

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

Zhang, Yong; Yang, Zhengxian; Ye, Guang

**DOI**

[10.1016/j.cemconres.2019.105919](https://doi.org/10.1016/j.cemconres.2019.105919)

**Publication date**

2020

**Document Version**

Accepted author manuscript

**Published in**

Cement and Concrete Research

**Citation (APA)**

Zhang, Y., Yang, Z., & Ye, G. (2020). Dependence of unsaturated chloride diffusion on the pore structure in cementitious materials. *Cement and Concrete Research*, 127, Article 105919. <https://doi.org/10.1016/j.cemconres.2019.105919>

**Important note**

To cite this publication, please use the final published version (if applicable). Please check the document version above.

**Copyright**

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

**Takedown policy**

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

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

2 Yong Zhang <sup>a,b,c</sup>, Zhengxian Yang <sup>a,b</sup>, Guang Ye <sup>c,\*</sup>

3 <sup>a</sup> Fujian Provincial University Research Center for Advanced Civil Engineering Materials, Fuzhou  
4 University, Fuzhou 350116, China

5 <sup>b</sup> College of Civil Engineering, Fuzhou University, Fuzhou 350116, China

6 <sup>c</sup> Microlab, Section of Materials and Environment, Faculty of Civil Engineering and Geosciences,  
7 Delft University of Technology, 2628 CN Delft, the Netherlands

8 \*Corresponding author: Guang Ye ([g.ye@tudelft.nl](mailto:g.ye@tudelft.nl))  
9

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

20 Keywords: Chloride diffusion; Pore structure; Degree of water saturation; Relative humidity;  
21 Supplementary cementitious materials  
22

## 23 1. Introduction

24 One major durability issue of marine concrete structures can be ascribed to the chloride-induced  
25 reinforcement corrosion, caused by chloride ions penetration in the concrete cover. After the  
26 publication by Collepardi et al. [1] who reported that the penetration of chloride ions into concrete  
27 follows Fick's diffusion law, the chloride diffusion coefficient ( $D_{Cl}$ ) has been commonly used to  
28 describe the capacity of concrete to resist chloride ions penetration. Numerous studies on this subject  
29 were based on the chloride ions penetration tests of saturated concretes [2]. The test results depend  
30 primarily on the pore structure of the concrete specimens. It is generally considered that lowering  
31 water-to-binder (w/b) ratio or adding pozzolanic materials will improve the durability, because of the  
32 refined pore structure and associated higher resistance to the chloride diffusion in *saturated* concretes  
33 [3]. Such consideration plays an important part in current concrete mixture design and durability  
34 assessment, e.g. DuraCrete [4] and Life-365 [5]. However, this consideration is not yet fully assured

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

38 For saturated cementitious materials the effects of pore features on the chloride diffusion have  
39 been well documented. Page et al. [6] may be the first who observed that in saturated ordinary  
40 Portland cement (OPC) pastes the chloride diffusion coefficient  $D_{Cl}$  almost linearly increases with  
41 increasing *total porosity*. By studying the profiles of the chloride ions penetrated from seawater to  
42 different mortars, Moukwa [7] concluded that the macro pores ( $> 30$  nm) play a major role in the  
43 chloride diffusion. Tang and Nilsson [8] proposed an approach correlating the profile of total chloride  
44 content to the *pore size distribution*. In the percolation concept described by Bentz and Garboczi [9],  
45 referred to by Ye [10], the *pore connectivity* is a key factor controlling mass transport phenomena.  
46 An experimental investigation from Neithalath and Jain [11] further confirmed that the pore  
47 connectivity has a higher impact on ionic transport compared to porosity and pore size. Hornain et al.  
48 [12] found that the reduction of chloride diffusion, caused by the addition of limestone filler, was  
49 attributed to the increased *tortuosity* of the pore system. Ma et al. [13] established a two-scale model  
50 for transport studies, in which the importance of tortuosity on chloride diffusion was highly  
51 emphasized.

