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Effects of Surface Layer on Moisture Transport in Cementitious Materials: Experimental Evidence and Simulation Results

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Abstract. *Moisture in concrete is the essential factor of many degradation mechanisms to reinforced concrete structures, such as carbonation, chloride ingress, and frost attack. Therefore, it is important to accurately determine and predict moisture state and moisture distribution inside the material. Most moisture transport models generally view concrete as a homogeneous material, which might be appropriate for the large scale. However, it is commonly found that the properties (chemical and microstructure) of the concrete surface layer are different from the bulk concrete. When considering the moisture exchange with the surrounding environment, this surface layer may unavoidably affect the process of moisture transport. In this study, water absorption tests were performed to investigate moisture transport in uncarbonated cement pastes and mortars. The results show that during the process of sample preparation, the microstructure of the surface layer was altered, leading to anomalous moisture transport, in which the conventional models can not predict the measured mass change. Based on the experimental results, the non-homogeneous simulation domain was created to represent the more realistic microstructure of concrete. The numerical simulation results show a similar trend of the mass change due to moisture transport to the experimental results. Therefore, the non-homogeneous microstructure of concrete, in particular the different microstructure of the surface layer from the bulk concrete, can be one of the reasons that cause the anomalous moisture transport in cementitious materials. This also emphasizes the importance of sample preparation in the lab, which must avoid creating a surface layer with the different microstructure from the bulk concrete.*

Keywords: *Moisture Transport, Durability, Anomalous, Surface Layer.*

1 Introduction

Moisture in concrete is closely related to many degradation mechanisms, such as carbonation, chloride ingress, steel corrosion, and frost attack. Therefore, it is important to accurately determine and predict moisture state and moisture distribution inside cementitious materials. Most moisture transport models generally view concrete as a homogeneous material and these conventional models that have been used for general porous media (e.g., soils, rocks) are used to simulate the moisture transport in cementitious materials (Zhang et al. 2015). However, it is commonly found that the measured moisture transport in cementitious materials does not follow the simulation results of these conventional models, which is termed as anomalous moisture transport (Wadsö 1992, Zhou et al. 2021). The anomalies of moisture transport in cementitious materials may be caused by different reasons, such as the dispersion of trapped air (Fagerlund 1982, Weiss 2014), the complex microstructure (Zhang and Angst, 2020a), cement rehydration upon the change of moisture content (Zeng and Xu 2017), and the change in microstructure due to the various moisture condition (Hall 2019, Zhang and Angst 2020b, Ren et al. 2021). Therefore, different moisture transport models have been proposed to catch the anomalous transport phenomena, such as the dual-porosity/dual-permeability models (Zhang and Angst

2020a) and the time-dependent models (Hall 2019, Zhang and Angst 2020b, Ren et al. 2021).

However, our recent results showed that the surface layer of cementitious specimen might significantly change the moisture transport process (the results will be presented in the following section). It has been widely recognized that the properties (chemical and microstructure) of the concrete surface layer are different from the bulk concrete (Kreijger 1984, Pigeon et al. 1996). When considering the moisture exchange with the surrounding environment, this surface layer may unavoidably affect the process of moisture transport. In this study, water absorption tests were performed to investigate moisture transport in uncarbonated mortars. Based on this, numerical simulations were carried out to study the effect of different microstructures of surface layer on moisture transport.

2 Experimental Study

2.1 Experiments

The mortar specimens were prepared from CEM II/B-LL cement with a water-to-cement ratio of 0.6, which were leftover materials of the previous study (Zhang and Angst 2022). The sand-to-cement ratio was 3 with the maximum river sand size of 2 mm. The fresh materials were cast in plastic cylindrical cups with a diameter of 33 mm. After a 6-month curing period, they were cut into roughly 2 cm long short cylinders. All cylindrical specimens were then sealed with the adhesive aluminum sheet with leaving one end open for water absorption. Before the water absorption tests, these short cylinders have been subjected to vacuum saturation, preconditioning in high relative humidity (RH), drying in different RHs, and oven drying at 65°C (see (Zhang and Angst 2022) for detailed sample preparation and the pre-moisture transport measurements). After their masses reached equilibrium, water absorption tests were conducted and repeated twice with oven drying at 65°C after each test.

