Multiscale modelling of ionic diffusivity in unsaturated concrete accounting for its hierarchical microstructure

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A B S T R A C T

This study presents an integrated multiscale framework for modelling ionic diffusivity in unsaturated concrete accounting for its microstructural features and 3D moisture distribution. The hierarchical microstructure of concrete at multiscale from nano- to meso-scale is mimicked, based on which the fluid-solid interaction and moisture distribution in pore network of concrete with various saturation levels are simulated using a lattice Boltzmann multiphase model. A lattice Boltzmann-finite difference model for diffusion is developed to mimic the ionic diffusion and predict the ionic diffusivity in unsaturated concrete. Results indicate that ionic diffusivity in unsaturated concrete highly depends on moisture content and distribution, pore structure, and aggregate content. As the water saturation level drops to around 90%, interfacial transition zone starts to retard ionic diffusion. Voids have a great contribution to water saturation level but less effect on ionic diffusivity. The simulation results of ionic diffusivity at each scale agree well with experimental data.

1. Introduction

Durability of concrete is associated with the coupled action of physical and chemical processes, where the transport of aggressive species plays a dominant role and thus transport properties are regarded as the indicators of concrete durability. Among them, ionic diffusivity is the most critical parameter for service life prediction and durability assessment of reinforced concrete structures. In the laboratory, the ionic diffusivity in concrete is usually measured at a saturated state [1]. However, due to self-desiccation [2] and change in the moisture of service environments, e.g. atmospheric and tidal marine conditions [3], the concrete structures in practice are partially saturated, where the ionic diffusion is highly associated with the moisture conditions in pore network of concrete including water content and moisture distribution [4]. Therefore, for accurate prediction of service life of reinforced concrete structures, it is vital to investigate the ionic diffusivity in unsaturated concrete.

Over the past decades, many attempts including experimental measurements and numerical predictions have been made for determining the ionic diffusivity in unsaturated concrete. To measure the ionic diffusivity in unsaturated concrete, natural diffusion tests [5–9] or electrical resistivity tests [10–14] are generally carried out on the concrete specimens preconditioned to a certain unsaturated state. The measured ionic diffusivity was found to be strongly dependent on the water content in pore network of concrete. Moreover, the change of ionic diffusivity in unsaturated concrete with water content in terms of water saturation level or internal relative humidity (RH) is significantly affected by water-to-cement (w/c) ratio [5,7,10,12], supplementary cementitious materials [10,11,13,14], interfacial transition zone (ITZ) [11], and aggregate content [8]. Nevertheless, the experimental procedure is usually very time-consuming and the desired water content in specimens during the testing process may be changed. Additionally, the use of these experimental measurements to characterise the ionic diffusivity in unsaturated concrete is still questionable. For instance, in the natural diffusion tests, the solution of Fick’s second law for diffusion is employed to fit the measured ionic concentration profile of unsaturated concrete, but there is no agreement on whether the binding of ions should be considered [13]. Regarding the electrical resistivity tests, the measured ionic diffusivity cannot fully represent the realistic diffusion property of concrete due to the presence of electrical double layer (EDL) induced by the nano-sized pores [15]. Furthermore, the underlying mechanisms of ionic diffusion in unsaturated concrete cannot be explored from the simple relationship between measured ionic diffusivity and water content.

In addition to experimental work, several analytical and numerical studies were undertaken to investigate the ionic diffusivity in unsaturated concrete...
unsaturated concrete in the past years. Through fitting the experimental results, some empirical equations were proposed to depict the relation of ionic diffusivity in concrete to water saturation level. For instance, Saetta et al. [16] found that there exists an S-shaped correlation between ionic diffusivity in concrete and RH, where a critical RH was obtained based on experimental data. Similarly, Baroghel-Bouny et al. [17] indicated that the change of ionic diffusivity in concrete with water saturation level follows a power function. Despite the simplicity and ease application, the applications of these equations are limited to certain conditions and the fitting parameters in these equations need to be further verified to consider microstructural characteristics of concrete [6, 13]. Recently, Zhang and Ye [18] proposed a new empirical equation for predicting the ionic diffusivity in unsaturated concrete accounting for pore structure features, where the fitting parameter was expressed as a function of average pore diameter of concrete measured by mercury intrusion porosimetry (MIP). It was indicated that the change of ionic diffusivity in unsaturated concrete with water saturation level is strongly dependent on the pore structure of concrete. Nevertheless, the used pore structure characteristics for this empirical equation were over-simplified and the pore size measured is not so accurate owing to the presence of ink-bottle effect and certain assumptions applied to MIP tests [19]. Moreover, besides water content, the ionic diffusivity in unsaturated concrete is also strongly dependent on the moisture distribution in pore network [4] that cannot be reflected in these empirical equations.

To tackle the limitations of empirical studies, numerical modelling was carried out to consider the 3D microstructure of cementitious materials and moisture distribution in them. For instance, Zhang et al. [20] present a lattice Boltzmann model for simulating the moisture distribution in capillary pores and ionic diffusivity in unsaturated cement paste. They demonstrated that there exists a critical water saturation level between 20% and 34.9%, where the depercolation of water-filled capillary pores for ionic diffusion takes place. However, the effect of gel pores on ionic diffusion was not taken into account in their model. It has been demonstrated that the contribution of gel pores to water saturation level and ionic diffusivity in concrete is significant and cannot be ignored [21, 22]. Recently, a modified microstructure-based lattice Boltzmann model was proposed to mimic the ionic diffusivity in unsaturated cement paste accounting for both capillary and gel pores as well as the EDL effect at nano-scale [23], where the EDL effect of gel pores on ionic diffusion was found to be significant at a low degree of water saturation and the critical water saturation level is around 8%. Nevertheless, the above-mentioned numerical studies were only focused on pure cement paste rather than concrete and the mechanism of ionic diffusion in partially saturated concrete has not been fully understood. For example, there exists ITZ with relatively higher porosity and larger pore size in the vicinity of aggregate surface resulting from the wall effect of aggregate, which would significantly affect ionic diffusivity in concrete [24]. However, the influence of ITZ on moisture distribution and its role in ionic diffusivity in unsaturated concrete have not been extensively addressed.

So far, different multiscale methods have been developed to investigate the ionic diffusion in concrete considering its hierarchical nature (see Fig. 1) [25]. Among them, multiscale homogenisation approaches including analytical models [26–29] and numerical models [30–32] are widely used to estimate the ionic diffusivity in saturated concrete because of their simplicity and easy implementation. The analytical predictions of ionic diffusivity in saturated concrete can be achieved based on the classical effective medium theory such as generalized Maxwell approximation, self-consistent scheme and generalized self-consistent scheme [1], while the numerical simulations can be performed using the computational homogenisation strategy to solve the governing equations. In this study, the multiscale computational homogenisation method is adopted as it can consider the complex microstructure of concrete at each scale and obtain the local information (e.g., ionic concentration distribution within concrete for diffusion) [33].