52 The above findings about the relationship between pore structure and ionic transport were based  
53 on the studies of saturated cementitious materials. For unsaturated cementitious materials explicit  
54 descriptions on the pore structure-dependent ionic transport can hardly be found [14]. Most of the  
55 previous studies intended to measure or evaluate the chloride/moisture transport properties in  
56 unsaturated cementitious materials [15-28], only that Olsson et al. [18] presented a preliminary  
57 description on the relationship between large pores, small pores and unsaturated ionic transport. In  
58 the literature the unsaturated state is characterized normally by the degree of water saturation ( $S_w$ ) or  
59 relative humidity (RH). The relative chloride diffusion coefficient ( $D_{rc}$ ), i.e.  $D_{Cl}$  at unsaturated state  
60 normalized to  $D_{Cl}$  at saturated state, is often adopted to describe the unsaturated chloride diffusion.  
61 In view of the results published, there is none consensus on the relationship between  $D_{rc}$  and  $S_w$  (or  
62 RH) [14,17,18,26-28]. The data about the  $D_{rc}$ - $S_w$  (or  $D_{rc}$ -RH) relationships show a large scatter [14].  
63 Buchwald [24] reported that the  $D_{rc}$  was decreased from 1 to 0.42 when the  $S_w$  decreased from 100 to  
64 70%, while Mercado et al. [25] found a drastic drop of  $D_{rc}$  from 1 to 0.03 in this saturation range. The  
65 role of w/b ratio in unsaturated chloride diffusion remains a point of controversy. Olsson et al. [18]  
66 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  
67 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  
68  $S_w$ . Up to date a satisfactory explanation on the phenomenon of unsaturated chloride diffusion is not  
69 available.

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

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

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

## 97 **2. Role of pore structure in water continuity**

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

$$101 \quad \eta_w = \frac{N_w}{N_{Sat}} \quad (1)$$

102 where  $N_w$  and  $N_{Sat}$  represents the number of channels available for ionic transport when the porous  
103 system is at a particular saturation level  $S_w$  and at saturated state, respectively.

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

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

#### 124 2.1. Effect of porosity on water continuity

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

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

#### 134 2.2. Effect of pore size on water continuity

135 Fig. 4 shows two porous systems (I and II) with different pore size distribution. System I has one  
 136 channel consisting of large pore (diameter  $d_L$ ) and small pore (diameter  $d_S$ ). System II has two  
 137 channels consisting of pores with diameters  $d_1 = d_L/2$ ,  $d_2 = \sqrt{3} d_L/2$ ,  $d_3 = d_S/2$  and  $d_4 = \sqrt{3} d_S/2$ .  
 138 **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**

139 pore  $d_L$  is equal to the sum of the volumes of the pores  $d_1$  and  $d_2$ , as  $V_{d_L} = V_{d_1} + V_{d_2}$ . At  $S_w = 100\%$ ,  
140  $\eta_w(\text{I}) = 1/1 = 1$  and  $\eta_w(\text{II}) = 2/2 = 1$ . With the decrease of  $S_w$  water loss starts from the centre part  
141 of the larger pore. At  $S_w = 70\%$  the pore  $d_2$  in system II is drained, i.e.  $N_w(\text{II}) = 1$  and  $\eta_w(\text{II}) = 1/2$ .  
142 In contrast, the pore  $d_L$  in system I remains partially water-filled allowing ionic transport, i.e.  $N_w(\text{I})$   
143  $= 1$  and  $\eta_w(\text{I}) = 1$ . Herein, it is noted that  $d_L$ ,  $d_1$  and  $d_2$  represent the diameters of large pores (as  
144 shown in Fig. 4) while they can also be regarded as the diameters of large transport channels in 3D-  
145 microstructure. At  $S_w = 60\%$  the pore  $d_L$  in system I becomes drained. In the meantime, the pores  $d_1$   
146 and  $d_2$  in system II are drained as well. It holds:  $\eta_w(\text{I}) = \eta_w(\text{II}) = 0$ . At low saturation levels, i.e.  $S_w$   
147  $< 60\%$ , further loss of water no longer influences the water continuity in both systems I and II. It  
148 holds:  $\eta_w(\text{I}) = \eta_w(\text{II}) = 0$ .

149 It is found that for a given degree of water saturation  $S_w$ , water continuity  $\eta_w$  tends to be lower in  
150 the system with a finer pore size distribution. This can be explained by the fact that water loss in a  
151 fine pore easily results in the pore to become drained and in this case  $\eta_w$  can be sensitive to water  
152 loss. Nevertheless, the effect of the pore size on  $\eta_w$  is pronounced at high saturation levels but  
153 becomes weak at low saturation levels.

### 154 2.3. Effect of pore connectivity on water continuity

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

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

## 174 2.4. Effect of pore tortuosity on water continuity

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

178 Fig. 6 shows two channels I and II. Both channels consist of small pore and large pore. Channel II  
179 has a higher tortuosity than channel I, i.e.  $\tau(\text{II}) > \tau(\text{I})$ . At saturated state, the water continuity of  
180 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  
181 large pores in channels I and II are drained. The water in both channels becomes discontinuous, i.e.  
182  $\eta_w(\text{I}) = \eta_w(\text{II}) = 0$ . Therefore, the dependence of water continuity on the pore tortuosity is  
183 insignificant since the water-filled pores in a channel, irrespective of its tortuosity, are no longer  
184 continuous only if one pore in the channel is drained (Fig. 6b).

