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Dependence of unsaturated chloride diffusion on the pore structure in cementitious materials

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Abstract: Conceptual analysis is performed to examine the effects of pore features on the water continuity in unsaturated porous systems. The roles of pore features in relative chloride diffusion coefficient (D_{rc}) of mortar specimens at various degrees of water saturation (S_w) were studied based on mercury intrusion porosimetry and resistivity tests. It is found that the role of pore structure in the D_{rc}-S_w relationship is a result of its effect on the water continuity. Porosity and tortuosity are not relevant to the D_{rc}-S_w relationship. A finer pore size distribution or lower pore connectivity tends to result in a lower D_{rc}. The pore size effect on the D_{rc} is pronounced primarily at high S_w, while the D_{rc} is dominated by the pore connectivity at low S_w. Cement mortar with a higher water-to-binder ratio shows larger chloride diffusion at high relative humidity levels but smaller chloride diffusion at low relative humidity levels.

Keywords: Chloride diffusion; Pore structure; Degree of water saturation; Relative humidity; Supplementary cementitious materials

1. Introduction

One major durability issue of marine concrete structures can be ascribed to the chloride-induced reinforcement corrosion, caused by chloride ions penetration in the concrete cover. After the publication by Collepardi et al. [1] who reported that the penetration of chloride ions into concrete follows Fick's diffusion law, the chloride diffusion coefficient (D_{Cl}) has been commonly used to describe the capacity of concrete to resist chloride ions penetration. Numerous studies on this subject were based on the chloride ions penetration tests of saturated concretes [2]. The test results depend primarily on the pore structure of the concrete specimens. It is generally considered that lowering water-to-binder (w/b) ratio or adding pozzolanic materials will improve the durability, because of the refined pore structure and associated higher resistance to the chloride diffusion in *saturated* concretes [3]. Such consideration plays an important part in current concrete mixture design and durability assessment, e.g. DuraCrete [4] and Life-365 [5]. However, this consideration is not yet fully assured

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when it comes to *unsaturated* concretes. Since concrete is seldom saturated in engineering practice, further research on the chloride transport in non-saturated concretes is essential for reliable durability design.

For saturated cementitious materials the effects of pore features on the chloride diffusion have been well documented. Page et al. [6] may be the first who observed that in saturated ordinary Portland cement (OPC) pastes the chloride diffusion coefficient D_{Cl} almost linearly increases with increasing *total porosity*. By studying the profiles of the chloride ions penetrated from seawater to different mortars, Moukwa [7] concluded that the macro pores (> 30 nm) play a major role in the chloride diffusion. Tang and Nilsson [8] proposed an approach correlating the profile of total chloride content to the *pore size distribution*. In the percolation concept described by Bentz and Garboczi [9], referred to by Ye [10], the *pore connectivity* is a key factor controlling mass transport phenomena. An experimental investigation from Neithalath and Jain [11] further confirmed that the pore connectivity has a higher impact on ionic transport compared to porosity and pore size. Hornain et al. [12] found that the reduction of chloride diffusion, caused by the addition of limestone filler, was attributed to the increased *tortuosity* of the pore system. Ma et al. [13] established a two-scale model for transport studies, in which the importance of tortuosity on chloride diffusion was highly emphasized.

The above findings about the relationship between pore structure and ionic transport were based on the studies of saturated cementitious materials. For unsaturated cementitious materials explicit descriptions on the pore structure-dependent ionic transport can hardly be found [14]. Most of the previous studies intended to measure or evaluate the chloride/moisture transport properties in unsaturated cementitious materials [15-28], only that Olsson et al. [18] presented a preliminary description on the relationship between large pores, small pores and unsaturated ionic transport. In the literature the unsaturated state is characterized normally by the degree of water saturation (S_{w}) or relative humidity (RH). The relative chloride diffusion coefficient (D_{rc}), i.e. D_{Cl} at unsaturated state normalized to D_{Cl} at saturated state, is often adopted to describe the unsaturated chloride diffusion. In view of the results published, there is none consensus on the relationship between D_{rc} and S_{w} (or RH) [14,17,18,26-28]. The data about the D_{rc}-S_{w} (or D_{rc}-RH) relationships show a large scatter [14]. Buchwald [24] reported that the D_{rc} was decreased from 1 to 0.42 when the S_{w} decreased from 100 to 70%, while Mercado et al. [25] found a drastic drop of D_{rc} from 1 to 0.03 in this saturation range. The role of w/b ratio in unsaturated chloride diffusion remains a point of controversy. Olsson et al. [18] stated that the w/b ratio (from 0.38 to 0.53) has little effect on the D_{rc}-S_{w} relation while others such as Zhang et al. [26] found that a higher w/b ratio (from 0.4 to 0.6) results in a larger D_{rc} for a given S_{w}. Up to date a satisfactory explanation on the phenomenon of unsaturated chloride diffusion is not available.

The pore structure dependence of ionic transport is more complex in unsaturated porous systems than in saturated porous systems. In saturated porous systems (Fig. 1a), all the connected pores are fully water-filled allowing chloride diffusion. In unsaturated porous systems (Fig. 1b), the gas phase preferentially fills the large pores while the small pores tend to be filled with water. The water-filled (small) pores are divided into one part that can form continuous paths for chloride diffusion and another part that cannot [29]. For a given S_w the continuity of water-filled pores, in short water continuity (η_w), governs the unsaturated chloride diffusion [29]. η_w is determined by the moisture distribution that depends on the pore structure of the porous system. Changes of the pore structure may alter the η_w-S_w relationship, leading to the changes of the D_rc-S_w (or D_rc-RH) relationship.