This study aims to provide a comprehensive understanding of ionic diffusion in unsaturated concrete and investigate the ionic diffusivity in unsaturated concrete accounting for its microstructural features at multiscale and 3D moisture distribution in the pore network. Firstly, the representative volume elements (RVEs) of concrete at multiple scales from nano- to meso-scale including calcium silicate hydrate (C-S-H), cement paste composed of bulk paste and ITZ, mortar, and concrete were simulated, as illustrated in Fig. 1. Afterwards, the fluid (water and

Fig. 1. Multiscale structures of concrete with four levels where the 2D images of hierarchical concrete from left to right (top) are collected from [34-37].
gas-solid interaction and moisture distribution in pore network of concrete with various water saturation levels were mimicked by means of a lattice Boltzmann (LB) multiphase model, based on which the ionic diffusivity in unsaturated concrete at each length scale was estimated using a LB-finite difference model for diffusion. The simulations were verified using the experimental data obtained from literature. Finally, the effects of various factors associated with microstructural features including pore structure and aggregate attributes on ionic diffusivity in unsaturated concrete were investigated and discussed in depth to explore the underlying mechanisms of ionic diffusion in unsaturated concrete.

2. Simulation of representative volume elements of hierarchical concrete

As illustrated in Fig. 1, the structure of concrete can be divided into four length levels [34–37]: (1) Level I (nano-scale): colloidal C-S-H consisting of C-S-H particles and gel pores (2) Level II (micro-scale): cement paste (bulk paste and ITZ) composed of unhydrated cement, C-S-H, other crystalline hydration products, and capillary pores; (3) Level III (meso-scale): mortar consisting of bulk paste, fine aggregates, ITZ, and voids; (4) Level IV (macro-scale): concrete composed of mortar and coarse aggregates. Herein, the 3D RVEs of concrete at multiscale from nano-scale to macro-scale were simulated.

2.1. C-S-H level

Based on the authors’ previous study [38], the RVE of colloidal C-S-H was simulated by means of the hardcore-softshell (HCSS) algorithm [39]. The individual C-S-H particle was assumed to be a sphere with a diameter of 5 nm consisting of an impenetrable hardcore surrounded by a concentric softshell. During the packing process, the new softshell can overlap arbitrarily with the existing softshells and hardcores, while the new hardcore can only overlap with the existing softshells. The desired porosity of packing was set as 28%, corresponding to the C-S-H gel formed in Portland cement paste at room temperature [40]. According to [41,42], the RVE size of C-S-H was regarded as 100 × 100 × 100 nm$^3$. A typical microstructure of C-S-H is shown in Fig. 1, the gel pore size of which ranges from 1 nm to 6 nm, comparable to 2.5–5 nm reported in [43].

2.2. Cement paste level

Because of the presence of aggregates, cement paste in concrete can be divided into bulk paste and ITZ, as demonstrated in Fig. 2a [36]. ITZ is a thin layer of paste with thickness of 10–50 μm around aggregate products induced by the so-called wall effect [44], which has a relatively higher porosity and contains less unhydrated cement and hydration products by contrast with bulk paste [45]. Due to the highly porous nature, ITZ is usually treated as an individual phase in concrete.

Here, the 3D microstructure of cement paste was simulated using the voxel-based CEMHYD3D model [46]. To mimic the wall effect, two parallel planes with a certain thickness were fixed in one direction of the cement paste to represent the neighbouring aggregates, as shown in Fig. 2b. Through changing the thickness of aggregate planes, the volume ratio between ITZ and bulk paste can be adjusted, which is kept consistent with that in mortar at meso-scale. The fine aggregate content in mortar is usually 50%–60% [47], as indicated in Table 1. The representative aggregate-to-aggregate spacing in mortar was found to be in the range of 120 μm to 168 μm (see Fig. 8 below). The RVE size of cement paste plus two parallel aggregate planes was thus set as 150 × 150 × 150 μm$^3$. In the direction perpendicular to the aggregate plane, i.e., Y-direction, the thickness sum of cement paste and two aggregate planes is 150 μm, as displayed in Fig. 2b. The default resolution of the digital RVE in the CEMHYD3D model (i.e. 1 μm/voxel) was employed. In the simulations, the cement particles regarded as rigid spheres were randomly placed in the cement paste region of RVE and cannot overlap with aggregate planes. After cement packing, the cement powders were segmented into tricalcium silicate (C$_3$S), dicalcium silicate (C$_2$S), tricalcium aluminate (C$_3$A), and tetracalcium aluminoferrite (C$_4$AF) based on the content and distribution of mineral phases. Finally, the computational cycles including dissolution, diffusion and reaction iteration manipulated by the cellular automaton-based evolution rules along with various empirical dissolution and reaction probabilities were used to mimic the hydration process and microstructural development. Herein, a parabolic function with a conversion factor ($\beta$) was used to link computational cycles (n) with real-time (t):

$$t = \beta n^2$$

(1)

For simulation, the attributes of cement need to be defined first. In this study, P.I. 52.5 Portland cement (Chinese standard) with a density of 3.15 g/cm$^3$ was employed, which is similar to ASTM Type I cement and composed of 53.72% C$_3$S, 24.09% C$_2$S, 7.61% C$_3$A, 8.98% C$_4$AF, and...
extra 5.6% C\textsubscript{3}S\textsubscript{4}H\textsubscript{2} by volume. The other inputs including intra-particle chemical phase distribution and particle size distribution of Portland cement, and conversion factor ($\beta = 0.00035$ h/cycle\textsuperscript{2}) are kept consistent with those reported in\cite{46,48}. Fig. 2b displays a typical example of hydrated cement paste with w/c ratio of 0.5 at 90 d.

To separate bulk paste and ITZ, it is necessary to determine the distribution of capillary porosity in 3D microstructure of cement paste, which was calculated by averaging the capillary porosity distribution in each 2D slice. Fig. 3 shows the distribution of capillary porosity in cement paste with w/c ratio of 0.4. As can be seen, there exists an obvious gradient in capillary porosity in pre-hydrated cement paste (0 d) within 12 \(\mu\)m away from the aggregate surface followed by a region with slight fluctuation. In hydrated cement paste at 90 d, the distribution of capillary porosity in the fluctuant region tends to be stable, while the region in the vicinity of the aggregate surface still has a higher capillary porosity. Additionally, the gradient of capillary porosity in the region with 12 \(\mu\)m near the aggregate surface is not significantly affected by the thickness of cement paste, i.e. sand content in mortar or concrete. For comparison, the experimental data obtained from the scanning electron microscopic images of concrete\cite{45} are also plotted in Fig. 3. As can be seen, the simulated distribution of capillary porosity in cement paste is in good agreement with experimental data. Fig. 4 shows the influence of w/c ratio on the distribution of capillary porosity, indicating that the capillary porosity at a given distance away from the aggregate surface increases with the increase of w/c ratio, while the gradient of capillary porosity in the region within 12 \(\mu\)m near the aggregate surface is less dependent on w/c ratio. Therefore, the thickness of ITZ can be considered as constant regardless of aggregate content and w/c ratio, consistent with the findings reported in\cite{24,49–51}, and the thickness of ITZ can be set as 12 \(\mu\)m based on the distribution of capillary porosity in cement paste shown in Figs. 3 and 4, which is between 10 \(\mu\)m and 50 \(\mu\)m\cite{44}.