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

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

## 193 3. Experimental program

### 194 3.1. Materials and samples

195 The raw materials used were CEM I 42.5N (OPC) and SCMs including ground granulated blast  
196 furnace slag (BFS), fly ash (FA) and limestone powder (LP). The chemical composition of the raw  
197 materials is given in Table 1. The mean particle sizes measured by laser diffraction were 24.1  $\mu\text{m}$  for  
198 OPC, 13.5  $\mu\text{m}$  for BFS, 25.0  $\mu\text{m}$  for FA and 33.5  $\mu\text{m}$  for LP. The crystalline fraction analyzed by  
199 quantitative X-ray diffraction was about 42 wt.% in FA, compared to merely 2 wt.% in BFS. The  
200 main content of LP, i.e.  $\text{CaCO}_3$ , was around 98 wt.%.

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

206 The one-year-old paste samples were crushed into pieces and then immersed in liquid nitrogen at  
207  $-195$  °C for 5 min. Next the paste pieces were placed in a freeze-dryer with  $-24$  °C and under vacuum

208 at 0.1 Pa. After the water loss was below 0.01% per day the paste pieces were ready for pore structure  
209 measurements (see Section 3.2).

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

### 225 3.2. Characterization of pore structure

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

$$231 \quad d = - \frac{4\gamma_{\text{Hg}} \cos \theta}{P} \quad (2)$$

232 where  $\gamma_{\text{Hg}}$  is the surface tension of mercury (0.48 N/m) and  $\theta$  is the contact angle between mercury  
233 and pore surface (139°) [40].

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



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

$$243 \quad d_a = \frac{4V_t}{S_t} \quad (3)$$

244 where  $V_t$  [ $\text{m}^3/\text{m}^3$ ] and  $S_t$  [ $\text{m}^2/\text{m}^3$ ] are the total pore volume and total pore surface area, respectively.

245 The pore connectivity  $\eta_p$  is often estimated as the quotient of the effective porosity  $\phi_e$  over the  
 246 total porosity  $\phi_t$  [42]:

$$247 \quad \eta_p = \frac{\phi_e}{\phi_t} \times 100\% \quad (4)$$

248 The pore tortuosity  $\tau$  can be determined from the CPSM model proposed by Salmas and  
 249 Androutsopoulos [43].

$$250 \quad \tau = 4.6242 \ln \left( \frac{4.996}{1 - \alpha_{en}} - 1 \right) - 5.8032 \quad (5)$$

251 where the  $\alpha_{en}$  is the mercury entrapment and equates to the ratio of the ink-bottle porosity  $\phi_{ink}$  over  
 252 the total porosity  $\phi_t$ .

### 253 3.3. Determination of relative chloride diffusion coefficient

#### 254 3.3.1 Method: Nernst-Einstein equation

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

$$257 \quad F_0 = \frac{\sigma_p}{\sigma} = \frac{D_p}{D} \quad (6)$$

258 where  $F_0$  is the formation factor;  $\sigma$  and  $\sigma_p$  [S/m] denote the conductivity of the cementitious material  
 259 and the pore solution, respectively;  $D$  and  $D_p$  [ $\text{m}^2/\text{s}$ ] are the chloride diffusion coefficient of the  
 260 cementitious material and the pore solution, respectively. The value of  $D_p$  is around  $1.5 \times 10^{-9} \text{ m}^2/\text{s}$   
 261 at room temperature when the chloride concentration (in the form of NaCl) of the pore solution is in  
 262 the range of 0.1~1.0 mol/L [45].

263 At a particular degree of water saturation  $S_w$  the diffusion coefficient  $D$  can be determined from  
 264 the conductivity  $\sigma$ , after correcting the  $\sigma_p$  for the saturation level  $S_w$ . The conductivity  $\sigma$  of  
 265 cementitious material is the inverse of its resistivity  $\rho$  [ $\Omega\text{m}$ ]. The non-destructive nature, rapid and  
 266 ease of performing a resistivity test make it an attractive method to determine the chloride diffusion  
 267 coefficient.

#### 268 3.3.2 Relative chloride diffusion coefficient $D_{rc}$

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

$$D_{rc} = \frac{D_{S_w}}{D_{Sat}} = \frac{\sigma_{S_w}}{\sigma_{Sat}} \cdot \frac{\sigma_{p,Sat}}{\sigma_{p,S_w}} \quad (7)$$

where  $\sigma_{S_w}$  and  $\sigma_{Sat}$  denote the conductivity of the cementitious material at a given saturation level  $S_w$  and at saturated state, respectively;  $\sigma_{p,S_w}$  and  $\sigma_{p,Sat}$  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  $R$  [ $\Omega$ ] of cylindrical mortar specimen ( $\phi 100 \times 50$  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  $\rho$  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.