2.2 Experimental Results

The results of two specimens are shown in **Figure 1**, which clearly shows that the curves from two repetitions (T1 and T2) are very different. If the pore structure of a material is rigid, meaning it remains unchanged regardless of the varying environment conditions, two curves for the same specimen should be very similar. The results shown here may suggest that the pore structure of the studied material has been modified during either sample preparation or tests. This change happened to all studied specimens (due to the limited space only the results of two specimens are provided here). After two repetitions, the surface layers of specimens (~ 5 mm) were removed by diamond saw cutting. Then, they were dried at 65°C again and the third round of water absorption tests were conducted, which are shown as blue triangle symbols in **Figure 1**. Clearly, curves from the third round raised very fast and followed a linear relation with the square root of time in the first stage. They then reach the second stage of water absorption and the increase rates are much lower. These results, in particular for the first stage, well follow the theoretical curves from the conventional models. By contrast, curves from the first and second tests raised very slow initially and then started rising quickly later, which is a typical case of anomalous moisture transport. In the following section, a moisture transport model will be proposed to study the effect of the surface layer on moisture transport.

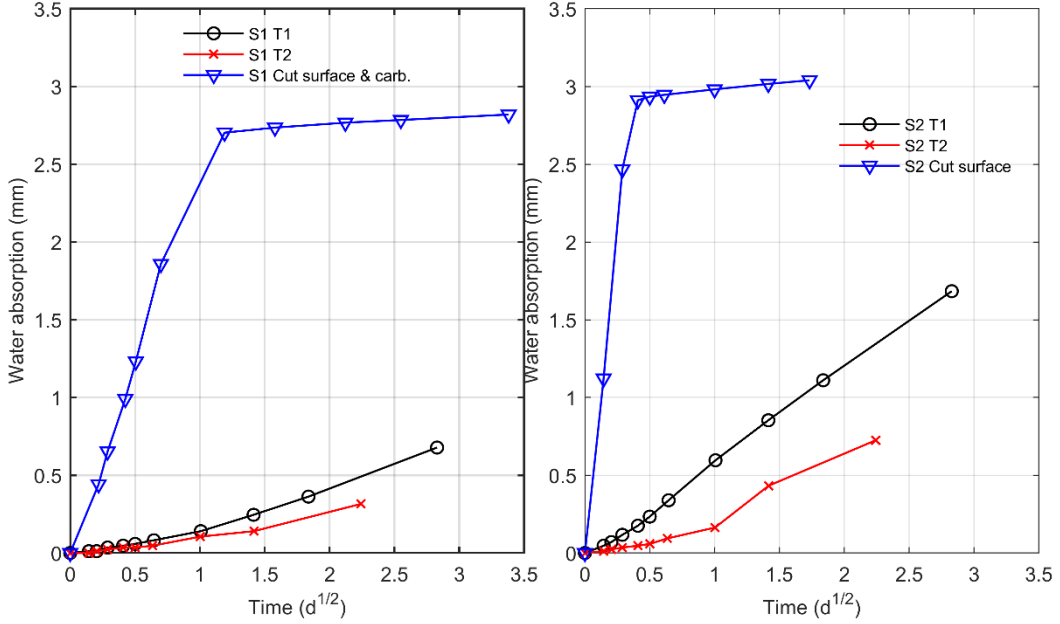


Figure 1. The water absorption results of two specimens with three repetitions.

3 The Moisture Transport Simulations

The moisture model presented here was initially developed based on the homogenization approach, which considers that an REV (representative elementary volume) could represent the moisture transport properties of a certain volume of the material, which is generally heterogeneous below the REV scale. As we only simulate the moisture transport, the solid skeleton is regarded as rigid so the heterogeneity of the porous medium is considered by the change of porosity at each element. Even though the resolution is lower than the pore network model, this method can cover a large simulation domain with varying pore structure.

