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Numerical investigation on tortuosity of transport paths in cement-based materials

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Abstract. Based on the compositions and structures of cement-based materials, the geometrical models of the tortuosity of transport paths in hardened cement pastes, mortar and concrete, which are associated with the capillary porosity, cement hydration degree, mixture particle shape, aggregate volume fraction and water-cement ratio, are established by using a geometric approach. Numerical simulations are carried out to investigate the effects of material parameters such as water-cement ratio, volume fraction of the mixtures, shape and size of aggregates and cement hydration degree, on the tortuosity of transport paths in hardened cement pastes, mortar and concrete. Results indicate that the transport tortuosity in cement-based materials decreases with the increasing of water-cement ratio, and increases with the cement hydration degree, the volume fraction of cement and aggregate, the shape factor and diameter of aggregates, and the material parameters related to cement pastes, such as the water-cement ratio, cement hydration degree and cement volume fraction, are the primary factors that influence the transport tortuosity of cement-based materials.

Keywords: tortuosity; cement-based materials; model; geometric approach; numerical simulation

1. Introduction

The service performance and durability of concrete structures, including bridges, dams, buildings and power plants, are significantly influenced by concrete material deterioration under permanently aqueous or chemically aggressive environments (Marchand *et al*. 2002, Bertron *et al*. 2005, Coussy *et al*. 2001, Shin *et al*. 2011). Concrete deterioration processes are associated with the transport behaviors of environmentally aggressive substances in concrete materials, such as the humidity, chloride and sulfate salts, acid rain, etc (Yoon 2009, Garrabrants *et al*. 2003, Moranville *et al*. 2003, Chen *et al*. 2007). Recently, due to the advance in concrete structure durability research, the transport behaviors of cement-based materials as porous multi-scale composite materials, such as the conductivity, permeability and diffusivity, have received extensive attentions

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(Guneyisi *et al*. 2010, Yamaguchi *et al*. 2009, Zheng *et al*. 2008, Neithalath *et al*. 2010). In cement-based materials such as hardened cement pastes, mortar and concrete, its transport behaviors are mainly controlled by the material microstructures (Quenard *et al*. 1998, Matte *et al*. 2000, Bentz *et al*. 2000). The microstructure of cement-based materials contains a very complicated pore structure, which is characterized by the porosity, tortuosity and connectivity of the pores (Zuo *et al*. 2010, Neithalath *et al*. 2010, Zhang *et al*. 2010). Therefore, it is essential to establish the relation between the transport behaviors and pore structure of cement-based materials for predicting the performance of cement-based materials and evaluating the concrete structure durability. The tortuosity of transport paths in cement-based materials is a key pore structure parameter (Yoon 2009, Coleman *et al*. 2008), and it plays a fundamental role in governing transport processes affecting the concrete durability (Stroeven *et al*. 2000, Igarashi *et al*. 2004). Modeling the tortuosity is a basis of analyzing quantitatively the transport behaviors and further calculating the in-service lifetime of concrete structure under chloride and sulfate attack.

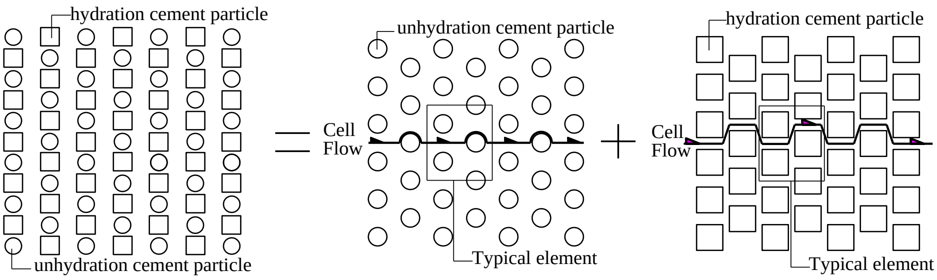
The concept of tortuosity was originally introduced by Carman to account for the sinuousness of individual flow channels and for cross-flow effects (Carman 1937). The tortuosity is usually defined by a ratio of the average diffusion path, L_e, of fluid particle to the corresponding straight and shortest distance, L, along the direction of macroscopic flux gradient, $\tau = L_e/L$ (Carman 1937, Barrande *et al*. 2007, Dullien 1979). Because the cement-based materials possess a porous system with the pore sizes ranging from nanometers to micrometers and the complicated porous networks, its actual transport path is extremely complicated or tortuous in both microscopic scale and macroscopic scale, which makes it very difficult to analytically find the tortuosity of cement-based materials. At present, the tortuosity of transport paths in cement- based materials were found by experiments (Garrouch *et al*. 2001, Amiri *et al*. 2005, Promentilla *et al*. 2007, Nakashima *et al*. 2007) or numerical simulations such as random walk (Promentilla *et al*. 2009) and Lattice boltzmann method (Weerts *et al*. 2001). However, the results from either experiment or numerical simulation are usually expressed as correlations with one or more empirical constants or as curves, thus the mechanisms behind the phenomena are often ignored. Therefore, seeking an analytical solution for quantifying the tortuosity of transport paths in cement-based materials is very necessary for modeling the permeability, diffusivity and durability of concrete materials.

For this purpose, this paper presents the geometrical models of tortuosity of transport paths in cement-based materials such as hardened cement pastes, mortar and concrete, and investigates numerically the effects of some material parameters, such as water-cement ratio, volumetric fraction of mixtures such as cement and aggregates, shape and size of aggregate, cement hydration degree, on the tortuosity of transport paths in hardened cement pastes, mortar and concrete.

