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Role of degree of water saturation**

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1 **New insights into long-term chloride transport in unsaturated cementitious materials:**  
2 **Role of degree of water saturation**

3  
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14  
15 **Abstract:** Concrete is rarely saturated. Reliable durability design of marine concrete  
16 structures requires a solid understanding of the long-term chloride transport in unsaturated  
17 concretes. This paper presents a critical analysis of the time-dependent chloride diffusion  
18 coefficient in unsaturated cementitious materials exposed to marine environment. Evolutions  
19 of pore structure and chloride diffusion coefficient in saturated cementitious materials, along  
20 with the role of the degree of water saturation in long-term chloride diffusion, are analyzed. It  
21 is emphasized that the long-term sharp decrease of the chloride diffusion coefficient in  
22 marine cementitious materials is not primarily caused by densification of the microstructure  
23 due to hydration, but by the decreasing degree of water saturation with depth in the surface  
24 part of the materials. The effects of water/binder ratio and supplementary cementitious  
25 materials on chloride diffusion coefficient are different between saturated and unsaturated  
26 cementitious materials.

27  
28 **Keywords:** Cementitious material; Chloride; Degree of water saturation; Pore structure;  
29 Long-term transport

30

## 31 **1. Introduction**

32 The present paper constitutes one part of a series of several interrelated papers devoted to  
33 examining the chloride transport in unsaturated concretes [1-4]. It is hoped that these papers,  
34 taken together, can constitute a coherent conceptual framework that enables to understand the  
35 chloride transport in a manner approaching to the realistic situation, and that it will provide a  
36 scientific background for service life prediction based on unsaturated chloride transport.

### 37 1.1 Chloride diffusion in concrete

38 Today, more than ever, the governments and the owners want to be assured of the long-  
39 term performances of the reinforced concrete infrastructures with life expectancy over 100  
40 years. Chloride penetration is an issue of primary concern in service life design. In present  
41 service life calculations, the chloride penetration in concrete structures, exposed to stable  
42 marine conditions such as submerged, tidal, splash zone, etc., is normally considered to be  
43 controlled by diffusion. Diffusion of chloride ions takes place, under a concentration gradient,  
44 via the continuous water-filled pores in concrete [2]. A certain percentage of the chloride ions  
45 interacts with the binder in terms of physical adsorption to e.g. calcium silicate hydrates [5],  
46 and chemical bound to aluminates as Friedel's salt or Kuzel's salt, and even reacts with  
47 calcium hydroxide [6]. The so-called free or water-soluble chlorides, which diffuse inwards,  
48 are detrimental to the reinforcement corrosion. The chloride diffusion coefficient, derived by  
49 using Fick's second law to describe the chloride profiles, was often used for service life  
50 design of reinforced concrete structures located in chloride-laden environments.

51 Considerable efforts have been dedicated to clarifying the fundamental aspects of  
52 chloride diffusion in saturated and non-saturated concretes [5-28]. The difficulties linked to  
53 accurate description of chloride diffusion can be attributed to the intrinsic complexity of the  
54 concrete microstructure and to the sophistication of the moisture condition (moisture content  
55 and its distribution), as well as to the intricate nature of the diffusion phenomena. In principle  
56 Fick's law of diffusion is valid only for non-ionic substances. For ionic diffusion the ion-ion  
57 interactions need to be involved accounting for the increase of diffusion with dilution. Tang  
58 [7,8] has proved a strongly concentration dependent chloride diffusion coefficient after a  
59 series of theoretical and experimental investigations. The chloride ions at the penetration  
60 front are mostly free. With ongoing penetration process accumulations of the chloride ions  
61 take place, resulting in a larger chloride binding, until saturation of chloride content is  
62 attained [9]. Diffusion of chloride ions is always accompanied with the movement of cations