3.1 Transport Equations

Unsaturated moisture transport in a rigid porous material can be formulated by different levels of complexities of models, including multiphase models, two-phase models and one phase models. The previous studies have concluded that for the general purposes of simulating moisture transport the Richards' equation is sufficient, which can be written as (Mainguy et al. 2001, Zhang et al. 2015)

$$\frac{\partial S_l}{\partial t} = \nabla[D_a(S_l)\nabla S_l] \quad (1)$$

where $D_a(S_l)$ is the apparent diffusivity, which is a function of S_l , the degree of moisture saturation. Here we choose a two-phase model, which can cover moisture transport in a large range of relative humidity (Zhang et al. 2016). Therefore, $D_a(S_l)$ needs to consider contributions from both liquid water and water vapor,

$$D_a(S_l) = D_l(S_l) + D_v(S_l) \quad (2)$$

with

$$D_l(S_l) = -k_{rl} \frac{K_l}{\phi \eta_l} \frac{dP_c}{dS_l} \quad (3)$$

$$D_v(S_l) = -\left(\frac{M_v}{\rho_l RT}\right)^2 D_{v0} \phi^{x_D} (1 - S_l)^{x_D+2} \frac{P_{vs} RH}{\phi} \frac{dP_c}{dS_l} \quad (4)$$

where η_l is the dynamic viscosity of liquid water, k_{rl} is relative permeability, K_l is the intrinsic permeability, M_v is the molar mass of water molecule, ρ_l is liquid water density, x_D is a resistant parameter to consider the microstructural effect on vapor diffusion (taking as 2.74 for cement-based materials based on the fitting of experimental data of CO₂ and oxygen diffusion), and P_{vs} is the saturated vapor pressure in air.

The sorption isotherm is here mathematically described by the van Genuchten equation (van Genuchten 1980)

$$S_l = \left[\left(\frac{P_c}{\alpha} \right)^{\frac{1}{1-m}} + 1 \right]^{-m} \quad (5)$$

where P_c (Pa) is capillary pressure, which is calculated from RH by the Kelvin's law, and α (Pa) and m are two fitting parameters.

Relative permeability k_{rl} is expressed as a function of S by using the van Genuchten - Mualem model (Mualem 1976, van Genuchten 1980).

$$S_l = k_{rl} = S_l^{0.5} \left[1 - (1 - S_l^{1/m})^m \right]^2 \quad (6)$$

where m is taken from the van Genuchten equation.

Here we consider a case that the microstructure of a material is changed due to the environmental effect. Assuming the original porosity is ϕ_m and the time-dependent porosity is ϕ , the porosity-related parameters need to be updated as well. The previous study has shown that, to consider the dependence of sorption isotherms on porosity, m can be viewed as a constant while taking α as a function of porosity ϕ (Zhang et al. 2022).

$$\alpha(\phi) = \alpha_0 e^{-c(\phi - \phi_m)} \quad (7)$$

where c is a constant and taken as 4.33 (Zhang et al. 2022).

Therefore, the intrinsic permeability K_l is the only unknown, which is commonly inversely determined by fitting a measured mass change curve of a specimen subjecting to drying or wetting/absorption if consider cementitious materials as homogeneous porous media (Mainguy et al. 2001). In this study, we consider the heterogeneity of concrete microstructure, so K_l as a function of porosity is assumed. Following the suggestion in (Zhang et al. 2022), the Kozeny-Carman (KC) equation is used to calculate K_l based on porosity.

$$K_l = \frac{\phi^3}{C_K \tau^2 \rho_s^2} \quad (8)$$

where C_K is the KC coefficient, ρ_s the bulk density of dried material, and τ the tortuosity which can be written as a function of porosity as well ($\tau = \phi^{-2.5}$ according to the results of fitting the Bruggeman relation to the measured tortuosity (Promentilla et al. 2009, Leupin et al. 2021)). Therefore, the only unknown is C_K whose value depends on the material properties.

Since there are not enough data for the material used in Section 2, this study takes data of a cement paste in the literature as an example (Baroghel-Bouny 2007). They are $\phi_m=0.41$, $\alpha_0 = 1.5 \times 10^7$ Pa, $\rho_s = 1750$ kg/m³, and $C_K = 2 \times 10^9$ m⁴/kg². The value of C_K was estimated to ensure the material has the intrinsic permeability in the order of 5×10^{-21} m² (see the permeability curve in **Figure 2** for the case of uniform porosity distribution).