2. Model description

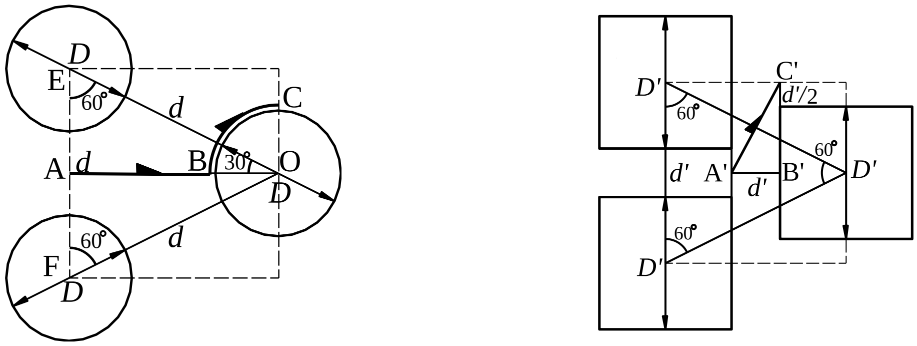
2.1 Tortuosity of transport paths in hardened cement pastes

The hardened cement pastes with a certain of hydration degree are mainly consisted of the unhydrated and hydrated cement particles. Based on SEM observation on the morphology of the cement particles in the process of the cement hydration, Authors have regarded the partly hydrated cement pastes as a mixture of the unhydrated circular cement particles with the average diameter and the square hydrated cement particles with the same length of a side (Zuo *et al*. 2011). In order to model easily the transport tortuosity, the hardened cement pastes are individually separated into



(a) Hardened cement pastes (b) Unhydrated cement particles (c) Hydrated cement pastes

Fig. 1 Ideal morphology and simplification of hardened cement pastes



(a) Hardened cement pastes (b) Unhydrated cement particles

Fig. 2 Representative unit cell for transport paths through unhydrated and hydrated cement medias

two parts: the unhydrated circular cement particles and fully hydrated square cement particles, as shown in Fig. 1. Therefore, the tortuosity of transport paths in hardened cement pastes can be obtained by modeling the transport tortuosity in unhydrated and fully hydrated cement particles.

For unhydrated circular cement particles given in Fig. 1(b), a possible configuration, namely a representative unit cell, for analyzing the transport tortousity of the penetrative water or diffusible ion in unhydrated cement particle deposits which are consisted of the circular cement partcles and the interconnected pores, is the dashed rectangle given in Fig. 2(a), in which the cement particles are arranged in an equilateral-triangle form. The penetrative water or diffusible ion moves along the maximum gradient direction under the gravity or chemical potential, namely, the transport path of the water or ion is $\mathrm{A} \rightarrow \mathrm{B} \xrightarrow{\text{along } 1/4 \text{ arc}} \mathrm{C}$, so the effective length of the transport path $L_e = (\overline{AB} + \overset{\frown}{BC})$, and the corresponding shortest distance $L = \overline{ABO}$. According to the definition of tortuosity (Barrande *et al*. 2007, Promentilla *et al*. 2009), the transport tortuosity in unhydrated circular cement particles can be obtained by

$$\tau'_{\text{uh-cp}} = \frac{L_e}{L} = 1 + \frac{\sqrt{3}(\pi - 2)}{6\left(1 + \dfrac{d}{D}\right)} \tag{1}$$

where $\tau'_{\text{uh-cp}}$ is the tortuosity of unhydrated circular cement particles in the loose state, D is the average diameter of unhydrated cement particles, d is the average gap among the unhydrated cement particles.

By using the porosity of the representative unit cell in Fig. 2(a), it can be obtained that

$$\frac{d}{D}=\sqrt{\frac{\pi}{2\sqrt{3}\left(1-\varphi_{\text{uh-cp}}\right)}}-1 \tag{2}$$

in which $\varphi_{\text{uh-cp}}$ is the porosity of unhydrated cement in the loose state, in general, the porosity of cement powers is about 58% (Zuo *et al*. 2010).

Substituting Eq. (2) into Eq. (1), the relation between the tortuosity $\tau'_{\text{uh-cp}}$ and the porosity $\varphi_{\text{uh-cp}}$ of the unhydrated circular cement particle deposites can be expressed by

$$\tau'_{\text{uh-cp}}=1+\frac{(\pi-2)\sqrt{\left(1-\varphi_{\text{uh-cp}}\right)}}{\sqrt{2\sqrt{3}\pi}} \tag{3}$$

when $\varphi_{\text{uh-cp}} = 58\%$, it can be obtained that $\tau'_{\text{uh-cp}} = 1.23$, it is in agreement with the tortuosity of the porous particles (Amiri *et al*. 2005, Zuo *et al*. 2010).

Similarly, for fully hydrated square cement particles given in Figure 1(c), its possible configuration or representative unit cell for analyzing the transport tortousity of the penetrative water or diffusible ion in fully hydrated cement particle deposits including the square particles and the interconnected pores, is also a dashed rectangle given in Fig. 2(b), in which the square particles are arranged in an equilateral-triangle form. Based on the actual condition that the tortuosity tends to infinity when the porosity of cement pastes approaches to zero ($\varphi_{\text{h-cp}}\rightarrow 0$, $\tau'_{\text{h-cp}}\rightarrow\infty$) (Yoon 2009), the paths $\text{A}'\rightarrow\text{C}'$ and $\text{A}'\rightarrow\text{B}'$ are respectively selected as the transport paths in the fully hydrated cement pastes and the shortest paths without the existence of the cement particles, namely, the effective length of the transport path $L_e=\overline{\text{A}'\text{C}'}$, and its direct length $L=\overline{\text{A}'\text{B}'}$, so the tortuosity in the fully hydrated cement pastes for the water penetration or ion diffusion can be expressed by

$$\tau'_{\text{h-cp}}=\frac{L_e}{L}=\sqrt{1+\frac{1}{4}\left(1+\frac{D'}{d'}\right)^2} \tag{4}$$

where $\tau'_{\text{h-cp}}$ is the transport tortuosity of the fully hydrated cement pastes, D' is the average side length of the square particles, and d' is the average gap among square particles.