![Fig. 3. Distribution of capillary porosity in cement paste in mortars with w/c ratio of 0.4 and sand contents of 50% and 60% at 90 d away from the aggregate surface.](image)

![Fig. 4. Distribution of capillary porosity distribution in cement paste in mortars with w/c ratios of 0.4, 0.5 and 0.6, and sand contents of 50% (a) and 60% (b) at 90 d away from the left aggregate surface.](image)
sand volume fractions of 50% and 60%, the volume fraction of ITZ is 10.88% and 12.67%, respectively (see Section 2.3) and thus the volume ratios between ITZ and bulk paste were calculated to be 0.278 and 0.464, corresponding to the thickness of cement paste of 102 μm and 70 μm, respectively. The distribution of capillary porosity in cement paste of mortars with sand contents of 50% and 60% at 90 d is shown in Fig. 4. Afterwards, the bulk paste and ITZ can be separated and the 3D microstructure and capillary pore structure of them can be extracted, as indicated in Fig. 5 for the case of mortar with w/c ratio of 0.5.

2.3. Mortar level

In general, mortar at meso-scale can be regarded as a four-phase material composed of bulk paste, ITZ, void, and fine aggregate (sand). In this study, sand and voids were both simplified as spheres. To simulate the RVE of mortar, a similar HCSS algorithm [39] was employed, where each hardcore (sand) is surrounded by a thin softshell of ITZ with thickness of 12 μm, while voids were treated as hardcores that can freely overlap with ITZ. To increase the packing density, the particles including sand and voids were placed in a cubic domain filled with cement paste in the sequence of size from the largest particle to the smallest one. Herein, the typical sand with a fineness modulus of 2.8 was used for modelling the mesostructure of mortar, the particle size of which is between 0.15 mm and 4.75 mm (see Fig. 6). As summarised in Table 1, the sand content of mortar specimens for measuring ionic diffusivity is in the range of 50% to 62%. To keep consistent with experiments, the mortar specimens with sand contents of 50% and 60% were considered in this study. Regarding voids in mortar, it was observed from X-ray computed tomography scanning by Kim et al. [52] that the void content is around 4% and the average diameter of voids is 0.134 mm, which were adopted for modelling the mesostructure of mortar here. To achieve a representative geometry, the size of mortar for simulation of ionic diffusion should be at least 6–10 mm [53,54]. Considering the thickness of ITZ (12 μm), the RVE size of mortar was set as 9 × 9 × 9 mm³, corresponding to 750 × 750 × 750 voxels as the resolution of 12 μm/voxel was adopted. Fig. 6 shows the simulated and measured particle size distribution of sand in mortar, which agrees very well with each other. The maximum size of sand in the mortar is 2.77
mm that is less than 1/3 the length size of RVE of mortar. It suggests that the selected RVE size of mortar can meet the criterion that the side length of RVE should be at least 3–5 times the maximum size of inclusion [55].

With these inputs, the RVE of mortar can be simulated using the HCSS algorithm. Taking the mortar with sand content of 60% as an example, its 3D mesostructure is displayed in Fig. 7. It can be observed that the inclusions including sand and voids were randomly distributed in RVE and ITZ (in orange) can overlap with each other. Fig. 8 shows the spatial distribution of aggregate-to-aggregate spacing in the mortars with sand contents of 50% and 60%, which indicates that the representative thickness of cement paste is between 120 μm and 168 μm and thus the simulated cement paste with length size of 150 μm can represent the real cement paste in mortar. For mortars with sand contents of 50% and 60%, the volume fractions of ITZ were calculated to be 10.89%, and 12.67%, respectively, which indicates that the representative thickness of cement paste is between 102 μm and 70 μm respectively for the mortars with sand contents of 50% and 60%, as demonstrated in Fig. 4.

2.4. Concrete level

Concrete is considered as a two-phase material consisting of mortar and coarse aggregate. Given that the thickness of interfacial layer between cement paste/mortar and each coarse aggregate is negligible in comparison with the coarse aggregate particle size and the volume fraction of ITZ in concrete is mainly dependent on fine aggregates because of their high specific surface area, the interfacial layer surrounding each coarse aggregate in concrete can be ignored and the contribution of ITZ in concrete can be included in mortar at meso-scale as an individual phase in mortar, as introduced in Sections 2.2 and 2.3. This is consistent with that adopted for multiscale modelling of physical and mechanical properties of concrete in literature, e.g., viscoelasticity [56] and creep [57]. In the simulations, the coarse aggregates were assumed as spheres and placed into a cube following the sequence from the largest particle to the smallest one. During the packing process, the spherical aggregates cannot overlap with each other and the periodic boundary condition was employed. In this study, a typical particle size ranging from 4.75 mm to 19 mm for coarse aggregates (see Fig. 6) was used to simulate the mesostructure of concrete. The RVE size of concrete was set as 60 mm with a resolution of 0.12 mm/voxel, which is over three times the maximum size of coarse aggregate [55]. A typical 3D mesostructure of concrete with coarse aggregate content of 40% is displayed in Fig. 9. A comparison between the simulated and measured particle size distribution of coarse aggregate in concrete shown in Fig. 6 indicates a good agreement between them. It is worth mentioning that
the irregular-shaped aggregates can be also simulated using the central
growth method \[58,59\] or Voronoi tessellation method \[60\] in this
modelling framework. Given that the ionic diffusivity in concrete is
mainly dependent on aggregate content and the shape and fineness of
aggregate have less influence on the ionic diffusivity \[53,61\], only the
spherical coarse aggregates were considered in this study.

3. Modelling of ionic diffusivity in unsaturated concrete

3.1. Modelling of moisture distribution in concrete at multiscale

The moisture distribution in concrete is strongly influenced by its
porous structure with a wide range of size including gel pores, capillary
pores, and voids. Considering the difference of their geometrical char-
acteristics, the water-gas distribution in gel and capillary pores was
simulated using a multiphase LB model, while the voids were regarded
to be completely occupied by water or gas as a result of the isolated
distribution of them in concrete.