3.2 Model Setup

In this study, we take a specimen with a length of 20 mm and the thickness of the surface layer is about 5 mm. The heterogeneity of the surface layer is considered in three ways as shown in **Figure 2**. For the first case, the surface layer has the same porosity as the interior. For the second case, the surface layer is denser, meaning porosity of the beginning part is lower. However, to keep the total pore volume the same as the first case, a coarser region after the denser region was created. For the third case, the surface layer is coarser so porosity is very high and then decrease with the distance from the surface. The varying porosity along with the depth causes the varying intrinsic permeability from the surface to the interior of the material. As shown in **Figure 2**, permeability changes by about 4 orders of magnitude for two heterogenous cases.

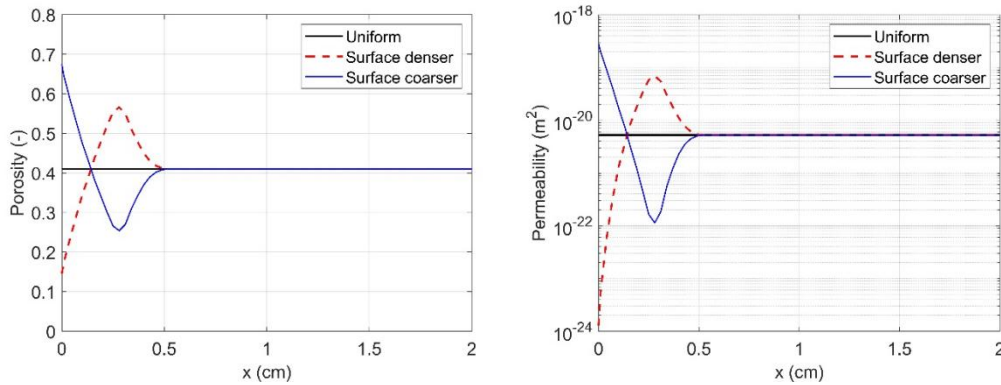


Figure 2. Porosity and permeability distributions along the distance from the specimen surface.

3.3 Modelling Results

The simulations followed the experimental condition in Section 2, in which the specimen was initially equilibrated with 20% RH and then exposed to liquid water, so water absorption caused the increase in the specimen mass as shown in **Figure 3** for three studied cases. For the homogeneous case with the uniform porosity distribution, the mass change curve shows exact the case of the theoretical curve with two linear stages, while for the other two cases, curves are very different from the first case. If the surface is denser, water uptake is very slow and the water absorption rate (the slope of the curve) gradually increases with time, which is similar to the experimental results reported in **Figure 1** for the first and second tests. Eventually the curve

will reach the same level as the first case, but it would take much longer time. If the surface layer is coarser, the specimen mass sharply raises in a very short period but then the water absorption rate decreases which may be due to water reaching the dense region. After water passed this region, the specimen mass quickly increases to the same level as the first case. These simulation results clearly demonstrate that the different porosity distributions are able to significantly affect the mass changes curves.

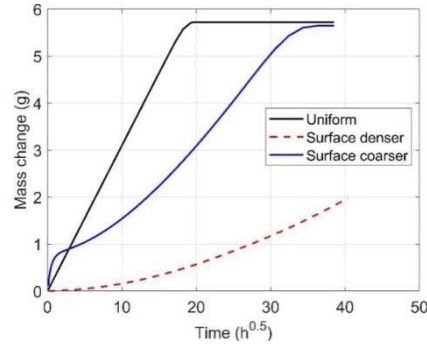


Figure 3. The mass change during water absorption for three studied cases.

The saturation profiles at different times are provided in **Figure 4** for the three simulation cases. Clearly, the initial saturation is very heterogeneous if the porosity distribution is not uniform. With the process of water absorption, the saturation profiles vary a lot depending on the porosity distribution. Compared to the case of coarser surface layer, the saturation inside the concrete increases very slow for the denser surface layer because of the blockage of the dense layer. This layer significantly reduces water permeability as shown in **Figure 1** so the moisture transport becomes very slow. If the surface layer is coarser, the saturation profiles show a fast initial absorption and a later retardation of the dense region, which agrees with the mass change curve in **Figure 3**.