Using the porosity of the representative unit cell in Fig.2(b), it can be obtained that

$$\frac{d'}{D'}=\sqrt{\frac{1}{1-\varphi_{\text{h-cp}}}}-1 \tag{5}$$

Substituting Eq. (5) into (4), the transport tortuosity $\tau'_{\text{h-cp}}$ of the fully hydrated cement pastes is expressed by

$$\tau'_{\text{h-cp}} = \frac{1}{1-\sqrt{1-\varphi_{\text{h-cp}}}}\sqrt{\left(1-\sqrt{1-\varphi_{\text{h-cp}}}\right)^2+\frac{1}{4}} \tag{6}$$

Eq. (6) demonstrates that when $\varphi_{\text{h-cp}} \to 1$, $\tau'_{\text{h-cp}} \approx 1$, and when $\varphi_{\text{h-cp}} \to 0$, $\tau'_{\text{h-cp}} \to \infty$. This is consistent with the fact of the defined tortuosity of cement pastes (Yoon 2009, Barrande *et al*. 2007). Therefore, it is reasonable for idealizing the hydrated cement particles as square shape and selecting the transport paths in fully hydrated cement pastes in Fig. 2(b).

As known from the above, the hardened cement pastes are mainly consisted of the unhydrated and hydrated cement particles. With the continuous hydration of cements, the hydrated products gradually increase and the unhydrated cements decrease, so the tortuosity of transport paths in hardened cement pastes changes with the cement hydration degree. Based on the separation of the hardened cement pastes in Fig. 1, the tortuosity of transport paths in hardened cement pastes can be obtained by the weighted average with the cement hydration degree between the tortuosities of unhydrated circular and fully hydrated square cement particles, namely

$$\tau'_{\text{cp}} = \left(1-h_\alpha\right)\tau'_{\text{uh-cp}} + h_\alpha \tau'_{\text{h-cp}} \tag{7}$$

where τ'_{cp} is the tortuosity of transport paths in hardened cement pastes with the ideal cement particles, $\tau'_{\text{uh-cp}}$ and $\tau'_{\text{h-cp}}$ are the transport tortuosity in unhydrated circular and hydrated square cement particles, which can be calculated by Eqs. (3) and (6), respectively, h_α is the cement hydration degree (Masi *et al*. 1997).

The tortuosity models, Eqs. (3), (6) and (7), are deduced from the ideal circular and square cement particles. But the real shapes of cement particles are very complicated and irregular, and the ideal shapes of both unhydrated and fully hydrated cement particles is quite different to their real morphology, so the calculating tortuosity from these models has an error with the real tortuosity. Therefore, in order to modify the tortuosity models, the shape factor is selected to correct the difference between the ideal shapes and the real morphology of cement particles (Mora *et al*. 2000, Chen *et al*. 2003). In addition, for the hydrated cement pastes, the water-cement ratio has an important influence on its microstructure and morphology (Zhang *et al*. 2010). Therefore, the model of tortuosity in hardened cement pastes, Eq. (7), is corrected by the shape factors and the adjustment coefficient associated with the water-cement ratio

$$\tau_{\text{cp}} = \eta_{\text{c}}\left(1-h_\alpha\right)\tau'_{\text{uh-cp}} + \omega_{\text{wc}}\eta_{\text{r}} h_\alpha \tau'_{\text{h-cp}} \tag{8}$$

where τ_{cp} is the modified tortuosity of transport paths in hardened cement pastes, η_{c} and η_{r} are respectively the shape factors of unhydrated and fully hydrated cement particles, which can be obtained by using the volume equivalence principle between the irregular cement particle and the ideal circular and square (Taleb *et al*. 2007, Stroeven *et al*. 2009), for the ordinary Portland cement, $\eta_{\text{c}} \approx 1.97$ and $\eta_{\text{r}} \approx 1.77$ (Zuo *et al*. 2011), ω_{wc} is the adjustment coefficient associated with the water-cement ratio, based on the fit of the MIP test results for the tortuosity in hardened cement pastes, it may be expressed by (Zuo *et al*. 2010)

$$\omega_{\mathrm{wc}} = \left(1+7h_{\alpha}\right)^{w_{\mathrm{c}}-0.35} \tag{9}$$

in which ω_{wc} is the adjustment coefficient, w_{c} is the water-cement ratio.

2.2 Tortuosity of transport paths in mortar and concrete

Depending on the compositions and structures of mortar, it can be assumed that the mortar is a composite embedding the circular sand particles with the average diameter D_{s} into the cement paste matrix, as shown in Fig. 3(a). Thus, a possible configuration, namely a representative unit cell for modeling the transport tortuosity of mortar, is displayed in Fig. 3(b), in which the particles are arranged in an equilateral-triangle form and the corresponding unit cell is in the dashed rectangle.