$$\rho = \frac{1}{\sigma} = \frac{AR}{L} \quad (8)$$

Based on the measured resistances  $R$  and Eq. (8), the conductivities of the mortar specimens at various saturation levels, i.e. values of  $\sigma_{p,S_w}$  and  $\sigma_{p,Sat}$ , 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  $Na^+$ ,  $K^+$  and  $OH^-$  [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  $Na^+$  and  $K^+$  were then obtained. The sum of the two alkali concentrations was determined as the concentration of  $OH^-$  [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]:

$$C_{Na} = \frac{n_{Na}^r}{\phi_t \cdot S_w + Rd \cdot m_{C-S-H}} \quad (9a)$$

$$C_K \cdot \phi_t \cdot S_w + K_f \cdot (C_K)^{0.24} \cdot m_{C-S-H} = n_K^r \quad (9b)$$

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

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

## 311 4. Experimental results

### 312 4.1 Pore structure of paste specimens

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

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

### 331 4.2 Conductivity of pore solution in unsaturated mortars

#### 332 4.2.1 Ionic concentration at various saturation levels

333 Fig. 8 shows the calculated ionic concentrations of pore solution as a function of the degree of  
334 water saturation for one-year-old cementitious mortars. Regardless of OPC or SCMs (FA, BFS or LP)  
335 binders, a similar tendency is found that the concentration of each ion species nonlinearly increases  
336 with decreasing  $S_w$ . The concentration of  $\text{K}^+$  is generally higher than that of  $\text{Na}^+$ . For all binders the  
337  $\text{K}^+/\text{Na}^+$  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  
338 as low as 30%. In cementitious systems  $\text{Na}^+$  is more readily released from the raw materials after mix  
339 with water, while  $\text{K}^+$  is more rapidly incorporated in hydrates C-S-H [52]. At lower  $S_w$ , the physically  
340 bound  $\text{K}^+$  is more susceptible to liberate from C-S-H into the pore solution as free  $\text{K}^+$ , resulting in a

341 higher  $K^+/Na^+$  ratio at lower  $S_w$ . This finding is a point well worthy of consideration as far as  
342 modelling cement hydration kinetics is concerned.

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

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

#### 358 4.2.2 Conductivity of pore solution at various saturation levels

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

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

#### 372 4.3 Relative chloride diffusion coefficient $D_{rc}$ in blended mortars

373 The conductivities of the partially-saturated mortar specimens and their pore solutions were  
374 measured. By using Eq. (7), the relative chloride diffusion coefficient  $D_{rc}$  as a function of the degree

375 of water saturation  $S_w$  was determined. The  $D_{rc}$ - $S_w$  relationships of mortar specimens containing  
376 different SCMs, i.e. fly ash, slag and limestone powder, are presented below.

#### 377 4.3.1 Effect of fly ash (FA)

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

383 Differences of the  $D_{rc}$ - $S_w$  relation between mortars MF5 and M5 can be attributed to changes of  
384 the pore structure formed with and without FA. Fig. 10b shows the MIP-derived pore size  
385 distributions in the pastes with plain OPC binder M5 and FA-blended binder MF5. The majority of  
386 the pore sizes are smaller than  $0.1 \mu\text{m}$  for both binders. Paste MF5 contains more small pores than  
387 paste M5. As already noted in Table 3, the average pore diameter  $d_a$ , indicating pore size fineness, is  
388 lower in paste MF5 (19.8 nm) than in paste M5 (24.5 nm). The pore connectivity  $\eta_p$  of paste MF5  
389 (45.8%) is also lower than that of paste M5 (57.1%). It is thus expected that mortar MF5 has lower  
390 water continuity  $\eta_w$  and lower relative chloride diffusion coefficient  $D_{rc}$  in the entire range of  $S_w$ ,  
391 compared to the reference mortar M5.

#### 392 4.3.2 Effect of slag (BFS)

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

406 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  
407 the pore size fineness. When the w/b ratio decreases from 0.6 to 0.4, the total porosity  $\phi_t$  decreases  
408 from 27.7 to 15.5% and from 15.9 to 7.8% for OPC pastes and BFS-blended pastes, respectively (see  
409 Table 3). Nevertheless, different dependences of the pore size fineness (indicated by average pore

410 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  
411 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  
412 with w/b ratios of 0.4, 0.5 and 0.6, respectively. For OPC binders, lowering w/b ratio significantly  
413 reduces the pore size. For BFS-blended binders, however, the w/b ratio does not affect the pore size  
414 fineness drastically.