Supplementary cementitious materials (SCMs) such as fly ash, slag and limestone powder are receiving increasing attention worldwide due to their economic and environmental benefits in concrete production. There is no doubt that partial replacement of OPC by SCMs, either reactive or inert, will affect the pore structure because of the changes in the particle size distribution and related changes of the particle packing, and changes of the hydration process and the microstructure formed. Consequently, η_w as well as D_rc can be very different between SCMs-blended concrete and OPC concrete.

To facilitate an in-depth understanding of unsaturated transport phenomena, the role of pore structure needs to be addressed clearly. The pore features under study include porosity, pore size, pore connectivity and tortuosity. The effects of these pore features on η_w are analyzed following the Kelvin law. The analytical results are verified against the experimental data derived in this work. One-year-old mortar samples with different w/b ratios (0.4~0.6) and SCMs were prepared. The mortar samples were preconditioned to different degree of water saturation S_w and the relative humidity RH of these partially saturated mortar samples was measured. The D_rc-S_w relationships, determined from resistivity measurements and using the Nernst-Einstein equation, are correlated to the pore structures obtained from mercury intrusion porosimetry (MIP) tests. The effects of various SCMs on the D_rc-S_w relationship are analyzed and compared. The influences of RH on unsaturated chloride diffusion are subsequently discussed.

2. Role of pore structure in water continuity

In unsaturated cementitious materials the water-filled pores are partly continuous and partly discontinuous. The continuous water-filled pores constitute into a number of channels that allow for ionic transport [28,29]. The water continuity η_w can be expressed as:

$$\eta_\mathrm{w} = \frac{N_\mathrm{w}}{N_\mathrm{Sat}} \tag{1}$$

where N_w and N_Sat represents the number of channels available for ionic transport when the porous system is at a particular saturation level S_w and at saturated state, respectively.

For a given degree of water saturation S_w, a higher water continuity η_w results in a higher relative chloride diffusion coefficient D_{rc} [29]. The water phase in cementitious materials can roughly be classified into three categories: capillary water, gel water and non-evaporable water [30]. Part of the capillary water is physically adsorbed on the pore walls. The free capillary water plays a dominant role in the ionic transport [31]. In unsaturated cementitious materials some of the capillary pores are fully water-filled, some are partially water-filled, and the rest is drained [32,33]. A pore is considered drained if only a thin water film is adsorbed on the pore wall [29]. The thickness (t) of the thin water film depends on RH in the porous system. Chloride diffusion is possible in the fully and partially water-filled pores but is hardly possible in a drained pore [29,31].

Fig. 2 illustrates the *idealistic* moisture distribution in a porous system. According to the Kelvin law, each RH corresponds to a particular radius (r_k) of a meniscus. The pores with radii $r < r_p$ ($r_p = r_k + t$) are saturated with water, whereas the pores with radii $r > r_p$ are drained (only thin water film is present). A lower degree of water saturation S_w tends to result in a lower relative humidity RH and lower water continuity η_w. The η_w-S_w relationship is controlled mainly by the pore structure. The pore features conventionally used for mass transport studies include porosity, pore size, pore connectivity and tortuosity. In the following the effects of these pore features on the η_w-S_w relationship will be analyzed. The analysis is carried out by varying the pore feature of interest while maintaining the other pore features unchanged. In addition, three assumptions are made: (1) Small pore and large pore coexist in a porous system; (2) Larger pore loses water as the degree of water saturation decreases; and (3) All pores are cylindrical in shape.

2.1. Effect of porosity on water continuity

Fig. 3 shows two porous systems (I and II) with different porosity. System I has one channel (porosity ϕ_I, $N_{Sat}(I) = 1$) and system II has two channels (porosity $\phi_{II} = 2\phi_I$, $N_{Sat}(II) = 2$). Each channel consists of small pore (diameter d_1) and large pore (diameter d_2). At saturated state, it holds: $N_w(I) = 1$ and $N_w(II) = 2$; $\eta_w(I) = \eta_w(II) = 1$. At unsaturated state, e.g. $S_w = 70\%$, systems I and II exhibit the same moisture distribution. The large pores (d_2) in both systems I and II are drained (gas-filled). It holds: $N_w(I) = N_w(II) = 0$ and $\eta_w(I) = \eta_w(II) = 0$.

It is found that for a given degree of water saturation S_w the porous systems with varying porosity (other pore features are the same) exhibit the same moisture distribution and the same water continuity η_w. In this case the porosity has no influence on the η_w-S_w relationship.

2.2. Effect of pore size on water continuity

Fig. 4 shows two porous systems (I and II) with different pore size distribution. System I has one channel consisting of large pore (diameter d_L) and small pore (diameter d_S). System II has two channels consisting of pores with diameters $d_1 = d_L/2$, $d_2 = \sqrt{3}\, d_L/2$, $d_3 = d_S/2$ and $d_4 = \sqrt{3}\, d_S/2$. Systems I and II have the same porosity (${d_L}^2 = {d_1}^2 + {d_2}^2$ and ${d_S}^2 = {d_3}^2 + {d_4}^2$). The volume of the pore d_{L} is equal to the sum of the volumes of the pores d_1 and d_2, as $V_{d_{\mathrm{L}}} = V_{d_1} + V_{d_2}$. At S_{w} = 100%, η_{w}(I) = 1/1 = 1 and η_{w}(II) = 2/2 = 1. With the decrease of S_{w} water loss starts from the centre part of the larger pore. At S_{w} = 70% the pore d_2 in system II is drained, i.e. N_{w}(II) = 1 and η_{w}(II) = 1/2. In contrast, the pore d_{L} in system I remains partially water-filled allowing ionic transport, i.e. N_{w}(I) = 1 and η_{w}(I) = 1. Herein, it is noted that d_{L}, d_1 and d_2 represent the diameters of large pores (as shown in Fig. 4) while they can also be regarded as the diameters of large transport channels in 3D-microstructure. At S_{w} = 60% the pore d_{L} in system I becomes drained. In the meantime, the pores d_1 and d_2 in system II are drained as well. It holds: η_{w}(I) = η_{w}(II) = 0. At low saturation levels, i.e. S_{w} < 60%, further loss of water no longer influences the water continuity in both systems I and II. It holds: η_{w}(I) = η_{w}(II) = 0.