Because the average diameter of sand particles is largely greater than that of cement particles (D_s • D), the transport path of mortar in Fig. 3(b) may be approximately selected as $\mathrm{A}\rightarrow\mathrm{B}\xrightarrow{\text{along } 1/4 \text{ arc}}\mathrm{C}$. Due to the obstacle of cement particles in mortar, the effect of filling cement pastes among the sand particles on its transport tortuosity needs to be taken into account, so in the representative unit cell, the effective length of transport path, $L_e = (\overline{\mathrm{AB}}+\widehat{\mathrm{BC}})\,\tau_{cp}$ and the direct length $L=\overline{\mathrm{AO}}$. The tortuosity of transport paths in mortar can be drawn as

$$\tau'_m = \frac{L_e}{L} = \left[1+\frac{\pi-2}{2\sqrt{3}\left(1+\dfrac{d_{\mathrm{s}}}{D_{\mathrm{s}}}\right)}\right]\tau_{\mathrm{cp}} \tag{10}$$

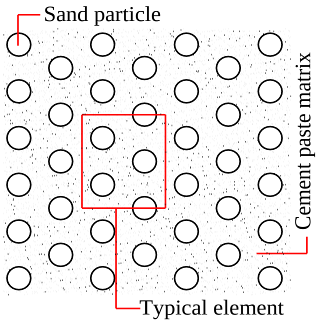
where τ'_m is the tortuosity of transport paths in mortar as the circular sand particles embedded in the cement paste matrix, and τ_{cp} is the tortuosity of transport paths in hardened cement pastes, determined by Eq. (8), D_{s} and d_{s} are the average diameter of the circular sand particles and the average gap among the sand particles, the ratio between them can be obtained by the volumetric faction of sand particles in the representative unit cell in Fig.3(b)

$$\frac{d_{\mathrm{s}}}{D_{\mathrm{s}}} = \sqrt{\frac{\pi}{2\sqrt{3}f_{sa}}}-1 \tag{11}$$

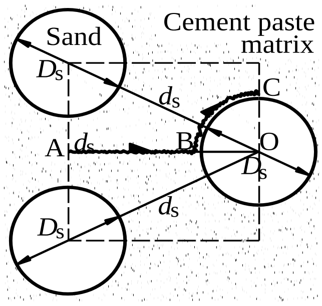
where f_{sa} is the volumetric faction of sand particles in the unit cell.

Substituting Eq. (11) into Eq. (10), the tortuosity of transport paths in mortar with the circular sand particles can be expressed by

$$\tau'_m = \left[1+\frac{(\pi-2)\sqrt{f_{\mathrm{sa}}}}{\sqrt{2\sqrt{3}\pi}}\right]\tau_{\mathrm{cp}} \tag{12}$$



(a) Ideal arrangement of sand in cement paste matrix



(b) Representative unit cell in typical element

Fig. 3 Configuration for the model of the tortuosity of transport paths in mortar with spherical sand particles in hardened cement paste matrix

Due to the great differences between the ideal circular in the tortuosity model and the real shape of sand particles, the circular sand particle, as a substitute for the irregular sand particles, produces great influences on the tortuosity of transport paths in mortar. Therefore, the effects of the shape of the sand particles on the tortuosity in model Eq. (12) need to be considered by the shape factor

$$\tau_{\mathrm{m}} = \eta_{\mathrm{sa}} \tau'_{m} = \eta_{\mathrm{sa}} \left[1 + \frac{(\pi - 2)\sqrt{f_{\mathrm{sa}}}}{\sqrt{2\sqrt{3}\pi}} \right] \tau_{\mathrm{cp}} \tag{13}$$

in which τ_{m} is the tortuosity of transport paths in mortar associated with the sand particle shape, η_{sa} is the shape factor of sand particle, which can be obtained by using the image analysis method (Mora *et al*. 2000, Taleb *et al*. 2007), for the ordinary river sand, its average shape factor $\eta_{\mathrm{sa}} \approx 1.1$ (Zuo *et al*. 2010).

In order to model the tortuosity of the transport paths in concrete, regarding mortar as a matrix, concrete is from the mortar embedded the circular stone particles with the average diameter D_{c} and average gap d_{c}, which are also arranged in an equilateral-triangle form. Similar to modeling the transport tortuosity of mortar, and considering the effect of stone shape on the tortuosity, the tortuosity of transport paths in concrete can be expressed by

$$\tau_{\mathrm{c}} = \eta_{\mathrm{st}} \tau'_{m} = \eta_{\mathrm{st}} \left[1 + \frac{(\pi - 2)\sqrt{f_{\mathrm{st}}}}{\sqrt{2\sqrt{3}\pi}} \right] \tau_{\mathrm{m}} \tag{14}$$

where τ_{c} is the tortuosity of transport paths in concrete, f_{st} is the volumetric faction of stone particles in concrete, η_{st} is the shape factor of the stone particles in concrete, τ_{m} is the transport tortuosity in mortar, as given in Eq. (13).

With the combinations of Eqs. (13) and (14), it can be obtained that

$$\tau_{\mathrm{c}} = \eta_{\mathrm{sa}} \eta_{\mathrm{st}} \left[1 + \frac{(\pi - 2)\sqrt{f_{\mathrm{sa}}}}{\sqrt{2\sqrt{3}\pi}} \right] \left[1 + \frac{(\pi - 2)\sqrt{f_{\mathrm{st}}}}{\sqrt{2\sqrt{3}\pi}} \right] \tau_{\mathrm{cp}} \tag{15}$$

3. Numerical result and discussion

3.1 Materials and properties

The cement used in this work was ordinary Portland cement, whose chemical compositions are given in Table 1. The fine aggregate in mortar and concrete is a kind of river sand with the maximum particle size being 2 mm and the apparent density 2.64g/cm^3, and its average shape factor is 1.1. The basalt with the maximum particle size being 15 mm and the apparent density 3.0g/cm^3 is selected as the coarse aggregate in concrete, and the average shape factor of the basalt particles is 1.4. The water used was potable laboratory tap water. The mix weight proportions, the cement paste, mortar and concrete with the water-cement ratios 0.35, 0.45, 0.55 and 0.65, are listed in Table 2. Using MIP tests, the porosity of hardened cement pastes with the water-cement ratio, 0.35, 0.45, 0.55 and 0.65 are respectively 15.58%, 20.17%, 26.38% and 35.36% (Zuo *et al*. 2011).