At nano- and micro-scale, a multiphase LB model \[23\] was employed
to simulate the equilibrium water-gas distribution in pore network of C-
S-H or cement paste. As the details about theory and implementation of
multiphase LB model have been given in a recent publication \[23\], only
the modelling procedure was briefly introduced here. In the simulations,
the pore voxels in the 3D microstructure of C-S-H or cement paste were
randomly converted into liquid and gas voxels according to a pre-set
distribution including water/gas density ratio and contact angle of water on
the surface of solid phases in cement paste, a series of input parameters
considering the difference of their geometrical characteristics, the water-gas distribution in gel and capillary pores was simulated using a multiphase LB model, while the voids were regarded to be completely occupied by water or gas as a result of the isolated distribution of them in concrete.

In mortar, the voids were randomly segmented into water-filled and
gas-filled voids according to the given volume ratio. As per the Kelvin-
Laplace equation \[62\], the gas-filled pores in porous media are gradu-
ally occupied with water, following an order from small pores to large
pores with the increase of water saturation level. Therefore, the gel
pores are first filled by water followed by capillary pores and voids in
sequence with the increasing water saturation level of concrete. As such,
the water content in pores at each scale can be calculated using the
known constituents of pore structure of concrete. This method has been
successfully used to investigate the moisture-related properties of con-
crete considering the hierarchical pore structure, e.g., water sorption
isotherm \[41\], drying shrinkage \[63\], and permeability \[64\].

3.2. Modelling of ionic diffusivity in concrete at multiscale

In this study, an integrated LB-finite difference modelling framework
was proposed to mimic the ionic diffusion and estimate the ionic
diffusivity in unsaturated concrete. At nano- and micro-scale, i.e. C-S-H
and cement paste, the LB model for diffusion was used, while the finite
difference model for diffusion was employed at meso-scale, i.e. mortar
and concrete. In the simulation, the simulated ionic diffusivity at the low
scale was employed as the input to estimate the ionic diffusivity at the high scale, as displayed in Fig. 1.

3.2.1. Modelling of ionic diffusivity in C-S-H and cement paste

Treating gas-filled gel and capillary pores as non-diffusive phases,
the LB method was employed to simulate the ionic diffusivity in un-
saturated C-S-H, bulk paste and ITZ \[48\]. A brief introduction to theory
and implementation of the LB model for diffusion is provided below. For
the pure diffusion phenomenon of porous media, the discretised Boltz-
mann equation is given as:

$$ f_i(x + c_v \delta t, t + \delta t) - f_i(x, t) = -\frac{1}{\tau} \left[ f_i(x, t) - f^{eq}_i(x, t) \right] $$  \hspace{1cm} (2)

where $f_i$ and $f^{eq}_i$ (equal to $\frac{1}{N} \sum f_i(x,t)$) are the non-equilibrium and equi-
lbrium particle distribution functions at position $x$ and time $t$, $c_v$ is the
lattice speed that is equal to $\delta x / \delta t$, $\delta x$ and $\delta t$ denote the grid spacing and
time step in lattice units $lu$ and $tu$, respectively, $\epsilon_v$ is the microscopic
velocity at position $x$ and time $t$, the subscript $i$ represents the ith discrete
lattice velocity direction, equal to 0, 1, ..., (b - 1), and $\tau$ is the relaxation
time within (0.5, 2) in lattice units \[48\]. A detailed mapping between the
lattice units and real physical units can be found in a previous study
\[20\], based on which the LB simulation results can be related to any
quantities in the physical system.

It has been demonstrated that the D3Q7 lattice model can be used
instead of D3Q19 to improve the computational efficiency when simul-
ating the pure diffusion process of porous media \[65\]. According to
Chapman-Enskog expansion \[65\], the relaxation time of D3Q7 lattice

model indicated in Eq. (2) is associated with the ionic diffusivity in lattice units ($\mathcal{D}$) as:

$$\mathcal{D} = \frac{2}{\tau} \left( \tau - \frac{1}{2} \right) \Delta t$$

(3)

where the lattice speed $c = \Delta x / \Delta t$ ($\Delta t = 1$ and $\Delta x = 1$) is set as 1 by default.

Regarding boundary conditions, the inlet/outlet boundary condition was applied at the inlet and outlet of the computational domain. To make sure no diffusive flux through the other four surfaces, the solid wall was added for each of them [66]. The periodic condition was applied in the direction corresponding to the concentration gradient so that the nodes on inlet and outlet boundaries were considered as neighbours. At the interface of diffusive and non-diffusive nodes inside the computational domain, the no-ship condition was imposed following the half-way bounce-back rule.

Once the steady-state diffusion is achieved, the diffusive flux across the computational domain ($\mathcal{J}$) can be obtained as [65]:

$$\mathcal{J} = - \sum_i \left[ \mathcal{D} _i \mathcal{C}_i - 0.5 \right] \tau_a$$

(4)

where $\tau_a$ represents the relaxation time of diffusive phase $a$ in the computational domain in lattice units.

Then, the ionic diffusivity in the computational domain in physical units ($D_0$) can be calculated by [48]:

$$\frac{D_0}{D_e} = \mathcal{J} / \Delta x$$

(5)

where $D_0$ is the ionic diffusivity in water-filled pore (set as $2.03 \times 10^{-10}$ m$^2$/s in water-filled gel pore [23] and $2.03 \times 10^{-9}$ m$^2$/s in water-filled capillary pore [67] for chloride ions), and $D_e$ is the diffusive flux across a water-saturated pore space with the same size as the computational domain.

### 3.2.2. Modelling of ionic diffusivity in mortar and concrete

At the meso-scale, a finite difference model [58] was employed to simulate the ionic diffusion through mortar and concrete and estimate the ionic diffusivity. In the simulations, the aggregates and gas-filled voids were regarded as non-diffusive inclusions and the ionic diffusivity in water-filled voids is $2.03 \times 10^{-9}$ m$^2$/s [67]. The steady-state ionic diffusion in mortar or concrete is satisfied with Fick’s first law:

$$\nabla (D \nabla C) = 0$$

(6)

where $\nabla$ is the gradient operator, $D$ denotes the ionic diffusivity matrix of the computational domain, and $C$ is the ionic concentration.

To numerically solve this governing equation, the finite difference method combined with the conjugate gradient method was used to simulate the ionic diffusivity in the computational domain by imposing an ionic concentration gradient along the diffusion direction. No ionic flux was allowed to pass through the other four surfaces. After achieving the steady-state, the ionic diffusivity in mortar or concrete ($D_e$) can be calculated as:

$$D_e = \frac{JL}{A \Delta C}$$

(7)

where $J$ is the steady-state ionic flux, $A$ is the cross-section area of the computational domain, and $L$ is the length over which the concentration gradient $\Delta C$ was imposed.