It is found that for a given degree of water saturation S_{w}, water continuity η_{w} tends to be lower in the system with a finer pore size distribution. This can be explained by the fact that water loss in a fine pore easily results in the pore to become drained and in this case η_{w} can be sensitive to water loss. Nevertheless, the effect of the pore size on η_{w} is pronounced at high saturation levels but becomes weak at low saturation levels.

2.3. Effect of pore connectivity on water continuity

Fig. 5 shows two porous systems (I and II), both of which consist of small pores (diameter d_1) and large pores (diameter d_2) but have different pore connectivity. For the same degree of water saturation S_{w} the water continuity η_{w} is very different between systems I and II. In system I, the small pores d_1 are highly interconnected and they have no connection with the large pores d_2. The water-filled small pores d_1 easily form continuous paths when water loss occurs in the large pores d_2. In system II, the small pores d_1 are connected through the large pores d_2. In the case of water loss in the large pores d_2, it is difficult for the water-filled small pores d_1 to form a continuous path. It is found that a higher pore connectivity (Fig. 5-I) tends to result in a higher water continuity η_{w} in unsaturated porous systems.

Whether the small pores are interconnected or connected with the large pores can be examined by the ink-bottle effect (i.e. pore entrapment) measured using MIP. High pore connectivity (Fig. 5-I) corresponds to small ink-bottle effect (i.e. low pore entrapment). Low pore connectivity (Fig. 5-II) corresponds to large ink-bottle effect (i.e. high pore entrapment). The distribution of pore connectivity as a function of pore diameter has been explored in a recent experimental study through repeated mercury intrusion-extrusion cycles [34,35]. It has been revealed that the connectivity of large pores (which lose water at high saturation levels S_{w}) differs slightly between different binders, but the connectivity of small pores (which lose water at low saturation levels S_{w}) differs significantly between different binders [34,35]. Accordingly, for different cementitious materials, their pore connectivity is very effective for comparing their water continuity at low saturation levels.

2.4. Effect of pore tortuosity on water continuity

Pore tortuosity, often noted as τ, is a property of a transport channel being tortuous. In its simplest way, the tortuosity is defined as the ratio of the length L of a channel to the straight distance C between the two ends of the channel, as $\tau = L/C$.

Fig. 6 shows two channels I and II. Both channels consist of small pore and large pore. Channel II has a higher tortuosity than channel I, i.e. $\tau(\text{II}) > \tau(\text{I})$. At saturated state, the water continuity of channel I ($\eta_w(\text{I}) = 1/1=1$) is equal to that of channel II ($\eta_w(\text{II}) = 1/1=1$). At unsaturated state, the large pores in channels I and II are drained. The water in both channels becomes discontinuous, i.e. $\eta_w(\text{I}) = \eta_w(\text{II}) = 0$. Therefore, the dependence of water continuity on the pore tortuosity is insignificant since the water-filled pores in a channel, irrespective of its tortuosity, are no longer continuous only if one pore in the channel is drained (Fig. 6b).

Based on the foregoing analyses (Sections 2.1, 2.2, 2.3 and 2.4), the pore structure dependence of the η_w-S_w relationship can be summarized as: (1) Porosity and tortuosity are not relevant to the η_w-S_w relationship; (2) Finer pore size distribution tends to result in lower water continuity. The pore size effect on water continuity is pronounced at high saturation levels but becomes weak at low saturation levels; (3) Lower pore connectivity tends to result in lower water continuity.

The addition of SCMs changes the pore size and pore connectivity. As a result, the water continuity and associated relative chloride diffusion coefficient can be very different in the cementitious materials with and without SCMs. More details are presented in the experimental program below.

3. Experimental program

3.1. Materials and samples

The raw materials used were CEM I 42.5N (OPC) and SCMs including ground granulated blast furnace slag (BFS), fly ash (FA) and limestone powder (LP). The chemical composition of the raw materials is given in Table 1. The mean particle sizes measured by laser diffraction were 24.1 μm for OPC, 13.5 μm for BFS, 25.0 μm for FA and 33.5 μm for LP. The crystalline fraction analyzed by quantitative X-ray diffraction was about 42 wt.% in FA, compared to merely 2 wt.% in BFS. The main content of LP, i.e. $CaCO_3$, was around 98 wt.%.

Cement pastes and mortars were prepared. The mortar samples were made with the same amount of siliceous sand, the particle size of which was in the range from 0.125 to 2 mm. A series of mixtures containing different binders and w/b ratios was designed, as outlined in Table 2. The replacement of OPC by SCMs was at dosage levels of 30% for FA, 70% for BFS and 5% for LP by mass of binder. All samples were placed in a standard curing room (20 ± 0.1 ˚C, RH > 98%) for 1 year.

The one-year-old paste samples were crushed into pieces and then immersed in liquid nitrogen at –195 ˚C for 5 min. Next the paste pieces were placed in a freeze-dryer with –24 ˚C and under vacuum at 0.1 Pa. After the water loss was below 0.01% per day the paste pieces were ready for pore structure measurements (see Section 3.2).