3.2 Effects of material parameters on the transport tortuosity

It can be known from the above tortuosity models of transport paths in cement-based materials such as hardened cement pastes, mortar and concrete that, several factors, such as water-cement ratio, volumetric fraction of mixtures, shape and size of aggregate, cement hydration degree, have an influence on the transport tortuosity in cement-based materials. Based on the above proposed model Eqs. (8), (13) and (15), the effects of water-cement ratio, volumetric fraction of mixtures such as cement and aggregates, shape and size of aggregate, cement hydration degree, on the tortuosity of transport paths in hardened cement pastes, mortar and concrete are numerically investigated, of which the mix weight proportions are listed in Table 2.

In numerical simulation and analysis, the related main parameters are summarized as follows. the cement stack porosity: $\varphi_{\text{uh-cp}}$ =0.58, the average shape factors of unhydrated and fully hydrated cement particles: η_c =1.97 and η_r =1.77, the average shape factors of sand and stone particles: η_{sa} =1.1 and η_{st} =1.4, when water-cement ratio w_c =0.35, the sand volume fraction in mortar: f_{sa} =0.39, and the sand and stone volume fraction in concrete: $f_{sa} = f_{st}$ =0.31, the water-cement ratios: w_c = 0.35, 0.45, 0.55, 0.65, when the cement hydration time: t =30days, the hydration degree: h_α = 0.785, and the porosities corresponding to water-cement ratios: $\varphi_{\text{h-cp}}$ =15.58%, 20.17%, 26.38%, 35.36%.

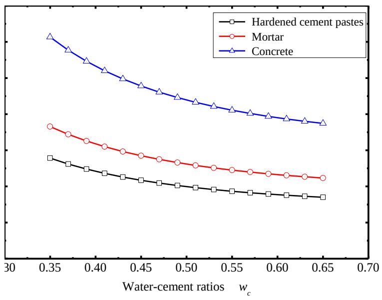


Fig. 4 Effects of water-cement ratio on the transport tortuosity in cement-based materials

3.2.1 Water-cement ratio

Fig. 4 presents the effects of water-cement ratio on the tortuosity of transport paths in hardened cement paste, mortar and concrete, in which the materials are cured for 30 days, and the cement hydration degree is 0.78. It is seen from Fig. 4 that, the transport tortuosities in cement-based materials decrease with the increasing of water-cement ratio, and when the water-cement ratio increases from 0.35 to 0.65, the tortuosities of transport paths in hardened cement pastes, mortar and concrete decrease respectively from 30.7, 18.3 and 13.9 to 18.7, 11.2 and 8.5, and the corresponding decrease ratios are basically 39%. Therefore, the water-cement ratio has an important impact on the transport tortuosity in cement-based materials. Because of the increasing of the water-cement ratio in cement-based materials, the capillary porosity increases and the pore space are better connected to each other, and the pore connectivity in cement-based materials with the low water-cement ratio 0.35 appears to be much lower than that with the high water-cement ratio 0.65. The pore connectivity will directly shorten the transport paths and cause the decrease of the transport tortuosity in cement-based materials (Nakarai *et al*. 2006). In addition, the aggregates such as sands and stones embedded in mortar and concrete will prolong the transport paths, which lead to the increasing of the tortuosity of mortar and concrete. The more aggregates, the larger tortuosity. So, the tortuosities of transport paths in mortar and concrete are obviously greater than that in hardened cement pastes, as shown in Figure 4, and this is in agreement with the experimental results (Promentilla *et al*. 2007, Zuo *et al*. 2010).

3.2.2 Volumetric fraction of mixtures

The content of the mixtures such as cement and aggregates in cement-based materials has a significant influence not only on its mechanical behavior like the strength and stiffness but also on its microstructure such as the tortuosity, porosity and connectivity. In order to describe quantitatively the effects of the mixtures on the transport tortuosity in cement-based materials, the volume fraction of cement and aggregates in cement-based materials is selected for analyzing the effects of mixture on the transport tortuosity, as shown in Figure 5 and 6. Figure 5 presents the effects of the cement volume fraction on the tortuosity of transport paths in hardened cement pastes, mortar and concrete. It can be made clear from the figure that the tortuosity of transport paths in hardened cement pastes, mortar and concrete increases with the cement volume fraction. When the cement volume fraction increases from 0.2 to 0.8, the transport tortuosities of hardened

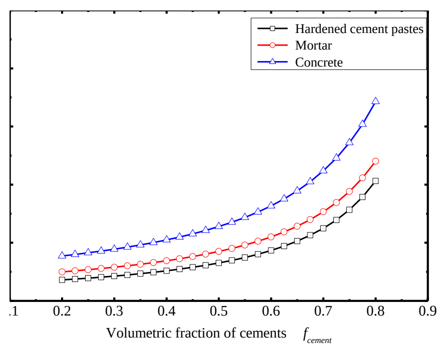


Fig. 5 Effects of water-cement ratio on the transport tortuosity in cement-based materials

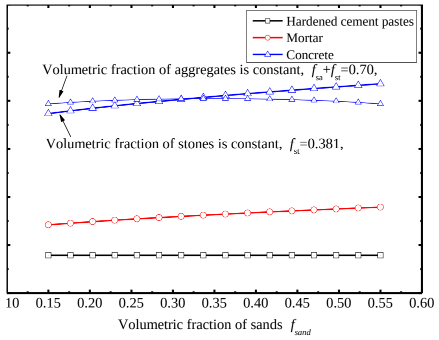


Fig. 6 Effects of water-cement ratio on the transport tortuosity in cement-based materials

cement pastes, mortar and concrete increase from 1.7, 2.7 and 3.8 to 10.4, 11.9 and 17.2, and the corresponding increments of tortuosity caused by the cement volume fraction are respectively 8.7, 9.2 and 13.4. Therefore, the change of the transport tortuosity in hardened cement pastes is basically the same as that of tortuosity in mortar, but they are less than the change of the transport tortuosity in concrete. Because the increases of cement volume fraction in cement-based materials decrease the porosity and connectivity of the materials and prolong the effective length of thetransport paths, the tortuosity of transport paths in cement-based materials will increase (Bejaoui *et al*. 2007). In addition, the average shape factors of the river sands and the basalt particles are respectively 1.1 and 1.4, so the sand shape has basically no obvious influence on the transport tortuosity in mortar while the stone shape has more obvious impact on the transport tortuosity in concrete.