63 in order to keep the electric charges balanced in the pore solution. The diffusivity of chloride  
64 ( $\text{Cl}^-$ ) is larger than that of sodium ( $\text{Na}^+$ ) [27]. When a concrete is exposed to an aqueous  
65 solution of NaCl, the cations (e.g. calcium  $\text{Ca}^{2+}$ ) can move to the down-stream side along  
66 with the  $\text{Cl}^-$  and the hydroxyl ( $\text{OH}^-$ ) will move to the up-stream side without any imposed  
67 concentration gradients [28]. The electrical double layer (EDL) formed on the particle surface  
68 plays an important part in chloride diffusion [29]. Hydrated cement particles are negatively  
69 charged so that the cations are more concentrated in the EDL than in the bulk solution.  $\text{Cl}^-$   
70 and  $\text{Ca}^{2+}$  are forced to diffuse together so that the diffusivity of  $\text{Cl}^-$  in the bulk solution is  
71 retarded and that of  $\text{Ca}^{2+}$  in the EDL is accelerated. The EDL effect on chloride diffusion is  
72 more pronounced in the smaller water-filled pores [3].

### 73 1.2 Long-term chloride diffusion

74 Laboratory measurements and field data have demonstrated that the chloride diffusion  
75 coefficient is not a constant but decreases with time. Takewake and Mastumoto [30] maybe  
76 the first who pointed out the time-dependency of chloride diffusion in concrete. A wide range  
77 of experimental data on this subject was reported by Mangat and Molloy [31]. Tang and  
78 Nilsson [32] proposed an expression, according to Crank's mathematics of diffusion, to  
79 quantify the decrease of chloride diffusion coefficient with age. Current service life design,  
80 e.g. DuraCrete [33], relies on the time-dependent chloride diffusion coefficient  $D(t)$ , which  
81 is described with a power equation:

$$D(t) = D_0 \cdot \left(\frac{t_0}{t}\right)^n \quad (1)$$

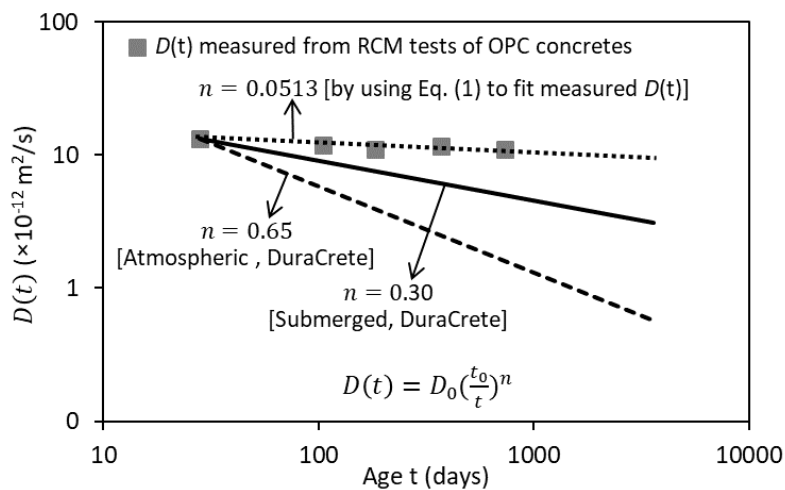
82 where  $n$  is the ageing factor, which stands for the decrease of chloride diffusion coefficient  
83 with age. The  $D(t)$  is extremely sensitive to small changes in the ageing factor  $n$ .  $D_0$  is a  
84 constant referring to the chloride diffusion coefficient at a reference age  $t_0$  (often  $t_0 = 28$   
85 days). The unsaturated state has been a significant obstacle for standardization of the  
86 measurement of the chloride diffusion coefficient in unsaturated concretes [2]. In practice the  
87  $D_0$ -value is usually determined based on chloride penetration testes (e.g. NT Build 492 [34])  
88 of concrete specimens after vacuum saturation.