The one-year-old mortar samples were prepared in two series. One series of the mortar samples (ϕ50 × 100 mm, moist-cured) was compressed under pressure by following the method proposed by Barneyback and Diamond [36]. Chemistry analysis was performed on the extracted pore solutions. Another series of the mortar samples (ϕ100 × 50 mm, moist-cured) was preconditioned to uniform moisture content with the S_w ranging from 18 to 100%. The sample preconditioning comprised two steps: an oven-drying step at 50 ˚C until a preassigned loss of water was attained and a moisture redistribution step to gain homogeneous moisture distribution, i.e. the RH is uniform in the samples. More details of the sample preconditioning procedures can be referred to a previous report [28]. The relative humidity of the mortar samples at different uniform moisture content, i.e. RH *vs* S_w, was recorded in the sample preconditioning [28]. A minimum relative humidity RH achievable for all mortar mixtures after the sample preconditioning was found to be 45%. This is reasonable given that at RH = 45%, corresponding to the Kelvin radius of around 1.7 nm (Kelvin-Cohan equation [37]), only gel water is left in the pore structure and it is difficult to evaporate when drying at 50 °C [38]. Resistivity measurements were conducted on all the mortar samples of different uniform moisture content.

3.2. Characterization of pore structure

MIP is one of the most widely used techniques for pore structure measurements in part due to its wide range pore size identification. Mercury is a non-wetting substance that would enter a small capillary pore only when external pressure is applied. Assuming cylindrical pore geometry, the intrusion pore diameter d [μm] and the applied pressure P [MPa] can be described by the Washburn equation [39]:

$$d = -\frac{4\gamma_{\mathrm{Hg}} \cos\theta}{P} \tag{2}$$

where γ_{Hg} is the surface tension of mercury (0.48 N/m) and θ is the contact angle between mercury and pore surface (139˚) [40].

In this work MIP measurements were applied to characterize the pore structure of one-year-old paste specimens made with different mixtures. Triplicate specimens of each paste mixture were examined. The porosimeter used enables to reach a maximum pressure of 210 MPa, corresponding to a minimum intrusion pore diameter of 7 nm. Fig. 7 shows an example of the cumulative pore volume measured by MIP test. The total porosity ϕ_{t}, effective porosity ϕ_{e} and ink-bottle porosity ϕ_{ink} can be determined.

Besides, the average pore diameter and the pore connectivity can also be estimated from MIP measurements. The average pore diameter d_a, an index indicating the fineness of pore size in a porous system, can be calculated as [41]:

$$d_{\mathrm{a}} = \frac{4V_{\mathrm{t}}}{S_{\mathrm{t}}} \tag{3}$$

where V_{t} [m^3/m^3] and S_{t} [m^2/m^3] are the total pore volume and total pore surface area, respectively.

The pore connectivity η_{p} is often estimated as the quotient of the effective porosity ϕ_{e} over the total porosity ϕ_{t} [42]:

$$\eta_{\mathrm{p}} = \frac{\phi_{\mathrm{e}}}{\phi_{\mathrm{t}}} \times 100\% \tag{4}$$

The pore tortuosity τ can be determined from the CPSM model proposed by Salmas and Androutsopoulos [43].

$$\tau = 4.6242 \ln\left(\frac{4.996}{1-\alpha_{\mathrm{en}}} - 1\right) - 5.8032 \tag{5}$$

where the α_{en} is the mercury entrapment and equates to the ratio of the ink-bottle porosity ϕ_{ink} over the total porosity ϕ_{t}.

3.3. Determination of relative chloride diffusion coefficient

3.3.1 Method: Nernst-Einstein equation

Ionic conductivity and ionic diffusion coefficient can be correlated with the Nernst-Einstein equation [44]:

$$F_0 = \frac{\sigma_{\mathrm{p}}}{\sigma} = \frac{D_{\mathrm{p}}}{D} \tag{6}$$

where F_0 is the formation factor; σ and σ_{p} [S/m] denote the conductivity of the cementitious material and the pore solution, respectively; D and D_{p} [m^2/s] are the chloride diffusion coefficient of the cementitious material and the pore solution, respectively. The value of D_{p} is around 1.5×10^{-9} m^2/s at room temperature when the chloride concentration (in the form of NaCl) of the pore solution is in the range of 0.1~1.0 mol/L [45].

At a particular degree of water saturation S_{w} the diffusion coefficient D can be determined from the conductivity σ, after correcting the σ_{p} for the saturation level S_{w}. The conductivity σ of cementitious material is the inverse of its resistivity ρ [Ωm]. The non-destructive nature, rapid and ease of performing a resistivity test make it an attractive method to determine the chloride diffusion coefficient.

3.3.2 Relative chloride diffusion coefficient D_{rc}

The relative chloride diffusion coefficient D_{rc} is expressed as the ratio of the chloride diffusion coefficient $D_{S_{\mathrm{w}}}$ at a particular degree of water saturation over the chloride diffusion coefficient D_{Sat} at saturated state. Both $D_{S_{\mathrm{w}}}$ and D_{Sat} can be calculated from Eq. (6), and then the D_{rc} can be determined as:

$$D_{\mathrm{rc}} = \frac{D_{\mathrm{S_w}}}{D_{\mathrm{Sat}}} = \frac{\sigma_{\mathrm{S_w}}}{\sigma_{\mathrm{Sat}}} \cdot \frac{\sigma_{\mathrm{p,Sat}}}{\sigma_{\mathrm{p,S_w}}} \tag{7}$$

where $\sigma_{\mathrm{S_w}}$ and σ_{Sat} denote the conductivity of the cementitious material at a given saturation level S_w and at saturated state, respectively; $\sigma_{\mathrm{p,S_w}}$ and $\sigma_{\mathrm{p,Sat}}$ represent the conductivity of the pore solution at a given saturation level S_w and at saturated state, respectively.