Fig. 6 shows the effects of the sand volume fraction on the transport tortuosity in mortar and concrete, in which the materials with the water-cement ratio 0.35 are cured for 30 days, and the sand volume fraction increases from 0.15 to 0.55 in mortar and concrete. The stone volume fraction in concrete include two cases: one is that the stone volume fraction always maintains 0.381; the other is that the total aggregate volume fraction maintains 0.7, namely the stone volume fraction varies from 0.55 to 0.15. It can be seen from Figure 6 that, when the sand volume fraction increases from 0.15 to 0.55, the tortuosity of transport paths in mortar increases from 17.1 to 18.9, whereas the transport tortuosity in concrete increases from 28.7 to 31.8 on the condition that the stone volume fraction always maintains 0.381; When the total volume fraction of the sand and stone is constant, namely $f_{sa} + f_{st}$=0.70, the transport tortuosity in concrete maintains basically 30.0. Similarly, the effect of the stone volume fraction on the transport tortuosity in concrete is basically the same as that of the sand volume fraction, and here, omitted. Therefore, the transport tortuosity in cement-based materials has an increase with the aggregate volume fraction, but the increasing degree is relatively small.

3.2.3 Shape and size of aggregates

In cement-based materials, the effects of the aggregates on the transport tortuosity are not only related to its volume fraction but also its shape and size (Taleb *et al*. 2007, Stroeven *et al*. 2009). Figure 7 presents the relations between the transport tortuosity in cement-based materials and the shape factor reflecting on the aggregate shape. It is seen from Figure 7 that, with the increasing of the sand shape factor from 1.0 to 4.0, the transport tortuosity in mortar increases linearly from 16.9 to 67.8, and for concrete, when the stone shape factor maintains 1.4, the transport tortuosity in concrete increases linearly from 27.4 to 109.5, but when the shape factor of stone and sand increases simultaneously from 1.0 to 4.0, the tortuosity of transport paths in concrete increases from 19.8 to 317.0. In addition, Fig. 7 also shows that, when the shape factor of both sand and stone is 1.0, namely the sand and stone are regarded as the sphere, the transport tortusoity in hardened cement pastes, mortar and concrete are 13.9, 16.9 and 19.8 respectively, so the smaller aggregate shape factor, the smaller differences between the transport tortuosities in hardened cement pastes, mortar and concrete. Therefore, the aggregate shape has very important influences on the transport tortuosity in cement-based materials, and the complicated and coarse aggregate surface, which has a great shape factor, not only improve the interfacial behavior of cement-based materials but also increase its transport tortuosity, thus it enhances the mechanical behavior and durability of cement-based materials (Barksdale *et al*. 1991, Stroeven *et al*. 2000).

When the shape factor of the aggregate is regarded as a constant in cement-based materials (here, $\eta_{sa} = 1.1$ and $\eta_{st} = 1.4$), and taking the diameter of sand particles as an example, the effects of the aggregate size on the transport tortuosity in materials are shown in Fig. 8. It can be obtained from Fig. 8 that, when the diameter of sand particles increases from 1.0 mm to 5.0 mm,

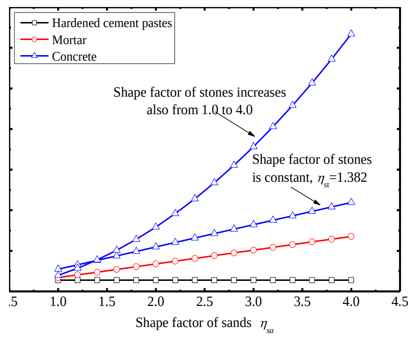


Fig. 7 Effects of aggregate shape on the tortuosity in cement-based materials

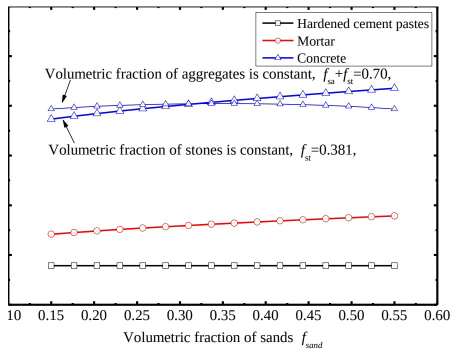


Fig. 8 Effects of sand particle diameter on the tortuosity in cement-based materials

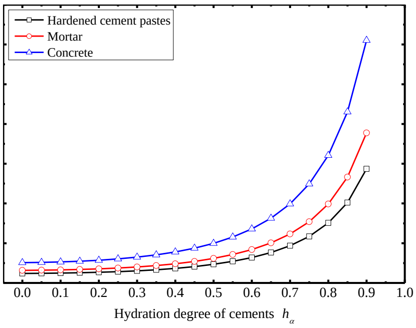


Fig. 9 Effects of cement hydration degree on the tortuosity in cement-based materials

the transport tortuosities in mortar and concrete increase respectively from 15.5 and 26.0 to 20.0 and 33.4. This is because, when the shape factor of the aggregates remains unchanged, the increasing of the aggregate size will bring about the increasing of the aggregate volume fraction in materials, which have a rise in the transport tortuosity according to the above-mentioned analytical results. Based on numerical analysis (Zuo *et al*. 2010), the transport tortuosity in concrete also increases with the stone particle diameter, and the relevant results are not repeated here. Therefore, for an invariable particle shape factor, the tortuosity of transport paths in cement-based materials increases with the aggregate size.