89 Densification of the microstructure due to continuous cement hydration has been long  
90 time considered an explanation for the decrease of the chloride diffusion coefficient  $D(t)$   
91 [14], and it is generally regarded as the main source used for determining the ageing factor  $n$ .  
92 It has been recognized, however, that the cement hydration is noticeable only in the first few

93 years [35]. A long-term sharp decrease in the  $D(t)$  value caused merely by cement hydration  
 94 is virtually inconceivable.

95 In the absence of long-term exposure data, determination of the ageing factor  $n$  largely  
 96 depends on our knowledge about evolutions of the chloride diffusion coefficient  $D$  measured  
 97 from laboratory specimens. Plenty of reports on this topic are available [36-38]. These reports  
 98 are generally based on regression analyses on experimental data, i.e. by using Eq. (1) to fit  
 99 the time-related chloride diffusion coefficient  $D$  measured from rapid chloride migration  
 100 (RCM) tests of concrete specimens. An example is provided in Fig. 1. An ageing factor  $n =$   
 101 0.0513 is obtained for the OPC concrete prepared under laboratory condition. In the  
 102 DuraCrete [33], however, the ageing factor  $n$  is considerably larger, i.e.  $n = 0.30$  for  
 103 submerged OPC concrete and  $n = 0.65$  for atmospheric OPC concrete. Obviously, the  
 104 diffusion coefficient  $D$  obtained from RCM tests of laboratory concretes shows a relatively  
 105 slow decrease with age, whereas the  $D$ -value predicted from the DuraCrete drops to a great  
 106 extent with age. Such significant differences in long-term chloride diffusion prediction have  
 107 been noticed for a long time [36]. One uttermost reason can be ascribed to the fact that a  
 108 well-prepared laboratory concrete specimen for RCM test is almost *saturated* while onsite  
 109 concrete is usually *unsaturated* owing to self-desiccation and/or wetting-drying cycles [1].  
 110 This makes it essential to consider a point, not explicitly addressed so far, namely that the  
 111 chloride diffusion coefficient  $D(t)$  can decrease with decreasing moisture content.

112



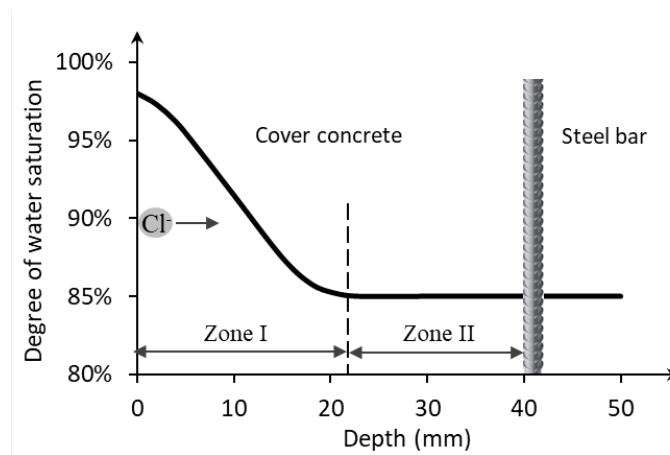
113

114 Fig. 1 Evolution of the chloride diffusion coefficient  $D(t)$  in OPC concretes (water/cement =  
 115 0.5) predicted based on different ageing factor  $n$ .

116

117 Fig. 2 shows an example of the moisture profile in the marine concrete. The near-surface  
118 part may have a high degree of water saturation  $S_w$  because of the moisture ingress from  
119 ambient environment. The internal concrete (Zone II), however, is relatively dry and has a  
120 saturation level  $S_w$  approximately the same as that caused by self-desiccation [39,40]. There  
121 is a moisture gradient in Zone I. The capillary absorption, owing to wetting-drying cycles,  
122 can accelerate the chloride penetration in cover concrete for the first few years of exposure.  
123 The absorption effect is strong when the moisture content of the near-surface concrete is low,  
124 but becomes increasingly weak with an increase of the wetting-drying cycles, since wetting-  
125 drying cycles normally lead to a continuous water supply and comparatively little evaporation  
126 [41,42]. In cases where high performance concretes are used, the influential depth of wetting-  
127 drying cycles will be limited only to the outermost part of the concrete and will play  
128 insignificant role in chloride penetration in the internal concrete [43]. During wetting and  
129 drying, there is a balance between water loss and intake after an equilibrium wetting-drying  
130 time ratio is reached [42]. The chloride penetration in Zone II is considered driven merely by  
131 diffusion.