3.3.3 Resistivity measurement of mortar specimens

The electrical resistivity measurement is based on the microstructure and moisture condition of the material under study [46-48]. The resistance R [Ω] of cylindrical mortar specimen (ϕ100 × 50 mm) at a given degree of water saturation S_w was measured with direct current by using one stainless steel electrode covering each surface of the specimen. Between each electrode and specimen surface, a wet sponge was used to obtain a resistance value. More details about the resistivity measurements can be referred to Refs. [28,49].

The resistivity ρ is a function of the resistance R, the length L [m] and the cross-sectional area A [m^2] of the specimen, as shown below.

$$\rho = \frac{1}{\sigma} = \frac{AR}{L} \tag{8}$$

Based on the measured resistances R and Eq. (8), the conductivities of the mortar specimens at various saturation levels, i.e. values of $\sigma_{\mathrm{p,S_w}}$and $\sigma_{\mathrm{p,Sat}}$, can be determined.

3.3.4 Conductivity of pore solution

The conductivity of cementitious pore solution is determined primarily by the concentrations of the ions $\mathrm{Na^+}$, $\mathrm{K^+}$ and $\mathrm{OH^-}$ [50]. These ionic concentrations nonlinearly change with changing degree of water saturation S_w [29].

For saturated state (S_w = 100%), the chemistry of the pore solutions expressed from saturated mortar specimens was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) [51]. The concentrations of the alkalis $\mathrm{Na^+}$ and $\mathrm{K^+}$ were then obtained. The sum of the two alkali concentrations was determined as the concentration of $\mathrm{OH^-}$ [50].

For unsaturated state (S_w < 100%), the alkali concentrations in the pore solution were predicted based on the nonlinear relationship between bound alkalis (mainly by C-S-H) and free alkalis (in the pore solution), as described by Eqs. (9a) and (9b) [29]:

$$C_{\mathrm{Na}} = \frac{n_{\mathrm{Na}}^{r}}{\phi_{\mathrm{t}} \cdot S_{\mathrm{w}} + Rd \cdot m_{\mathrm{C-S-H}}} \tag{9a}$$

$$C_{\mathrm{K}} \cdot \phi_{\mathrm{t}} \cdot S_{\mathrm{w}} + K_{\mathrm{f}} \cdot (C_{\mathrm{K}})^{0.24} \cdot m_{\mathrm{C-S-H}} = n_{\mathrm{K}}^{\mathrm{r}} \tag{9b}$$

where C_{Na} and C_{K} denote the alkali concentration (mol/L) in the pore solution for $\mathrm{Na^+}$ and $\mathrm{K^+}$, respectively; Rd is the distribution ratio (0.45 × 10^{-3} L/g); K_{f} is the adsorption coefficient (0.20 × 10^{-3} L/g); $n_{\mathrm{Na}}^{\mathrm{r}}$ and $n_{\mathrm{K}}^{\mathrm{r}}$ are the mole of alkalis released during the hydration process for $\mathrm{Na^+}$ and $\mathrm{K^+}$, respectively; $m_{\mathrm{C-S-H}}$ is the mass of C-S-H.

Synthetic solutions were prepared by mixing solids NaOH and KOH with distilled water proportionally to achieve the same concentrations of the ions Na^+, K^+ and OH^- in the pore solution of various degrees of water saturation S_w. The conductivity of pore solution as a function of saturation level S_w, i.e. values of $\sigma_{\mathrm{p,S_w}}$ and $\sigma_{\mathrm{p,Sat}}$, was determined from conductivity tests on the synthetic solutions.

4. Experimental results

4.1 Pore structure of paste specimens

The pore structure of various paste mixtures was characterized by MIP measurements. The porosity, average pore diameter (Eq. (3)), pore connectivity (Eq. (4)) and tortuosity (Eq. (5)) were determined. Table 3 gives a summary of the results. As observed, the pore structure parameters vary tremendously between different mixtures. It seems that changes of the pore structure are more significant by adding SCMs than by altering w/b ratio. A higher total porosity does not necessarily correspond to a coarser pore structure, as can be seen from the data shown in Table 3. The blended binders MBL5 and MF5 have larger total porosity, but lower average pore diameter (finer pore size distribution), compared to the plain OPC binder M5 of the same w/b ratio of 0.5.

Of all binders those containing slag (MB4, MB5 and MB6) have the smallest average pore diameter and the lowest pore connectivity. By increasing the w/b ratio from 0.4 (MB4) to 0.6 (MB6), the average pore diameter shows a marginal increase from 11.1 to 11.9 nm while the pore connectivity shows a substantial increase from 25.6 to 40.7%. For OPC binders (M4, M5 and M6), in contrast, both average pore diameter and pore connectivity show a considerable increase with the rise in w/b ratio. Regardless of OPC or slag-blended binders, the total porosity increases clearly when the w/b ratio increases from 0.4 to 0.6, an expected observation. In the presence of FA, the binary binder MF5 exhibits a smaller average pore diameter and lower pore connectivity than the reference OPC binder M5. Compared to MF5, further addition of LP (MFL5) significantly increases both the average pore diameter and the pore connectivity.

4.2 Conductivity of pore solution in unsaturated mortars

4.2.1 Ionic concentration at various saturation levels

Fig. 8 shows the calculated ionic concentrations of pore solution as a function of the degree of water saturation for one-year-old cementitious mortars. Regardless of OPC or SCMs (FA, BFS or LP) binders, a similar tendency is found that the concentration of each ion species nonlinearly increases with decreasing S_w. The concentration of K^+ is generally higher than that of Na^+. For all binders the K^+/Na^+ ratio varies in the range 1.5~2.3 at $S_w = 100\%$, while in a wider range 2.1~3.5 when the S_w is as low as 30%. In cementitious systems Na^+ is more readily released from the raw materials after mix with water, while K^+ is more rapidly incorporated in hydrates C-S-H [52]. At lower S_w, the physically bound K^+ is more susceptible to liberate from C-S-H into the pore solution as free K^+, resulting in a higher K^+/Na^+ ratio at lower S_w. This finding is a point well worthy of consideration as far as modelling cement hydration kinetics is concerned.