3.2.4 Cement hydration degree

Fig. 9 illustrates the effects of the cement hydration degree on the tortuosity of transport paths in cement-based materials, in which the water-cement ratio is 0.35, and the sand volume fraction in mortar is 0.39, and both of the sand and stone volume fractions in concrete are 0.31. It may be made out from Figure 9 that, with the increasing of the cement hydration degree from 0.0 to 0.9, the tortuosity of transport paths in hardened cement pastes, mortar and concrete increases from 2.4, 3.2 and 5.1 to 28.7, 37.8 and 61.0 respectively, and the increasing degrees of the transport tortuosity become larger when the cement hydration degree is more than 0.55. This is because, with the increasing of the cement hydration degree, the capillary porosity decreases and the pore connectivity becomes relatively poor (Bentz *et al*. 2000, Beaudoin *et al*. 1994), it leads to the decrease of the transport torutuosity in cement-based materials.

4. Conclusions

(1) Based on the constituents and microstructures of cement pastes, geometrical model for the tortuosity of transport paths in hardened cement pastes is firstly proposed. Then considering the compositions and geometric features of mortar and concrete, the cement pastes are regarded as a matrix, and the sands and stones are respectively embedded in the cement pastes and mortar to form mortar and concrete. On the basis, the geometric models for the tortuosity of transport paths in mortar and concrete are finally established. The proposed models of transport tortuosity in cement-based materials are expressed as a function of capillary porosity, cement hydration degree,

mixture particle shape, and aggregate volume fraction and water-cement ratio.

(2) Based on the proposal tortuosity models of transport paths in cement-based materials, numerical analysis has been carried out to investigate the effects of water-cement ratio, volume fraction of the mixtures, shape and size of aggregates and cement hydration degree on the tortuosity of transport paths in hardened cement pastes, mortar and concrete. Results indicate that the transport tortuosity in cement-based materials decreases with the water-cement ratio, and increases with the cement hydration degree, the volume fraction of mixtures, the shape factor and diameter of the aggregates, and the water-cement ratio, cement hydration degree and cement volume fraction related to cement pastes are the main factors influencing the transport tortuosity of cement-based materials. The proposal models can be helpful for understanding the physical mechanism for the tortuosity of transport paths in cement-based materials.

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References

Amiri, O., Aït-Mokhtar, A. and Sarhani, M. (2005), "Tri-dimensional modeling of cementitious materials permeability from polymodal pore size distribution obtained by mercury intrusion porosimetry tests", *Adv Cem. Res*, **17**(1), 39-45.

Barksdale, R.D. and Kemp, M.A. (1991), Sheffield W J, Hubbard J L. Measurement of aggregate shape, surface area, and roughness, Transportation Research Record 1301, National Research Council, Washington, D.C., 107-116.

Barrande, M., Bouchet, R. and Denoyel, R. (2007), "Tortuosity of porous particles", *Analy. chem.*, **79**(23), 9115-9121.

Beaudoin, J.J., Feldman, R.F. and Tumidajski, P.J. (1994), "Pore structure of hardened portland cement pastes and its influence on properties", *Adv. Cem. Based Mater.*, **1**, 224-236.

Bejaoui, S. and Bary, B. (2009), "Modeling of the link between microstructure and effective diffusivity of cement pastes using a simplified composite model", *Cement Concrete Res.*, **37**(3), 469-480.

Bentz, D.P., Quenard, D.A., Kunzel, H.M., Baruchel, J., Peyrin, F., Martys, N.S. and Garboczi, E.J. (2000), "Microstructure and transport properties of porous building materials. II: three-dimensional X-ray tomographic studies", *Mater. Struct.*, **33**, 147-153.

Bertron, A., Duchesne, J. and Escadeillas, G. (2005), "Attack of cement pastes exposed to organic acids in manure", *Cement Concrete Compos.*, **27**(9-10), 898-909.

Carman, P.C. (1937), "Fluid flow through a granular beds", *Tran. Inst. Chem. Eng.*, **15**, 150.

Chen, D. and Mahadevan, S. (2007), "Cracking analysis of plain concrete under coupled heat transfer and moisture transport processes", *J. Struct. Eng.-ASCE*, **133**(3), 400-410.

Chen, Y.B. and Xu, P.T. (2003), "Study on expression of morphology of cement particles", *Cement*, **2**, 17-19 (in Chinese).

Coleman, S.W. and Vassilicos, J.C. (2008), "Tortuosity of unsaturated porous fractal materials", *Phy. Review E*, **78**(016308), 1-11.

Coussy, O. and Ulm, F.J. (2001), "Elements of durability mechanics of concrete structures", *Proceeding of*

Creep, Shrinkage and Durability Mechanics of Concrete and other Quasi-Brittle Materials, Amsterdam, Netherlands, 3993-4009.

Dullien, F.A.L. (1979), Porous media, fluid transport and pore structure, San Diega, CA: Academic.

Garrabrants, A.C. and Kosson, D.S. (2003), "Modeling moisture transport from a Portland cement-based material during storage in reactive and inert atmospheres", *Drying Technol*., **21**(5), 775-805.

Garrouch, A.A., Ali, L. and Qasem, F. (2001), "Using diffusion and electrical measurements to assess tortuosity of porous media. Materials and Interfaces", *Ind. Eng. Chem. Res*., **40**, 4363-4369.