The simulation results, in particular for the case of denser surface layer, show the similar tendency of experimental results in **Figure 1** that the specimen mass increases very slowly at the beginning and gradually increases faster after a certain time. This work confirms that the denser surface caused by sample preparation and pre-conditioning is one of the reasons that the anomalous moisture transport was observed in the experimental results. The dense surface layer may be induced by carbonation and/or the leaching and redistribution of ions inside cementitious materials. Either way, the dense surface layer may have a certain durability benefit. For instance, it could delay the increase of moisture content at the surface of embedded steel bar and therefore steel corrosion would be less pronounced.

The coarse surface layer may also exist due to casting and the environmental effects. For instance, when concrete is poured into the formwork, a layer of concrete with less aggregates naturally forms at the surface of concrete. This layer generally has a higher porosity than the bulk concrete. During the service of the concrete structures, ions leaching is a common process if water persistently remains on concrete. The coarse surface layer may impair the resistance to harmful ions and gases, such as chloride and CO_2 . Therefore, the generation of coarse surface layer should be avoided by the appropriate construction approach or applying surface coating

to make the surface water tight. However, the effects of the natural environment on the microstructure of the surface layer are complicated. To further investigate these effects, more studies are still needed.

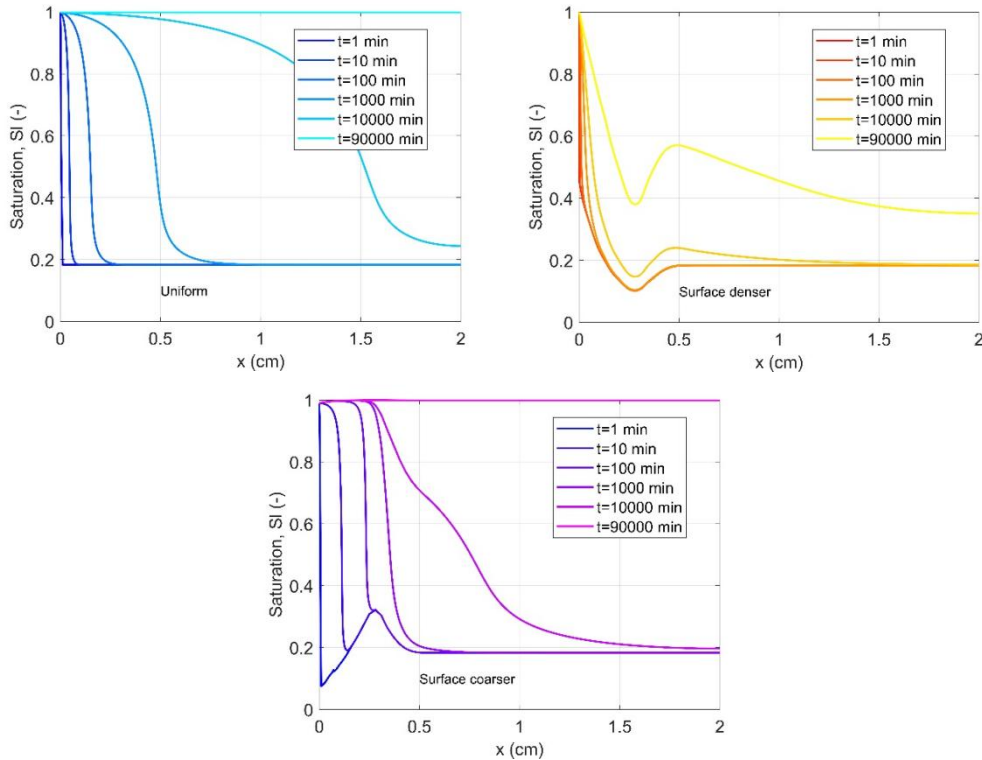


Figure 4. Water saturation profiles during water absorption for three studied cases.

4 Conclusions

- Water absorption tests were carried out and the experimental results showed that the microstructure of the surface layer was modified by sample preparation and preconditioning, so the anomalous moisture transport was observed.
- By considering the denser or the coarser surface layer, the numerical simulations could reveal that the anomalous moisture transport observed in this studied was most likely caused by the denser surface layer.
- The denser surface layer may have a certain durability benefit, while the coarser surface layer may impair concrete durability. More studies will be carried out on this topic.

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