As seen from Fig. 8, the ionic concentration decreases sharply with the addition of SCMs and particularly with BFS. This observation is in good agreement with those reported previously [52]. Of particular interest is that irrespective of the saturation level S_w the concentration of K^+ in the pore solution is nearly twice in OPC mortar M5 than in FA-blended mortar MF5, although the K_2O content of the raw OPC is only half that of the raw FA (Table 1). This can be related to the higher alkali uptake by the hydrates C-S-H, including the C-S-H formed by OPC hydration and the secondary C-S-H formed by pozzolanic reaction of FA and calcium hydroxide. The alkali adsorption capacity might be different between the secondary C-S-H (by pozzolanic reaction) and the C-S-H (by OPC hydration). In this respect, more research can be done in future for quantitative descriptions.

The OH^- concentration, a major factor related to the chloride-induced corrosion initiation (controlled by the Cl/OH ratio [53]), differs significantly between all the binders tested. At $S_w = 100\%$ the OH^- concentration varies by a factor of 5, from 0.104 (ternary binder MBL5) to 0.517 (OPC binder M4). An alteration by a factor of 6.7 between MBL5 and M4 is found for the OH^- concentration at a low S_w of 40%. The OH^- concentrations obtained in the present work are comparable to those of the w/b 0.58 paste specimens (OPC, BFS and FA) as reported by Scott and Alexander [54].

4.2.2 Conductivity of pore solution at various saturation levels

Fig. 9 presents the conductivity σ_p of the synthetic pore solution in cementitious mortars at different S_w. For any particular S_w, the binders blended with SCMs (FA, BFS or LP) generally show lower σ_p-values than the reference OPC binders of the same w/b ratio. The lowest σ_p-values are found in the BFS-blended binders. The value of σ_p increases nonlinearly with decreasing S_w. Especially for $S_w < 60\%$, a relatively rapid increase of the σ_p-value is observed as the S_w further decreases. The σ_p-value is almost doubled when the S_w decreases from 100 to 30%, regardless of the w/b ratio or the type of cement.

A factor of 4.3~5.1 is found for the differences of the conductivity of pore solution in all mortars at S_w = 60~100%, a normal saturation range of onsite cementitious materials. This demonstrates a considerable impact of the pore solution chemistry on the resistivity measurement results of cementitious materials. The need for taking pore solution chemistry into account when using resistivity measurements for judging the transport-related durability properties is also emphasized recently by Olsson et al. [19].

4.3 Relative chloride diffusion coefficient D_{rc} in blended mortars

The conductivities of the partially-saturated mortar specimens and their pore solutions were measured. By using Eq. (7), the relative chloride diffusion coefficient D_{rc} as a function of the degree of water saturation S_w was determined. The D_{rc}-S_w relationships of mortar specimens containing different SCMs, i.e. fly ash, slag and limestone powder, are presented below.

4.3.1 Effect of fly ash (FA)

Fig. 10a shows the D_{rc}-S_w relationships in the mortars with OPC binder M5 and FA-blended binder MF5. Like the reference mortar M5, the mortar MF5 also shows three-stage D_{rc}-S_w relationship: a slight decrease at stage I, a sharp drop at stage II and a slight decline at stage III. However, the mortar MF5 exhibits lower D_{rc} than the mortar M5 throughout the S_w range. For example, at S_w = 80% the D_{rc} of mortar MF5 is 35%, compared to 54% in mortar M5.

Differences of the D_{rc}-S_w relation between mortars MF5 and M5 can be attributed to changes of the pore structure formed with and without FA. Fig. 10b shows the MIP-derived pore size distributions in the pastes with plain OPC binder M5 and FA-blended binder MF5. The majority of the pore sizes are smaller than 0.1 μm for both binders. Paste MF5 contains more small pores than paste M5. As already noted in Table 3, the average pore diameter d_a, indicating pore size fineness, is lower in paste MF5 (19.8 nm) than in paste M5 (24.5 nm). The pore connectivity η_p of paste MF5 (45.8%) is also lower than that of paste M5 (57.1%). It is thus expected that mortar MF5 has lower water continuity η_w and lower relative chloride diffusion coefficient D_{rc} in the entire range of S_w, compared to the reference mortar M5.

4.3.2 Effect of slag (BFS)

Fig. 11a compares the D_{rc}-S_w relations between OPC mortars (M4, M5 and M6) and BFS-blended mortars (MB4, MB5 and MB6). Substantial differences can be observed. For BFS-blended mortars the D_{rc} shows a rapid drop when the S_w decreases in the high levels. This observation is similar to the results reported in Ref. [19]. The D_{rc}-value drops by a factor of around 20 when the S_w is reduced from 100 to 80%, followed by a slight slow decrease at lower S_w. For OPC mortars, in contrast, the D_{rc}-value changes clearly from 100 to 60%. For a given S_w in the range of 60~100%, the D_{rc} of BFS-blended mortars is appreciably lower than that of OPC mortars. The strong dependence of the D_{rc} on the S_w in BFS-blended mortars results from the fact that the BFS-blended paste matrix has a markedly fine pore size distribution (nearly all pores are smaller than 0.02 μm, see Fig. 11b) and a very low pore connectivity (see Table 3). In addition, the roles of the w/b ratio in the D_{rc}-S_w relation are different between OPC and BFS-blended mortars. The OPC mortar with a higher w/b ratio shows a higher D_{rc} for a given S_w. For BFS-blended mortars, in contrast, the D_{rc}-S_w relation (especially at high saturation levels, S_w = 80~100%) changes little when the w/b ratio increases from 0.4 to 0.6.