Guneyisi, E., Gesoglu, M. and Mermerdas, K. (2010), "Strength deterioration of plain and metakaolin concretes in aggressive sulfate environments", *J. Mater. Civ. Eng*., **22**(4), 403-407.

Igarashi, S., Kawamura, M. and Watanabe, A. (2004), "Analysis of cement pastes and mortars by a combination of backscatter-based SEM image analysis and calculations based on the Powers model", *Cement Concrete Compos*., **26**, 977-985.

Marchand, J., Samson, E., Maltais, Y., Lee, R.J. and Sahu, S. (2002), "Predicting the Performance of Concrete Structures Exposed to Chemically Aggressive Environment-Field Validation", *Mater. Struct*., **35**(3), 623-631.

Masi, M., Colella, D., Radaelli, G. and Bertolini, L. (1997), "Simulation of chloride penetration in cement-based materials", *Cement. Concrete Res*., **27**(10), 1951-1601.

Matte, V., Moranville, M. and Adenot, F. (2000), "Simulated microstructure and transport properties of ultra-high performance cement-based materials", *Cement. Concrete Res*., **30**(12), 1947-1954.

Mora, C.F. and Kwan, A.K.H. (2000), "Sphericity, shape factor, and convexity measurement of coarse aggregate for concrete using digital image processing", *Cement. Concrete Res*., **30**(3), 351-358.

Moranville, M., Kamali, S. and Guillon, E. (2004), "Physicochemical equilibria of cement-based materials in aggressive environments-experiment and modeling", *Cement. Concrete Res*., **34**(9), 1569-1578.

Nakarai, K., Ishida, T. and Maekawa, K. (2006), "Modeling of calcium leaching from cement hydrates coupled with micro-pore formation", *J. Adv. Concr. Technol*., **4**(3), 395-407.

Nakashima, Y. and Kamiya, S. (2007), "Mathematica programs for the analysis of three dimensional pore connectivity and anisotropic tortuosity of porous rocks using X-ray microtomography", *J. Nucl. Sci. Technol*., **44** (9), 1233-1247.

Neithalath, N., Sumanasooriya, M.S. and Deo, O. (2010), "Characterizing pore volume, sizes, and connectivity in pervious concretes for permeability prediction", *Mater. Charact*., **61**(8), 802-813.

Promentilla, M.A.B. and Sugiyama, T. (2007), "Evaluation of tortuosity of cement-based materials with X-ray synchrotron radiation microtomography", *Proceedings of the 1st International Conference on Recent Advances in Concrete Technology*, Washington D C, USA, 101-112.

Promentilla, M.A.B., Sugiyama, T., Hitomi, T. and Takeda, N. (2009), "Quantification of tortuosity in hardened cement pastes using synchrotron-based X-ray computed microtomography", *Cement Concr. Res*., **39**, 548-557.

Quenard, D.A., Xu, K., Künzel, H.M., Bentz, D.P. and Martys, N.S. (1998), "Microstructure and transport properties of porous building materials", *Mater. Struct*., **31**, 317-324.

Shin, K.J., Kim, J.S. and Lee, K.M. (2011), "Probability-based durability design software for concrete structures subjected to chloride exposed environments", *Comput. Concr*., **8**(5), 511-524.

Stroeven, P. (2000), "A stereological approach to roughness of fracture surfaces and tortuosity of transport paths in concrete", *Cement. Concrete Compos*., **22**, 331-341.

Stroeven, P., Hu, J. and Guo, Z. (2009), "Shape assessment of particles in concrete technology: 2D image analysis and 3D stereological extrapolation", *Cement Concrete Compos*., **31**, 84-91.

Taleb, A.R., Masad, E., Tutumluer, E. and Pan, T. (2007), "Evaluation of image analysis techniques for quantifying aggregate shape characteristics", *Constr. Build. Mater*., **21**(5), 978-990.

Weerts, A.H., Kandhai, D. and Bouten, W. (2001), "Tortuosity of an unsaturated sandy soil estimated using gas diffusion and bulk soil electrical conductivity: comparing analogy-based models and lattice-boltzmann simulations", *Soil. Sci. Soc. Amer. J*., **65**(6), 1577-1584.

Yamaguchi, T., Negishi, K., Hoshino, S. and Tanaka, T. (2009), "Modeling of diffusive mass transport in micropores in cement based materials", *Cement Concrete Res*., **39**, 1149-1155.

Yoon, I.S. (2009), “Simple approach to calculate chloride diffusivity of concrete considering carbonation”, *Comput. Concr.*, **6**(1), 1-18.

Zhang, W.M., Sun, W. and Chen, H.S. (2010), “3D visualisation of pore structures in cement-based materials by LSCM”, *Adv. Cement Res.*, **22**(1), 53-57.

Zheng, J.J. and Zhou, X.Z. (2008), “Analytical method or prediction of water permeability of cement paste”, *ACI Mater. J.*, **105**(2), 200-206.

Zuo, X.B. (2010), *Modeling and Numerical Investigation on Diffusion-reaction Behaviors in Concrete Subjected to Couplings of Sulfate Attack and Mechanical Loading*, Postdoctoral Research Report, College of Materials Science and Engineering, Southeast University, Nanjing, China, 18-31.

Zuo, X.B., Sun, W., Li, H. and Zhou, W.J. (2011), “Geometrical models for tortuosity of transport paths in hardened cement pastes”, *Adv. Cement Res.*, **24**(3), 145-154.

Zuo, X.B., Sun, W. and Yu, C. (2010), “Modeling of ion diffusion coefficient in saturated concrete”, *Comput. Concr.*, **7**(5), 421-435.

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