown in Figure 7.

(a) Water absorption **(b)** Sorptivity

Figure 1. Influence of k^*_{init} on capillary absorption and sorptivity

(a) Water absorption **(b)** Sorptivity

Figure 2. Influence of k^*_{final} on capillary absorption and sorptivity

(a) Water absorption **(b)** Sorptivity

Figure 3. Influence of τ^* on capillary absorption and sorptivity

(a) Water absorption **(b)** Sorptivity

Figure 4. Influence of ϕ^* on capillary absorption and sorptivity

(a) Water absorption

(b) Sorptivity

Figure 5. Influence of ζ^* on capillary absorption and sorptivity

(a) Distribution of α^*_{vg} and γ^*_{vg}

(b) Water absorption

Figure 6. α^*_{vg} and γ^*_{vg} distribution and their influence on capillary absorption

(a) Influence of α^*_{vg} **(b)** Influence of γ^*_{vg}

Figure 7. Influence of related WRC parameters on sorptivity

5 Sensitivity of sorptivity to random variables

The statistical properties, including mean value, standard deviation and coefficient of variation $C_{\mathrm{v,S^*}}$ (%) of different S^*_1 and S^*_2 simulated by different parameters are calculated, respectivily. To analyze the sensitivity of sorptivity to random variables, the ratios of $C_{\mathrm{v,S^*}}$ to coefficient of variation of parameters $C_{\mathrm{v,para}}$ are calculated and compared in Figure 8.

Both S_1 and S_2 are most sensitive to γ_{vg}, followed by α_{vg} and ζ with similar effects. The variations of ϕ, γ_{vg}, α_{vg} and ζ simultaneously affect the dispersions of S^*_1 and S^*_2. However, the sensitivities of S_1 and S_2 to permeability parameters are not identical. S_1 is obviously more sensitive to k_{init} than k_{final} and τ, while S_2 is more responsive to the changing of k_{final} and τ.

6 Conclusions

- The WRC parameters in VG model can be fitted as variables based on values of reference cases. Then the random WRC parameters can be used to study the effect of measuring errors of saturation degree on the prediction of capillary water absorption.
- From numerical results, S_1 increases with initial permeability and porosity, while S_2 grows with final permeability. Greater tortuosity factor can reduce both S_1 and S_2 .
- Both S_1 and S_2 are sensitive to parameters related to WRC and pore structure. S_1 only responsive to initial permeability, while the sensitivity of S_2 to final permeability and swelling time are more significant.

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Figures/CV/fig_cv_ratio_sorptivity-eps-converted-to.pdf

Figure 8. Ratios of $C_{\mathrm{v,S^*}}$ to $C_{\mathrm{v,para}}$

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