### 4. Results and discussion

#### 4.1. Ionic diffusivity in unsaturated C-S-H

The equilibrium distribution of water and gas phases in C-S-H with various water saturation levels can be simulated using the multiphase LB model. Fig. 10 shows the simulated equilibrium water-gas distribution in the microstructure and gel pore structure of C-S-H with degrees of water saturation of 90%, 70%, and 50%. It can be observed that the water phase tends to cover the C-S-H surface and fill the small pores, while the gas phase tends to form the gas clusters and fill the large pores. This agrees well with the finding obtained from the simulations based on porous geometry and Kelvin-Laplace equation that water is gradually removed from the large pores and then the small pores with the drop in degree of water saturation [68]. Treating the water-filled gel pores as a diffusive phase, Fig. 11 displays the steady-state ionic concentration distribution in unsaturated C-S-H corresponding to that shown in Fig. 10. The ionic diffusivity in unsaturated C-S-H against degree of water saturation is presented in Fig. 12. As can be seen, the ionic diffusivity in C-S-H reduces with the decrease of degree of water saturation, which can be attributed to the decreasing effective water-filled gel porosity as a result of the decreasing water-filled porosity and connectivity of water-filled pores [23]. In addition, as the water saturation level reduces to 24%, the ionic diffusivity becomes zero, suggesting that the water-filled gel pores are disconnected at this critical water saturation level. This finding is consistent with that reported by Martyts [69] that for the porous media consisting of overlapping spherical inclusions, the critical water saturation level is around 25%. By fitting the simulation results, a quadratic polynomial correlation between ionic diffusivity ($D_{CSH}$) and degree of water saturation in C-S-H at nano-scale ($S_w$) can be obtained as:

$$D_{CSH} = D_{CSH,5} \times (1.29 \times S_{w,2} - 0.28 \times S_{w} - 0.01)$$

(8)

where $D_{CSH,5}$ represents the ionic diffusivity in saturated C-S-H, equal to $1.83 \times 10^{-11}$ m$^2$/s.

This agrees well with the finding given in [18,70] that the ionic diffusivity in porous media consisting of overlapping spherical inclusions can be described using a quadratic polynomial function of water saturation level.

#### 4.2. Ionic diffusivity in unsaturated cement paste

#### 4.2.1. Effect of water saturation level

Considering the contribution of gel pores to water saturation level, the volume fraction of water-filled capillary pores in cement paste can be calculated according to a desired degree of water saturation. Taking cement paste of mortar with sand content of 60% and w/c ratio of 0.5 at 90 d as an example, the equilibrium water-gas distribution in bulk paste and ITZ at water saturation levels of 90%, 70%, and 50% is displayed in Fig. 13. As can be seen, the water-gas distribution in cement paste is heterogeneous and ITZ is easier to have gas clusters than bulk paste at a given water saturation level. Fig. 14 shows the distribution of water saturation level in the regions of bulk paste and ITZ with w/c ratio of 0.5 at 90 d. Compared to the relatively homogeneous distribution in bulk paste, the degree of water saturation exhibits a significant increase in ITZ away from the aggregate surface, which can be ascribed to the heterogeneous distribution of pores in cement paste, including capillary pores and gel pores (C-S-H). On one hand, the capillary porosity in ITZ is higher than that in bulk paste and displays a gradient away from the aggregate surface (see Figs. 7 and 8). Since the water phase tends to fill the small pores in porous media [62], the large capillary pores in ITZ are thus first occupied by the gas phase with the decrease of water saturation level, resulting in a relatively lower water saturation level in ITZ than bulk paste when the capillary pores are partially saturated, e.g. water saturation levels of 50%, 70%, and 90% (see Fig. 14). On the other hand, when the capillary pores in cement paste are completely occupied by gas phase, C-S-H containing gel pores starts to play an important role in water-gas distribution and ionic diffusion. For cement paste with w/c ratio of 0.5 at 90 d, the pores are composed of 63% capillary pores and 37% gel pores by volume. When the degree of water saturation is below...
37%, there is no water phase in capillary pores and the gel pores become partially saturated. The corresponding volume fractions of C-S-H in ITZ and bulk paste were calculated to be 0.42 and 0.50, respectively. Due to the less C-S-H in ITZ [45], ITZ has a lower water saturation level than bulk paste when the water saturation level of cement paste is below 37%, as shown in Fig. 14.

**Fig. 10.** Equilibrium distribution of water and gas phases in microstructure (top) and gel pore network (middle), and water-filled gel pores (bottom) in colloidal C-S-H with degrees of water saturation of 90% (a), 70% (b), and 50% (c) at 90 d (blue, grey and yellow colours represent water, gas and C-S-H particle, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 11.** Steady-state distribution of ionic concentration in C-S-H with degrees of water saturation of 90% (a), 70% (b), and 50% (c) along X-direction.
The presence of ITZ can promote ionic diffusion in saturated concrete due to the high porosity and large pore size in ITZ [24,26,53,61]. Nevertheless, the ionic diffusion in partially saturated concrete may not follow this trend, as the difference in effective water-filled porosity between ITZ and bulk paste would be reduced due to the lower degree of water saturation of ITZ in comparison with bulk paste. To estimate the ionic diffusivity in unsaturated cement paste, the LB model for diffusion was employed to mimic the ionic diffusion in partially saturated bulk paste and ITZ, respectively. Fig. 15 shows the steady-state ionic concentration distribution in bulk paste and ITZ at water saturation levels of 90%, 70%, and 50% corresponding to that illustrated in Fig. 13. The ionic diffusivity in unsaturated bulk paste and ITZ against degree of water saturation is displayed in Fig. 16b. It can be observed that the ionic diffusivity in bulk paste and ITZ is significantly reduced with the decrease of water saturation level due to the less effective diffusion paths for ions as a result of the decreasing water-filled porosity and pore connectivity [20]. As demonstrated in [23], with the reduction of water saturation level, the ionic diffusion in pure cement paste undergoes a gradual change in terms of available diffusion paths: connected capillary pore network, combination of water-filled capillary pores and saturated C-S-H network, and partially saturated C-S-H network as the main ionic diffusion paths, followed by the depercolation of water-filled gel pores. However, due to the difference in pore structure between bulk paste and ITZ, the change of ionic diffusivity in them with water saturation level follows different trends. Compared to bulk paste, a sharper drop in ionic diffusivity can be observed in ITZ, especially at water saturation levels of 89%–100%. With the decrease of water saturation level from 100% to 89%, the ionic diffusivity in ITZ is reduced by 12 times, while a 200% reduction in ionic diffusivity in bulk paste can be found. It can be ascribed to the relatively large capillary pore clusters and high capillary porosity in ITZ, which facilitate the formation of gas clusters in ITZ at the initial decrease stage of water saturation level from the saturated state [62].