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

#### 417 4.3.3 Effect of combined fly ash (FA) and limestone powder (LP)

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

421 Compared with the plain OPC mortar M5, the ternary mortar MFL5 shows a comparable  
422 (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  
423 III). This is reasonable against the background of their pore structure characteristics. A coarser pore  
424 size distribution is present in the binder MFL5 than in the binder M5 (see Fig. 12b), i.e.  $d_a = 24.7$  nm  
425 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  
426 fact that the pore connectivity is lower for MFL5 ( $\eta_p = 55.1\%$ ) than for M5 ( $\eta_p = 57.1\%$ ), as shown  
427 in Table 3, supports the lower  $D_{rc}$ -values at  $S_w < 55\%$  for MFL5 than for M5. The ternary mortar  
428 MFL5 shows larger  $D_{rc}$ -value in the entire  $S_w$  range as compared to the binary mortar MF5. This is a  
429 consequence of the coarser pore size distribution (see Fig. 12b) and lower pore connectivity (see  
430 Table 3) for the binder MFL5 than for the binder MF5.

#### 431 4.3.4 Effect of combined slag (BFS) and limestone powder (LP)

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

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

#### 441 4.4 Formation factor

442 Fig. 14 shows the formation factor  $F_0$  as a function of the degree of water saturation  $S_w$  for different  
443 mortars. The  $F_0$ -value is not a constant but increases with decreasing saturation level  $S_w$ . The  
444 changing  $F_0$ -value against varying saturation level  $S_w$  can be ascribed to the fact that the determination

445 of  $F_0$ -value depends on the electrical conductivity, which varies with different saturation level  $S_w$ .  
446 The  $F_0$ -values are generally lower for the OPC binder (M5) than for the blended binders, regardless  
447 of the saturation level  $S_w$ . The  $F_0$ - $S_w$  relationship enables to obtain the ionic conductivity/diffusion  
448 coefficient in a cementitious material directly from the ionic conductivity/diffusion coefficient in the  
449 pore solution.

## 450 **5. Discussion of $D_{Cl}$ -RH relation**

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

### 461 5.1 $D_{Cl}$ -RH relation in OPC mortars

462 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  
463 and 0.6. At high RH levels ( $> 95\%$ ) the diffusion coefficient  $D_{Cl}$  is higher in higher w/b ratio cement  
464 mortars. At low RH levels ( $< 85\%$ ), on the contrary, the higher diffusion coefficient  $D_{Cl}$  is found for  
465 lower w/b ratio cement mortars. This is acceptable given the fact that ionic diffusion occurs most  
466 readily within the largest continuous water-filled channels. At high RH levels the ionic diffusion in  
467 the large pores dominates the transport process. The cement mortar with a higher w/b ratio has more  
468 large pores, resulting in a larger  $D_{Cl}$ -value. The cement mortar with a lower w/b ratio has more small  
469 pores. Below a certain RH level these small pores control the ionic transport process and the  $D_{Cl}$ -  
470 value can be larger in the lower w/b ratio cement mortar [18]. Note that the connectivity of (water-  
471 filled) small pores is not much different for OPC mortars with different w/b ratios (0.4~0.6) [34,35].

### 472 5.2 $D_{Cl}$ -RH relation in blended mortars

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

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

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

489 Between OPC and blended mortars, the differences of the diffusion coefficient  $D_{Cl}$  diminish with  
490 decreasing RH level. The pronounced influence of the SCMs on the  $D_{Cl}$ -RH relation is found mainly  
491 when  $RH > 75\%$ . These are reasonable from a pore structure point of view. For saturated state ( $RH >$   
492  $98\%$ ), the pore connectivity controls the ionic transport. The addition of FA or BFS substantially  
493 reduces the pore connectivity, leading to a drastic reduction of the diffusion coefficient  $D_{Cl}$  in  
494 saturated mortars. Such reduction, however, will be partly counteracted for a lower RH level ( $< 98\%$ ),  
495 due to the presence of more water-filled small pores by adding FA or BFS.