132



133

134 Fig. 2 An example of the moisture profile in concrete after 2-year exposure to marine  
135 environment and transport of chloride ( $\text{Cl}^-$ ) [40,44].

136

### 137 1.3 Research significance

138 A critical review on models and equations regarding the time-dependence of chloride  
139 diffusion has been reported by Nilsson [18]. These models/equations may be useful in many  
140 practical applications, but they will fail, wholly or in part, when used for predictions of large-  
141 scale concrete infrastructures with a long-expected service life. The main weaknesses of these  
142 models/equations are the ignorance of the influences of moisture content on long-term

143 chloride penetration. Interestingly most of the concrete structures built in recent decade are of  
144 low water/binder ratio and the internal moisture content is low. Supplementary cementitious  
145 materials, widely incorporated into concrete to meet sustainable development goals, may also  
146 reduce the moisture content in concrete [45]. The microclimate, i.e. profile of the degree of  
147 water saturation  $S_w$ , should be a key element involved in the ageing factor  $n$ . Disregarding the  
148 microclimate implies that the models/equations are, by definition, inadequate to describe the  
149 chloride diffusion, and can give rise to misinterpretations of observed transport phenomena.

150 Chatterji [46], from a series of experimental studies, reported an obvious drop of chloride  
151 diffusion coefficient after a comparatively short interval of rapid chloride penetration and  
152 explained as due to the unsaturated state of concrete, i.e. water content decreases with depth.  
153 Nilsson [47] observed a similar trend of a very slow chloride penetration after an initial rapid  
154 rate based on examinations of under-water concrete structures. Chrisp et al. [48] found a  
155 decrease of electrical conductivity with depth owing to a gradient of the moisture content in  
156 cover concrete. The need for caution and concern with respect to inaccurate prediction of  
157 long-term chloride diffusion is apparent. Correct understanding of the unsaturated state, and  
158 hence an appropriate description of the time-dependent unsaturated chloride diffusion, are  
159 essential for reliable service life prediction of marine concrete structures.

160 The time-dependency of chloride diffusion in marine concrete is influenced by many  
161 factors. The present work deals with the analysis of the role of the degree of water saturation,  
162 a key influencing factor, in long-term chloride diffusion. An analytical model previously  
163 reported in Ref. [3] will be extended to analyze the time-dependent chloride diffusion  
164 coefficient  $D(t)$  in unsaturated cementitious materials. Effects of the degree of water  
165 saturation on  $D(t)$  are discussed in depth. The results will be compared with those  
166 determined from the well-known DuraCrete model, in order to ensure the reliability and the  
167 efficiency of the proposed approach. A deep insight into the effect of unsaturated state on the  
168 time-dependent chloride diffusion will help to predict the service life towards a scientific  
169 manner, rather than merely based on long-term exposure data.

## 170 **2. Time-dependent unsaturated chloride diffusion**

171 Chloride diffusion in a cementitious system is mainly determined by the moisture content  
172 (degree of water saturation  $S_w$ ) and the microstructure (changing with the degree of hydration  
173  $\alpha$ ). With the addition of supplementary cementitious materials, the hydration process  
174 becomes complicated. Accurate determination of the  $\alpha$  of each raw material is far from easy.