The role of the w/b ratio in the D_{rc}-S_w relation at high S_w stems from the effect of the w/b ratio on the pore size fineness. When the w/b ratio decreases from 0.6 to 0.4, the total porosity ϕ_t decreases from 27.7 to 15.5% and from 15.9 to 7.8% for OPC pastes and BFS-blended pastes, respectively (see Table 3). Nevertheless, different dependences of the pore size fineness (indicated by average pore diameter d_a) on the w/b ratio are found. The d_a-value is determined as 23.2, 24.5 and 27.6 nm for OPC pastes with w/b ratios of 0.4, 0.5 and 0.6, compared to 11.1, 11.6 and 11.9 nm for BFS-blended pastes with w/b ratios of 0.4, 0.5 and 0.6, respectively. For OPC binders, lowering w/b ratio significantly reduces the pore size. For BFS-blended binders, however, the w/b ratio does not affect the pore size fineness drastically.

The above analyses help to understand the controversial findings about the role of the w/b ratio in the D_{rc}-S_w relation as previously reported by different workers [18,26-28].

4.3.3 Effect of combined fly ash (FA) and limestone powder (LP)

Fig. 12a gives the D_{rc}-S_w relations in the mortars with OPC binder M5, binary binder MF5 and ternary binder MFL5. All the three binders show a three-stage D_{rc}-S_w relation. On the other hand, differences in the D_{rc}-S_w relation exist between these binders.

Compared with the plain OPC mortar M5, the ternary mortar MFL5 shows a comparable (marginally larger) D_{rc}-value at $S_w \geq 55\%$ (stages I and II) but a smaller D_{rc}-value at $S_w < 55\%$ (stage III). This is reasonable against the background of their pore structure characteristics. A coarser pore size distribution is present in the binder MFL5 than in the binder M5 (see Fig. 12b), i.e. $d_a = 24.7$ nm *vs.* $d_a = 24.5$ nm (Table 3). This explains the higher D_{rc}-values at $S_w \geq 55\%$ in MFL5 than in M5. The fact that the pore connectivity is lower for MFL5 ($\eta_p = 55.1\%$) than for M5 ($\eta_p = 57.1\%$), as shown in Table 3, supports the lower D_{rc}-values at $S_w < 55\%$ for MFL5 than for M5. The ternary mortar MFL5 shows larger D_{rc}-value in the entire S_w range as compared to the binary mortar MF5. This is a consequence of the coarser pore size distribution (see Fig. 12b) and lower pore connectivity (see Table 3) for the binder MFL5 than for the binder MF5.

4.3.4 Effect of combined slag (BFS) and limestone powder (LP)

Fig. 13a shows the D_{rc}-S_w relations in the mortars with OPC binder M5, binary binder MB5 and ternary binder MBL5. The D_{rc}-S_w curve of MBL5 falls in between the D_{rc}-S_w curves of M5 and MB5. In other words, at a given saturation level S_w the D_{rc}-value shows an ascending order in the binders as: D_{rc} (MB5) < D_{rc} (MBL5) < D_{rc} (M5). This observation is intimately related to the water continuity, which depends on the pore size fineness and pore connectivity in these specimens.

Fig. 13b shows the pore size distribution in the pastes of the same binders. A shift in distribution toward larger pore size is observed in the binary binder MB5 ($d_a = 11.6$ nm), ternary binder MBL5 ($d_a = 17.0$ nm) and OPC binder M5 ($d_a = 24.5$ nm). The same larger order also holds for the pore connectivity η_p: 37.3, 54.4 and 57.1% for MB5, MBL5 and M5, respectively (see Table 3).

4.4 Formation factor

Fig. 14 shows the formation factor F_0 as a function of the degree of water saturation S_w for different mortars. The F_0-value is not a constant but increases with decreasing saturation level S_w. The changing F_0-value against varying saturation level S_w can be ascribed to the fact that the determination of F_0-value depends on the electrical conductivity, which varies with different saturation level S_w. The F_0-values are generally lower for the OPC binder (M5) than for the blended binders, regardless of the saturation level S_w. The F_0-S_w relationship enables to obtain the ionic conductivity/diffusion coefficient in a cementitious material directly from the ionic conductivity/diffusion coefficient in the pore solution.

5. Discussion of D_{Cl}-RH relation

The *relative* chloride diffusion coefficient D_{rc} of the cementitious materials at various degrees of water saturation S_w has been studied. In parallel, the chloride diffusion coefficient D_{Cl} as a function of degree of water saturation S_w can also be obtained. Besides the degree of water saturation S_w, the relative humidity RH is another parameter used for studying the unsaturated chloride diffusion coefficient D_{Cl}. In practice the moisture exchange between cementitious materials and ambient environment highly depends on the ambient RH level. A lower ambient RH corresponds to a lower saturation level S_w of the material. The RH-S_w relations of all mortar mixtures were measured in the experimental program. By making use of the RH-S_w relation, the D_{Cl}-S_w relation can be converted into the D_{Cl}-RH relation. The D_{Cl}-RH relations, as discussed below, can be a valuable supplement to the traditional understanding of the durability of marine cementitious materials.