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

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

## 507 **6. Conclusions**

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



- 513 • Higher water continuity ( $\eta_w$ ) leads to higher relative chloride diffusion coefficient ( $D_{rc}$ ) for a given  
514 degree of water saturation ( $S_w$ ). The porosity and tortuosity are not relevant to  $\eta_w$  in partially  
515 saturated porous systems. A finer pore size distribution or lower pore connectivity tends to result  
516 in a lower  $\eta_w$  and hence a lower  $D_{rc}$ . The effect of pore size on  $\eta_w$ , as well as on the  $D_{rc}$ -value, is  
517 pronounced primarily for high  $S_w$ . For low  $S_w$ ,  $\eta_w$  and associated  $D_{rc}$ -value are dominated by the  
518 pore connectivity.
- 519 • Variation of the pore solution conductivity by a factor of 4.3~5.1 is found for different  
520 cementitious binders. Using resistivity measurements to compare the ionic diffusion coefficient  
521 between binders with vastly different pore solution chemistry is therefore not reliable.
- 522 • The role of the w/b ratio in the  $D_{rc}$ - $S_w$  relation differs for different binders. A higher w/b ratio  
523 (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  
524 effect on the  $D_{rc}$ - $S_w$  relation for binders blended with 70% slag. Various SCMs such as fly ash,  
525 slag and limestone powder have significantly different influences on the  $D_{rc}$ - $S_w$  relationship due  
526 to their different effects on the pore structure.
- 527 • At high relative humidity (RH) levels (> 95%) a higher w/b ratio OPC mortar has a larger chloride  
528 diffusion coefficient. At low RH levels (< 85%) a lower w/b ratio OPC mortar can have a larger  
529 chloride diffusion coefficient.
- 530 • Utilization of fly ash or slag enables to gain a higher resistivity to chloride diffusion in saturated  
531 cementitious materials. However, this advantage becomes less pronounced in cementitious  
532 materials with lower RH levels, owing to the presence of more water-filled small pores in the  
533 refined pore structure by adding fly ash or slag.
- 534 • The dependences of chloride diffusion on pore structure characteristics are substantially different  
535 between saturated and unsaturated cementitious materials. There is a high need to study the  
536 unsaturated chloride diffusion coefficient in order to more effectively utilize SCMs for designing  
537 durable marine concrete.

538

### 539 **Acknowledgements**

540 The authors gratefully acknowledge the financial support provided by the Chinese Scholarship  
541 Council and the Talent-Introduction Program of Fuzhou University (grant No. 0050-510781). The  
542 first author would like to express sincere thanks to Gerrit Nagtegaal for his considerable help with  
543 the experimental work. The valuable comments from Dr. Mingzhong Zhang in University College  
544 London are highly appreciated.

545

546 **References**

- 547 [1] M. Collepardi, A. Marcialis, R. Turriziani, The kinetics of penetration of chloride ions into the  
548 concrete (in Italian), *Il Cemento* (1970) 157–164.
- 549 [2] R.A. Patel, Q.T. Phung, S.C. Seetharam, J. Perko, D. Jacques, N. Maes, G. de Schutter, G. Ye,  
550 K. van Breugel, Diffusivity of saturated ordinary Portland cement-based materials: a critical  
551 review of experimental and analytical modelling approaches, *Cem. Concr. Res.* 90 (2016) 52-72.
- 552 [3] F. Moodi, A. Ramezaniapour, E. Jahangiri, Assessment of some parameters of corrosion  
553 initiation prediction of reinforced concrete in marine environments, *Comput. Concr.* 13 (2014)  
554 71-82.
- 555 [4] DuraCrete R17, DuraCrete Final Technical Report, The European Union – Brite EuRam III,  
556 DuraCrete – Probabilistic Performance based Durability Design of Concrete Structures,  
557 Document BE95-1347/R17, May 2000, CUR, Gouda, the Netherlands.
- 558 [5] Life 365, Service life prediction—state-of-the-art report, Manual of Concrete Practice, ACI  
559 Committee 365. 1R-00-44, 2001.
- 560 [6] C.L. Page, N.R. Short, A. El Tarras, Diffusion of chloride ions in hardened cement pastes, *Cem.*  
561 *Concr. Res.* 11 (1981) 395-406.
- 562 [7] M. Moukwa, Penetration of chloride ions from sea water into mortars under different exposure  
563 conditions, *Cem. Concr. Res.* 19 (1989) 894-904.
- 564 [8] L. Tang, L.O. Nilsson, A new approach to the determination of pore distribution by penetrating  
565 chlorides into concrete, *Cem. Concr. Res.* 25 (1995) 695-701.
- 566 [9] D.P. Bentz, E.J. Garboczi, Percolation of phases in a three-dimensional cement paste  
567 microstructural model, *Cem. Concr. Res.* 21 (1991) 325-344.
- 568 [10] G. Ye, Percolation of capillary pores in hardening cement pastes, *Cem. Concr. Res.* 35 (2005)  
569 167-176.
- 570 [11] N. Neithalath, J. Jain, Relating rapid chloride transport parameters of concretes to microstructural  
571 features extracted from electrical impedance, *Cem. Concr. Res.* 40 (2010) 1041-1051.
- 572 [12] H. Hornain, J. Marchand, V. Duhot, M. Moranville-Regourd, Diffusion of chloride ions in  
573 limestone filler blended cement pastes and mortars, *Cem. Concr. Res.* 25 (1995) 1667-1678.
- 574 [13] H.Y. Ma, D.S. Hou, Z.J. Li, Two-scale modeling of transport properties of cement paste:  
575 formation factor, electrical conductivity and chloride diffusivity, *Comput. Mater. Sci.* 110 (2015)  
576 270-280.
- 577 [14] Y. Zhang, M. Zhang, Transport properties in unsaturated cement-based materials – a review,  
578 *Constr. Build. Mater.* 72 (2014) 367–379.