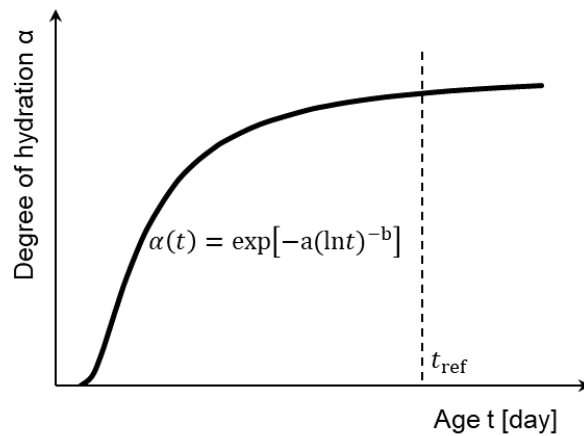
175 Nevertheless, the  $\alpha$  value in the entire cementitious system, by fitting against relative non-  
 176 evaporable water content, can generally be formulated with the expression proposed by  
 177 Jonasson [49]:

$$\alpha(t) = \exp[-a(\ln t)^{-b}] \quad (2)$$

178 where  $t$  is the age;  $a$  and  $b$  are fitting positive parameters.

179 An example of the hydration curve according to Eq. (2) is shown in Fig. 3. The curve  
 180 indicates that the degree of hydration  $\alpha(t)$  shows limited change after a reference age  $t_{\text{ref}}$ .  
 181 The change of the microstructure at later ages ( $t > t_{\text{ref}}$ ) is small. In the following the  
 182 evolution of the chloride diffusion will, therefore, not be described as a function of the degree  
 183 of hydration  $\alpha(t)$ , but described instead as a function of the degree of water saturation  $S_w$ .

184



185

186 Fig. 3 Changes of the degree of hydration with age in cementitious systems.

187

188 In previous work [3] a model of the chloride diffusion coefficient at various degrees of  
 189 water saturation  $S_w$  has been proposed. Here this model is extended considering the material  
 190 age  $t$ . The time-dependent unsaturated chloride diffusion coefficient can then be formulated  
 191 as:

$$D(t, S_w) = D_{\text{Sat}}(t) \cdot S_w \cdot \exp \left[ \frac{(1-S_w)^2}{2 \cdot [0.01 d_a(t) - 0.05]^2} \right] \quad (3)$$

192 where:

- 193 ▪  $S_w$  [-] is the degree of water saturation. The  $S_w$  value can change with self-desiccation  
 194 and/or moisture exchange with ambient environment.



- 195 ▪  $D(t, S_w)$  [ $m^2/s$ ] is the chloride diffusion coefficient in the unsaturated cementitious  
 196 material. The  $D(t, S_w)$  value changes with time  $t$  and degree of water saturation  $S_w$ .  
 197 ▪  $D_{Sat}(t)$  [ $m^2/s$ ] is the chloride diffusion coefficient of the cementitious material at  
 198 saturated state, which can be obtained from resistivity measurements, steady-state  
 199 diffusion or migration cell methods. The  $D_{Sat}$  value usually decreases with increasing  
 200 degree of hydration  $\alpha$  in the cementitious material.  
 201 ▪  $d_a(t)$  [ $nm$ ] is the average pore diameter, which can be obtained from mercury  
 202 porosimetry measurements. The  $d_a$  value usually decreases with increasing degree of  
 203 hydration  $\alpha$  in the cementitious material.

204 To understand the  $D(t, S_w)$ , experiments will be carried out to examine the values of  
 205  $D_{Sat}(t)$  and  $d_a(t)$ . Regarding the time-dependency of the degree of water saturation  $S_w(t)$ , a  
 206 simple discussion will be provided afterwards in the comparative study.

### 207 3. Experimental

#### 208 3.1 Materials and samples

209 Cement paste and mortar samples according to European Standard EN 196-1 were cast.  
 210 Details of the mixture proportions for the binders are listed in Table 1. CEM I 42.5 N (OPC)  
 211 was the essential part in all the binders under study. Supplementary cementitious materials  
 212 (SCMs) with typical replacement levels were studied, i.e. 30% for fly ash (FA), 70% for  
 213 ground granulated blast furnace slag (BFS) and 5% for limestone powder (LP). Three  
 214 different water/binder (w/b) ratios were considered, i.e. 0.4, 0.5 and 0.6. Paste and mortar  
 215 samples were cured in a humid room at  $20 \pm 0.1$  °C.