To assess the role of ITZ in ionic diffusion in concrete, the ionic diffusivity ratio of ITZ to bulk paste ($D_{ITZ}/D_{BP}$) is usually used [24,51]. Fig. 17b shows the ionic diffusivity ratio of ITZ to bulk paste as a function of water saturation level. The change of ionic diffusivity ratio of ITZ to bulk paste with the decrease of water saturation level can be divided into three stages: a sharp drop from 3.99 to 0.88 with decreasing water saturation from 100% to 89%, a slight drop to 0.53 with a further reduction of water saturation level to 37%, and a plateau, where the sharp drop can be attributed to the more significant decrease in the water saturation level of ITZ compared to bulk paste. For instance, with the decrease of water saturation level of cement paste from 100% to 89%, the water saturation level of ITZ is decreased from 100% to 81% compared to that of bulk paste from 100% to 93%. Considering the relatively high capillary porosity in ITZ, the effective water-filled porosity in ITZ is thus decreased more dramatically in the initial decrease stage of water saturation level. After the large capillary pores in ITZ are occupied by gas, the remaining water-filled capillary pores in bulk paste and ITZ have a similar trend to lose water with decreasing water saturation level, leading to a similar decreasing trend in ionic diffusivity in ITZ and bulk paste, as indicated in Fig. 16b. Since the ionic diffusivity in ITZ is lower than that in bulk paste in this stage, the ionic diffusivity ratio thus exhibits a slight decrease. When the capillary pores in cement paste are completely occupied by gas, the partially saturated C-S-H network acts as the diffusion path for ions. The moisture distribution in C-S-H is homogeneous at micro-scale, resulting in a constant ionic diffusivity ratio within this stage.

Regarding the role of ITZ in ionic diffusion in unsaturated concrete, it can be found that the ionic diffusivity in ITZ is greater than that in bulk paste only at a high water saturation level between 90% and 100%. As the water saturation level decreases to a critical value, i.e. 90%, the ionic diffusivity ratio of ITZ to bulk paste becomes less than 1, suggesting that the presence of ITZ can retard the ionic diffusion in concrete. This is an important finding for practical concrete structures. As reported in [71], the internal area of cover concrete exposed to marine environment where the chloride penetration is driven by diffusion has a constant degree of water saturation, close to that caused by self-desiccation [72], i.e., around 50–70% for mature concrete [4]. Therefore, ITZ would not facilitate the ionic diffusion in practical concrete, despite of the relatively higher porosity compared to bulk paste.

4.2.2. Effect of water-to-cement ratio

To estimate the effect of w/c ratio on ionic diffusivity in partially saturated cement paste, simulations were also carried out on cement paste with w/c ratios of 0.40 and 0.60, besides 0.5. The simulation results are shown in Fig. 16b in terms of ionic diffusivity in ITZ and bulk paste against degree of water saturation. In general, a similar relationship between ionic diffusivity and water saturation level can be found, while the cement paste with a higher w/c ratio exhibits a higher ionic diffusivity, which can be attributed to the increase in water-filled porosity [23] and connectivity of water-filled pores [73] at a given water saturation level as a result of the increasing w/c ratio. Fig. 17b shows the ionic diffusivity ratio of ITZ to bulk paste against degree of water saturation, indicating that the ionic diffusivity ratio at the saturated state is increased with increasing w/c ratio. This finding is consistent with that reported in [74]. Regarding the partially saturated state, the increasing w/c ratio decreases the critical water saturation level at which the ionic diffusivity ratio is equal to 1. For instance, with the increase of w/c ratio from 0.4 to 0.6, the critical water saturation level is decreased from 91% to 86% for cement paste of mortar with sand content of 60%, which can be explained by the fact that the difference in capillary pore network between ITZ and bulk paste is reduced with increasing w/c ratio. As demonstrated in [75], the ratio of capillary porosity in ITZ to that in bulk paste as an indicator for estimating the difference in capillary pore network of ITZ and bulk paste is decreased from 1.42 to 1.27. Thus, the moisture distribution in cement paste tends to become uniform at a certain water saturation level, which helps keep a relatively higher water-filled capillary porosity in ITZ. When the capillary pores are fully occupied by gas, C-S-H network will serve as the dominant diffusion channel for ions. As shown in Fig. 17b, the ionic diffusivity ratio is smaller for cement paste with a higher w/c ratio, mainly due to the increasing difference in C-S-H network between ITZ and bulk paste. For instance, as the w/c ratio increases from 0.4 to 0.6, the ratio of C-S-H content in ITZ to that in bulk paste is increased from 1.1 to 1.2.

4.2.3. Validation of simulations with experimental data

For validation, the simulated ionic diffusivity in unsaturated bulk
Fig. 13. Equilibrium distribution of water and gas phases in microstructure (top) and capillary pore network (middle), and water-filled capillary pores (bottom) in bulk paste and ITZ in mortar with w/c ratio of 0.5, sand content of 60%, and degrees of water saturation of 90% (a), 70% (b), and 50% (c) at 90 d (blue, grey and red colours represent water, gas and solid phases, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
paste was compared with the experimental data for pure cement paste with w/c ratio of 0.4 obtained from literature [9], as illustrated in Fig. 16. The detailed information on experimental program in terms of testing samples, sample preconditioning, and test method is given in Table 1. Note that in [9] lithium was selected as a tracer to characterise the effective ionic diffusivity in cement paste using the natural diffusion method, while the chloride natural diffusion in cement paste was simulated in this study. It was reported that the effective diffusivity of anion is 5–20 times that of cation in saturated cement paste with w/c ratio of 0.4 [76,77]. Therefore, a factor of 10 was selected to calibrate the effective diffusivity of lithium and chloride here, as plotted in Fig. 16. The simulated ionic diffusivity agrees well with the measured data as the water saturation level is greater than 70%, while the simulation results become slightly higher than the experimental data for the degree of water saturation below 70%. It can be attributed to the fact that the simulated ionic diffusivity in bulk paste indicated in Fig. 16 is expressed as a function of water saturation level of cement paste (bulk paste plus ITZ) rather than that of bulk paste and the water saturation level of cement paste is slightly lower than that of bulk paste. For example, as displayed in Fig. 14, for the cement paste with water saturation level of 50%, the water saturation level of bulk paste is calculated to be 55%. Therefore, the curve of simulated ionic diffusivity in bulk paste slightly shifts to the zone of low water saturation level. In addition, because of the presence of ITZ in concrete, the effective w/c ratio of bulk paste is lower than 0.4 and the coarser cement particles tend to distribute in bulk paste [45]. Thus, the change of ionic diffusivity in bulk paste with water saturation level is not identical to that in pure cement paste. Furthermore, the attributes of raw materials, curing age of specimens, and sample pre-conditioning used in literature would not be identical to that for simulations in this study, which would also result in a discrepancy between simulated and experimental results, as the microstructure of cement paste is greatly affected by these factors [78].