- 579 [15] M.A. Climent, G. de Vera, J.F. Lopez, E. Viqueira, C. Andrade, A test method for measuring  
580 chloride diffusion coefficients through non-saturated concrete: Part I. The instantaneous plane  
581 source diffusion case, *Cem. Concr. Res.* 37 (2002) 714-724.
- 582 [16] G. de Vera, M.A. Climent, E. Viqueira, C. Antón, C. Andrade, A test method for measuring  
583 chloride diffusion coefficients through partially saturated concrete. Part II. The instantaneous  
584 plane source diffusion case with chloride binding consideration, *Cem. Concr. Res.* 37 (2007)  
585 714–724.
- 586 [17] A.T.C. Guimarães, M.A. Climent, G. de Vera, F.J. Vicente, F.T. Rodrigues, C. Andrade,  
587 Determination of chloride diffusivity through partially saturated Portland cement concrete by a  
588 simplified procedure, *Constr. Build. Mater.* 25 (2011) 785–790.
- 589 [18] N. Olsson, V. Baroghel-Bouny, L.O. Nilsson, M. Thiery, Non-saturated ion diffusion in concrete  
590 – a new approach to evaluate conductivity measurements, *Cem. Concr. Compos.* 40 (2013) 40-  
591 47.
- 592 [19] N. Olsson, B. Lothenbach, V. Baroghel-Bouny, L.O. Nilsson, Unsaturated ion diffusion in  
593 cementitious materials – the effect of slag and silica fume, *Cem. Concr. Res.* 108 (2018) 31-37.
- 594 [20] V. Baroghel-Bouny, M. Thiéry, X. Wang, Modelling of isothermal coupled moisture-ion  
595 transport in cementitious materials, *Cem. Concr. Res.* 41 (2011) 828-841.
- 596 [21] E.P. Nielsen, M.R. Geiker, Chloride diffusion in partially saturated cementitious material, *Cem.*  
597 *Concr. Res.* 33 (2003) 133-138.
- 598 [22] P. Zhang, F.H. Wittmann, M. Vogel, H.S. Müller, T. Zhao, Influence of freeze-thaw cycles on  
599 capillary absorption and chloride penetration into concrete, *Cem. Concr. Res.* 100 (2017) 60-67.
- 600 [23] C.S. Zhou, Predicting water permeability and relative gas permeability of unsaturated cement-  
601 based material from hydraulic diffusivity, *Cem. Concr. Res.* 58 (2014) 143-151.
- 602 [24] A. Buchwald, Determination of the ion diffusion coefficient in moisture and salt loaded masonry  
603 materials by impedance spectroscopy, *Proc. 3rd Int. PhD symposium, Vienna, Austria, 2000*, pp.  
604 475-482.
- 605 [25] H. Mercado-Mendoza, S. Lorente, X. Bourbon, Ionic aqueous diffusion through unsaturated  
606 cementitious materials – a comparative study, *Constr. Build. Mater.* 51 (2014) 1-8.
- 607 [26] M. Zhang, G. Ye, K. van Breugel, Modeling of ionic diffusivity in non-saturated cement-based  
608 materials using lattice Boltzmann method, *Cem. Concr. Res.* 42 (2012) 1524-1533.
- 609 [27] M. Zhang, Pore-scale modelling of relative permeability of cementitious materials using X-ray  
610 computed microtomography images, *Cem. Concr. Res.* 95 (2017) 18-29.
- 611 [28] Y. Zhang, M. Zhang, G. Ye, Influence of moisture condition on chloride diffusion in partially  
612 saturated ordinary Portland cement mortar, *Mater. Struct.* (2018) 51:36.