5.1 D_{Cl}-RH relation in OPC mortars

Fig. 15 shows the D_{Cl}-RH relations in the one-year-old OPC mortars with the w/b ratios of 0.4, 0.5 and 0.6. At high RH levels (> 95%) the diffusion coefficient D_{Cl} is higher in higher w/b ratio cement mortars. At low RH levels (< 85%), on the contrary, the higher diffusion coefficient D_{Cl} is found for lower w/b ratio cement mortars. This is acceptable given the fact that ionic diffusion occurs most readily within the largest continuous water-filled channels. At high RH levels the ionic diffusion in the large pores dominates the transport process. The cement mortar with a higher w/b ratio has more large pores, resulting in a larger D_{Cl}-value. The cement mortar with a lower w/b ratio has more small pores. Below a certain RH level these small pores control the ionic transport process and the D_{Cl}-value can be larger in the lower w/b ratio cement mortar [18]. Note that the connectivity of (water-filled) small pores is not much different for OPC mortars with different w/b ratios (0.4~0.6) [34,35].

5.2 D_{Cl}-RH relation in blended mortars

Fig. 16 shows the D_{Cl}-RH relations for one-year-old OPC (M5) and blended mortars (MB5, MF5 and MFL5). All mortars have a constant w/b ratio of 0.5. The blended mortars generally show lower diffusion coefficient D_{Cl} than the OPC mortar M5 for RH > 60%. The diffusion coefficients D_{Cl} of the three blended mortars MB5, MF5 and MFL5 are almost the same at saturated state (RH > 98%) but differ at lower RH levels. With decrease of the RH level, the diffusion coefficient D_{Cl} decreases rapidly in the OPC mortar M5 while decreases slowly in the blended mortars. Particularly for the

BFS-blended mortar MB5, the diffusion coefficient D_{Cl} shows a slight change for RH > 83%, but it decreases drastically at lower RH.

The above observations indicate a strongly RH-dependent ionic transport (which is associated with the pore structures). The majority of the pores in the BFS-blended paste MB5 are smaller than 13 nm (see Fig. 11b), corresponding to RH = 83% by following the Kelvin-Cohan equation [37]. Compared to OPC mortar M5, the BFS-blended mortar MB5 shows lower diffusion coefficients D_{Cl} at low RH levels (< 83%), although MB5 has more small pores (< 13 nm) (see Fig. 13b). This can be explained by the considerably low water continuity of MB5, caused by its very fine pore size and low pore connectivity (see Table 3). A much lower connectivity of small pores in BFS-blended systems than in OPC systems has been demonstrated in a recent report [35].

Between OPC and blended mortars, the differences of the diffusion coefficient D_{Cl} diminish with decreasing RH level. The pronounced influence of the SCMs on the D_{Cl}-RH relation is found mainly when RH > 75%. These are reasonable from a pore structure point of view. For saturated state (RH > 98%), the pore connectivity controls the ionic transport. The addition of FA or BFS substantially reduces the pore connectivity, leading to a drastic reduction of the diffusion coefficient D_{Cl} in saturated mortars. Such reduction, however, will be partly counteracted for a lower RH level (< 98%), due to the presence of more water-filled small pores by adding FA or BFS.

A comparison of the data between Fig. 15 and Fig. 16 clearly indicates that the D_{Cl}-RH relation is affected more strongly by adding SCMs than by altering w/b ratio. The effects of both w/b ratio and SCMs on chloride diffusion differ significantly between saturated and unsaturated cementitious materials. Current specifications on the mixture design of concrete (often unsaturated when serving in marine environment) are normally based on the chloride diffusion coefficient of *saturated* concrete specimens. This may lead to misjudgements of the durability of marine concrete structures. A reliable durability assessment of a concrete mixture should consider the influence of *unsaturated* state on the chloride diffusion process.

Research aimed at clarifying the role of unsaturated state in service life prediction of marine concrete structures is in progress. It is hoped that this research may contribute to a more effective utilization of SCMs when designing new concrete structures in chloride-laden environments.

6. Conclusions

Experiments and analysis were carried out to investigate the role of pore structure, as well as supplementary cementitious materials (SCMs), in the chloride diffusion in unsaturated cementitious materials. This work helps to understand why the data previously reported about unsaturated chloride diffusion showed a large scatter and were partly controversial. The following conclusions can be drawn from the present work:

- Higher water continuity (η_w) leads to higher relative chloride diffusion coefficient (D_{rc}) for a given degree of water saturation (S_w). The porosity and tortuosity are not relevant to η_w in partially saturated porous systems. A finer pore size distribution or lower pore connectivity tends to result in a lower η_w and hence a lower D_{rc}. The effect of pore size on η_w, as well as on the D_{rc}-value, is pronounced primarily for high S_w. For low S_w, η_w and associated D_{rc}-value are dominated by the pore connectivity.
- Variation of the pore solution conductivity by a factor of 4.3~5.1 is found for different cementitious binders. Using resistivity measurements to compare the ionic diffusion coefficient between binders with vastly different pore solution chemistry is therefore not reliable.
- The role of the w/b ratio in the D_{rc}-S_w relation differs for different binders. A higher w/b ratio (0.4~0.6) results in a higher D_{rc} for OPC binders of a given S_w. The w/b ratio, however, has little effect on the D_{rc}-S_w relation for binders blended with 70% slag. Various SCMs such as fly ash, slag and limestone powder have significantly different influences on the D_{rc}-S_w relationship due to their different effects on the pore structure.
- At high relative humidity (RH) levels (> 95%) a higher w/b ratio OPC mortar has a larger chloride diffusion coefficient. At low RH levels (< 85%) a lower w/b ratio OPC mortar can have a larger chloride diffusion coefficient.
- Utilization of fly ash or slag enables to gain a higher resistivity to chloride diffusion in saturated cementitious materials. However, this advantage becomes less pronounced in cementitious materials with lower RH levels, owing to the presence of more water-filled small pores in the refined pore structure by adding fly ash or slag.
- The dependences of chloride diffusion on pore structure characteristics are substantially different between saturated and unsaturated cementitious materials. There is a high need to study the unsaturated chloride diffusion coefficient in order to more effectively utilize SCMs for designing durable marine concrete.

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