4.3. Ionic diffusivity in unsaturated mortar

4.3.1. Effect of water saturation level

Considering the contribution of gel pores and capillary pores to water saturation level of mortar, the water-filled void content in mortar can be calculated according to a pre-set water saturation level and the pore structure constituents of cement paste explained in Section 4.2. Taking the mortar with w/c ratio of 0.5 and sand content of 60% as an example, its mesostructure with water-filled void contents of 100%, 50%, and 0% is shown in Fig. 18, the corresponding water saturation levels of which are 100%, 88%, and 76% as the cement paste is saturated. Fig. 19 presents the ionic concentration distribution in 3D mortar at the steady state, indicating that the sand particles retard the ionic diffusion in mortar, leading to tortuous diffusion paths, and the increasing number of gas-filled voids also hinder the ionic diffusion as the water saturation level of mortar decreases.

Fig. 20 shows the change of ionic diffusivity in mortar with water saturation level. It was observed that with the decrease of water saturation level of mortar from 100% to 76%, there is a slight decrease in ionic diffusivity from $4.7 \times 10^{12} \text{m}^2/\text{s}$ to $3.4 \times 10^{12} \text{m}^2/\text{s}$, followed by a significant decrease to $6.3 \times 10^{13} \text{m}^2/\text{s}$ with a further reduction of water saturation level to 68%. When the water saturation level continues to drop, the change of ionic diffusivity in mortar is similar to that in bulk paste, as indicated in Fig. 14. The slight decrease in ionic diffusivity at water saturation level between 100% and 76% can be attributed to the formation of gas-filled voids that has less effect on the connected diffusion paths for ions. As indicated in [79], the effective diffusivity in concrete with void content of 4% is only increased by a factor of less than 2, compared to the reference concrete with void content of 0.46%. However, the voids have a great contribution to the water saturation level. To evaluate the influence of voids on ionic diffusivity,
the simulation results for mortar without voids are also plotted in Fig. 20. The curve of ionic diffusivity with degree of water saturation is significantly altered, especially at a high water saturation level and the ionic diffusivity in unsaturated mortar without considering the voids is much lower than that considering the voids, which significantly deviates from the experimental data [6,10,12]. Therefore, the voids cannot be ignored when predicting the ionic diffusivity in unsaturated mortar and concrete. The sharp drop of ionic diffusivity in mortar at water saturation level between 76% and 68% can be ascribed to ITZ that has a relatively higher ionic diffusivity than bulk paste but is more sensitive to the decrease of degree of water saturation (Fig. 17). When the water saturation level of mortar drops to below 68%, the change of ionic diffusivity in mortar is mainly dominated by bulk paste as ITZ has a lower ionic diffusivity than bulk paste in this range of water saturation level.

4.3.2. Effect of sand content

The sand content has a twofold effect on ionic diffusivity in unsaturated mortar. At micro-scale, the effective w/c ratio of bulk paste of mortar is dependent on the sand content, which may affect the moisture distribution and ionic diffusivity in cement paste [53]. At meso-scale, the increasing sand content can alter diffusion paths for ions (i.e. cement paste) in mortar due to non-diffusive nature of sand and increase the ITZ content in mortar [80].

To explore the influence of sand content on ionic diffusivity in unsaturated mortar at micro-scale, LB simulations were further carried out on the cement paste of mortar with sand content of 50% (see Figs. 16a and 17a) in addition to 60%. It can be found that at the saturated state
the ionic diffusivity in bulk paste is lower for the mortar with a higher sand content. For example, for mortar with w/c ratio of 0.5, the ionic diffusivity in saturated bulk paste is reduced from $8.88 \times 10^{-12}$ m$^2$/s to $6.81 \times 10^{-12}$ m$^2$/s with the increase of sand content from 50% to 60%. It can be attributed to the decreasing effective w/c ratio of bulk paste resulting from the increasing sand content, which reduces the ionic diffusivity in bulk paste [53]. However, as the water saturation level drops, the influence of sand content on ionic diffusivity in bulk paste becomes less significant. As the water saturation level is below 80%, the change of ionic diffusivity in bulk paste is identical for mortars with different sand contents. As ITZ is easier to have gas clusters than bulk paste (see Fig. 14), the water saturation level of bulk paste is higher for mortar with a higher sand content at a given degree of water saturation. The increase in water saturation level of bulk paste can decrease the discrepancy in ionic diffusivity in mortar as a result of the decreasing effective w/c ratio. It can be confirmed by the ionic diffusivity ratio of ITZ to bulk paste indicated in Fig. 17, which tends to be similar for mortars with different sand contents with the reduction of water saturation level.

To estimate the influence of sand content on ionic diffusivity in mortar at meso-scale, finite difference simulations were also carried out on the mesostructure of mortar with sand content of 50% in addition to 60%, the results of which are shown in Fig. 20. Compared to the water saturation level, sand content has an insignificant influence on the ionic diffusivity in mortar, which is slightly reduced with the increase of sand content in general because of the reduction in volume fraction but increased tortuosity of cement paste [59] and the slightly decreased ionic diffusivity in bulk paste at a high water saturation level (see Fig. 16). However, at the water saturation level between 68% and 77%, the increase of sand content can lead to a rise in ionic diffusivity in mortar. Since the void content in mortar was set as 4% in the simulations, the contribution of voids to the water saturation level of mortar is increased with the increasing sand content, which slows the decrease of water-filled capillary porosity. For example, the water saturation level at which no water-filled void is present is decreased from 80% to 76% with the increase of sand content from 50% to 60%. This finding is in good agreement with the experimental observation [8] that there is no consistent ranking of ionic diffusivity in concrete with different sand contents but same coarse aggregate content at a given water saturation level.

4.3.3. Validation of simulations with experimental data

For comparison, the simulated ionic diffusivity in unsaturated mortar with sand content of 60% is shown in Fig. 20, together with the experimental data obtained from literature [6,10,12], the details on experiments of which are summarised in Table 1. Note that this study is to simulate the ionic natural diffusion, while the experimental data reported in [10,12] were characterised using non-steady-state electrical migration tests, which were found to be higher than those obtained from natural diffusion tests with a contract ratio of 1.5–6, depending on the applied ionic concentration gradient [81]. As suggested by Castellote et al. [81], a ratio of 3 was adopted here to convert the measured data by means of electrical migration tests [10,12] to ionic diffusivity considering the applied catholyte solution of 10% NaCl [82]. After such calibration, the simulation results of ionic diffusivity in mortar against degree of water saturation agree well with the experimental data collected from [12] and show a similar changing trend but are slightly
lower in comparison with the literature data [6,10,12], which could be ascribed to the difference in void content. For instance, the measured void content of mortar in [10] is 6.1%, which is lower than the pre-set value for the simulations, i.e. 4%. As discussed above, the voids have a great contribution to water saturation level and would influence the change of ionic diffusivity in unsaturated mortar with water saturation level.