- 613 [29] Y. Zhang, G. Ye, A model for predicting the relative chloride diffusion coefficient in unsaturated  
614 cementitious materials, *Cem. Concr. Res.* 115 (2019) 133-144.
- 615 [30] T.C. Powers, Studies of water vapour adsorption of hardened Portland cement paste, Research  
616 Laboratories of the Portland Cement Association, Bulletin, 22 (1945).
- 617 [31] N.S. Martys, Diffusion in partially-saturated porous materials, *Mater. Struct.* 32 (1999) 555-562.
- 618 [32] A.M. Neville, *Properties of Concrete*, Fourth Edition Addison Wesley Longman Ltd., 1995.
- 619 [33] M. Zhang, K. Xu, Y. He, A.P. Jivkov, Pore-scale modelling of 3D moisture distribution and  
620 critical saturation in cementitious materials, *Constr. Build. Mater.* 64 (2014) 222-230.
- 621 [34] Y. Zhang, G. Ye, Experimental study on pore connectivity and its influence on chloride transport  
622 in saturated cementitious system. 3rd Int. RILEM Conf. on Microstructure Related Durability of  
623 Cementitious Composites (Microdurability2016), China, October 24-26, 2016.
- 624 [35] Y. Zhang, G. Ye. Characterization of pore structure in cementitious materials by intrusion-  
625 extrusion cyclic mercury porosimetry (IEC-MIP). Symposium on Concrete Modelling and  
626 Material Behaviour (CONMOD2018), Delft, the Netherlands, 2018.
- 627 [36] Jr.R.S. Barneyback, S. Diamond, Expression and analysis of pore fluids from hardened cement  
628 pastes and mortars, *Cem. Concr. Res.* 11 (1981) 279-285.
- 629 [37] A.V. Neimark, P.I. Ravikovitch, A. Vishnyakov, Bridging scales from molecular simulations to  
630 classical thermodynamics: density functional theory of capillary condensation in nano pores, *J.*  
631 *Phys. Condens. Matter* 15 (2003) 347-365.
- 632 [38] T.C. Powers, T.L. Brownyard, Studies of the physical properties of hardened Portland cement  
633 paste. Part 2. Studies of water fixation, *J. Amer. Concr. Inst.* 18 (3) (1947):249–303.
- 634 [39] E.W. Washburn, Note on method of determining the distribution of pore size in porous materials,  
635 *Proc. Natl. Acad. Sci.* 7 (1921) 115-116.
- 636 [40] G. Ye, Experimental study and numerical simulation of the development of the microstructure  
637 and permeability of cementitious materials, PhD thesis, Delft University of Technology, the  
638 Netherlands, 2003.
- 639 [41] K.K. Aligizaki, *Pore structure of cement-based materials: testing, interpretation and requirements*,  
640 Taylor & Francis, London, 2006.
- 641 [42] E.J. Garboczi, *Performance criteria for concrete durability*, edited by J. Kropp and H.K. Hilsdorf,  
642 Published by E & FN Spon, London, 1995.
- 643 [43] C. Salmas, G. Androustopoulos, Mercury Porosimetry: Contact Angle Hysteresis of Materials  
644 with Controlled Pore Structure, *J. Colloid Interf. Sci.* 239 (2001) 178–189.
- 645 [44] R.A. McKee, A generalization of the Nernst-Einstein equation for self-diffusion in high defect  
646 concentration solids, *Solid State Ionics* 5 (1981) 133-136.
- 647 [45] R.C. Weast, *Handbook of chemistry and physics*, 56th edition, CRC Press, Cleveland, 1975.

- 648 [46] W.J. McCartert, S. Garvin, Dependence of electrical impedance of cement-based materials on  
649 their moisture condition, *J. Phys. D: Appl. Phys.* 22 (1989) 1773-1776.
- 650 [47] P. Zhang, F.H. Wittmann, P. Lura, H.S. Müller, S. Han, T. Zhao, Application of neutron imaging  
651 to investigate fundamental aspects of durability of cement-based materials: A review, *Cem.*  
652 *Concr. Res.* 108 (2018) 152-166.
- 653 [48] J. Weiss, K. Snyder, J. Bullard, D. Bentz, Using a saturation function to interpret the electrical  
654 properties of partially saturated concrete, *J. Mater. Civil Eng.* 25 (2013) 1097-1106.
- 655 [49] R.B. Polder, Test methods for onsite measurement of resistivity of concrete – a RILEM TC-154  
656 technical recommendation, *Constr. Build. Mater.* 15 (2001) 125-131.
- 657 [50] K.A. Snyder, X. Feng, B.D. Keen, T.O. Mason, Estimating the electrical conductivity of cement  
658 paste pore solutions from  $\text{OH}^-$ ,  $\text{K}^+$  and  $\text{Na}^+$  concentrations, *Cem. Concr. Res.* 33 (2003) 793-798.
- 659 [51] X.D. Hou, B.T. Jones, *Inductively coupled plasma optical emission spectrometry*, John Wiley &  
660 Sons Ltd, Chichester, 2000.
- 661 [52] J. Duchesne, M.A. Bérubé, The effectiveness of supplementary cementing materials in  
662 suppressing expansion due to ASR: another look at the reaction mechanisms part 2: pore solution  
663 chemistry, *Cem. Concr. Res.* 24 (1994) 221-230.
- 664 [53] U. Angst, B. Elsener, C.K. Larsen, Ø. Vennesland, Critical chloride content in reinforced  
665 concrete - a review, *Cem. Concr. Res.* 39 (2009) 1122-1138.
- 666 [54] A. Scott, M.G. Alexander, Effect of supplementary cementitious materials (binder type) on the  
667 pore solution chemistry and the corrosion of steel in alkaline environments, *Cem. Concr. Res.* 89  
668 (2016) 45-55.