4.4. Ionic diffusivity in unsaturated concrete

Fig. 21 shows the steady-state ionic concentration distribution in concrete with coarse aggregate content of 40%, based on which the ionic diffusivity in concrete can be calculated as introduced in Section 3.2.2. The simulation results of ionic diffusivity in unsaturated concrete with coarse aggregate content of 40%, sand content of 30%, and w/c ratios of 0.4 and 0.5 are shown in Fig. 22. Since the concrete at meso-scale is only comprised of mortar and coarse aggregate, the moisture conditions in pore network are not altered. The change of ionic diffusivity in concrete with water saturation level is thus analogous to that in mortar with sand content of 50% indicated in Section 4.3. The ratio of ionic diffusivity at a given water saturation level between mortar and concrete is constant and less than 1 as a result of the reduced volume fraction but increased tortuosity of mortar caused by coarse aggregates [59], i.e. 0.48 for coarse aggregate content of 40%.

For comparison, the experimental data of ionic diffusivity in unsaturated concrete obtained from literature [11] were also plotted in Fig. 22, which all lie within the range of simulation results at a high water saturation level but are approximately 4–10 times lower than simulation results when the degree of water saturation is below 60%. It can be ascribed to the following uncertainties between experimental
measurements and numerical simulations. The experimental data reported in [11] were measured using electrical resistivity tests that relate the conductivity in concrete to its effective ionic diffusivity [14]:

\[
D_C = \frac{D_C,S}{\sigma_{p,S}} \frac{\sigma_{p}}{\sigma_C}
\]  

(9)

where \(D_C\) and \(D_{C,S}\) denote the ionic diffusivity in concrete at water saturation levels of \(S_w\) and 100% respectively, \(\sigma_C\) and \(\sigma_{C,S}\) represent the conductivity in concrete at water saturation levels of \(S_w\) and 100% respectively, and \(\sigma_p\) and \(\sigma_{p,S}\) stand for the conductivity in pore solution of concrete at water saturation levels of \(S_w\) and 100%, respectively.

In the electrical resistivity tests, the attributes of pore solution of concrete were assumed to be the same as those in free water regardless of the pore structure of concrete, based on which the conductivity in pore solution can be directly calculated according to the ionic concentration of pore solution [10,12]. This assumption makes sense for the concrete samples at a high water saturation level because the water conduction is dominantly controlled by the water-filled larger pores [23], which is less affected by the EDL effect [83]. However, as the water saturation level reaches a low value, the water-filled smaller pores become the main diffusion paths for ions. Due to the significant EDL effect of water-filled smaller pores, the actual conductivity in pore solution of concrete at a low water saturation level is lower than the calculated one according to the ionic concentration of pore solution [84]. Therefore, the corresponding experimental data of ionic diffusivity in unsaturated concrete at a low water saturation level are remarkably underestimated.

Additionally, concrete samples are inevitable to undergo extra drying during the whole testing process as it generally lasts a long time [85]. The actual water saturation level is thus lower than the desired one, leading to the underestimation of measured ionic diffusivity in concrete at a given water saturation level. Moreover, the continued hydration of cement particles during the exposure to humid conditions can densify the microstructure of concrete samples [86]. For example, as demonstrated in [87], the ionic diffusivity in mature concrete would be decreased by over 200% with the increasing curing age from 91 d to 181 d. Since this effect was not taken into account in the simulations, the simulated ionic diffusivity in concrete would be overestimated.

Furthermore, it is worth mentioning that the simulated ionic diffusivity in non-saturated concrete presented in this study does not consider the potential effects of ion binding (e.g., for chloride ions) and ionic concentration in pore solution which would change as the water saturation level in pores varies. Taking chloride ions as an example, when the chloride ions ingress into concrete, the physical and chemical binding can take place between chloride and hydration products, which would result in a reduction in concentration of free chloride ions in pore solution and changes in pore structure of concrete as well as chloride diffusivity in concrete [88–90]. For concrete with a lower water saturation level, the binding effect is more significant due to the relatively higher ionic concentration in pore solution. Therefore, it is necessary to consider these effects in order to predict the ionic diffusivity in concrete at various saturation levels more accurately, which can be achieved by implementing the modelling procedure proposed by Zhang et al. [31,90] into the integrated multiscale framework of this study. This is a subject of ongoing work and will be presented in a future publication.

5. Conclusions

In this study, an integrated multiscale framework was present to mimic the ionic diffusivity in unsaturated concrete accounting for the hierarchical microstructure of concrete and moisture distribution in pore network. The effects of microstructural features on ionic diffusivity in partially saturated concrete are quantitatively investigated. Based on the simulation results in comparison with experimental data obtained from literature, the main conclusions can be drawn as follows:

- The ionic diffusivity in C-S-H is strongly dependent on the water saturation level. The relationship between ionic diffusivity in C-S-H and degree of water saturation can be described using a quadratic polynomial equation. The depercolation of gel pores in C-S-H occurs at a critical degree of water saturation of 24%, corresponding to a zero ionic diffusivity.

- The moisture distribution in cement paste of concrete is heterogeneous due to the difference in pore network between bulk paste and ITZ. The degree of water saturation exhibits a significant increase in ITZ away from the aggregate surface as compared to the homogeneous distribution in bulk paste. And thus, the change of ionic diffusivity in bulk paste and ITZ with decreasing water saturation level is different. As the water saturation level of cement paste drops to a critical value (around 90%), ITZ starts to retard ionic diffusion in concrete. The critical water saturation level is slightly decreased with the increase of w/c ratio.

- The presence of voids has a great contribution to water saturation level but less influence on ionic diffusivity in mortar. The ionic diffusivity in saturated mortar is decreased with increasing sand content due to the decrease in effective w/c ratio of bulk paste and the increasing tortuosity but decreasing content of diffusion paths for ions. However, the increasing sand content has an insignificant effect on ionic diffusivity in unsaturated mortar because the increase in water saturation level of bulk paste can decrease the difference in ionic diffusivity induced by the decreasing effective w/c ratio. The simulation results of ionic diffusivity in unsaturated mortar are in good agreement with the experimental data obtained from literature.

- The change of ionic diffusivity in concrete with water saturation level is analogous to that in mortar. There exists a constant ratio (less than 1) between the ionic diffusivity values of mortar and concrete at a certain water saturation level as a result of the reduction in volume fraction and the increase in tortuosity of mortar caused by coarse aggregates.

CRediT authorship contribution statement

- Cheng Liu: Conceptualization, Methodology, Investigation, Data curation, Visualization, Writing – original draft. Mingzhong Zhang: Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial
interests or personal relationships that could have appeared to influence the work reported in this paper.

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