216  
 217 Table 1 Mixture proportions used for the binders.

Mixtures	Raw materials and replacement by weight				w/b
	OPC	FA	BFS	LP	
M4	100%	-	-	-	0.4
M5	100%	-	-	-	0.5
M6	100%	-	-	-	0.6
MF5	70%	30%	-	-	0.5
MB5	30%	-	70%	-	0.5
MFL5	65%	30%	-	5%	0.5

218

219 The paste samples at desired ages were crushed into small pieces (around 1 cm<sup>3</sup>). The  
220 small pieces were moved into liquid nitrogen to stop hydration and then placed in a freeze-  
221 drier with -24 °C and under vacuum at 0.1 Pa. After the mass loss was below 0.01% per day,  
222 the paste pieces were used for pore structure measurements. The mortar samples were made  
223 with the same amount of siliceous sand but varied with paste mixtures. Standard quartz sand  
224 0-2 mm (EN 196-1) with a density of 2.63 g/cm<sup>3</sup> was used as aggregate. The paste/sand ratio  
225 was fixed at 1:3 by weight. All mortar samples were moist-cured for desired ages before they  
226 were used for rapid chloride migration tests.

### 227 3.2 Pore structure characterization

228 Mercury intrusion porosimetry (MIP) was applied for characterizing the pore structure of  
229 various cementitious pastes. The paste specimens were at the ages of 28, 105, 182 and 370  
230 days. MIP measurements were performed with Micromeritics PoreSizer<sup>®</sup> 9320. Each  
231 measurement was conducted in two stages: a manual low pressure run from 0 to 0.15 MPa  
232 and an automated high pressure run from 0.15 to 210 MPa. The raw data produced from  
233 mercury intrusion were calculated by using the Washburn equation [50], with a contact angle  
234 of 139° and a surface tension of mercury of 0.48 N/m<sup>2</sup>. The minimum pore diameter hence  
235 measured by the apparatus was 7 nm. The dried paste specimens used for MIP were in the  
236 range of 4~8 g by mass with the expectation that the intrusion volume of mercury was about  
237 60~90% of the stem volume in complying with the regulations of the apparatus. Due to the  
238 ink-bottle effect, MIP measurements tend to underestimate the large pores and overestimate  
239 the small pores [51]. In this study, MIP was utilized with the main purpose to monitor the  
240 trend of the pore size changes with age due to hydration.

241 For the total pore volume  $V_t$  [m<sup>3</sup>/m<sup>3</sup>] and total surface area  $S_t$  [m<sup>2</sup>/m<sup>3</sup>] of the pores, the  
242 average pore diameter  $d_a$  is calculated as [3]:

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

### 243 3.3 Rapid chloride migration tests

244 Rapid chloride migration (RCM) tests were carried out on mortar specimens ( $\phi 100 \times 50$   
245 mm) according to the method described in NT Build 492 [34]. The set-up is shown in Fig. 4.  
246 The correspondence of this test method with the natural diffusion of chloride ions has been  
247 validated previously [52,53]. The mortar specimens were at the ages of 28, 105, 182 and 370

248 and 730 days. Vacuum-saturation was performed on the mortar specimens with saturated  
 249  $\text{Ca}(\text{OH})_2$  solution. During RCM tests the chloride ions were forced to migrate into the  
 250 specimens by an external electrical potential (30 V). Three specimens of each mixture were  
 251 tested simultaneously. After a limited test duration, e.g. 24 h, the specimens were axially split.  
 252 A 0.1 M  $\text{AgNO}_3$  solution was sprayed on the freshly split surface. When the white  $\text{AgCl}$ ,  
 253 precipitated on the surface, was clearly visible, the chloride penetration depth was measured  
 254 from the center to both edges at intervals of 10 mm.

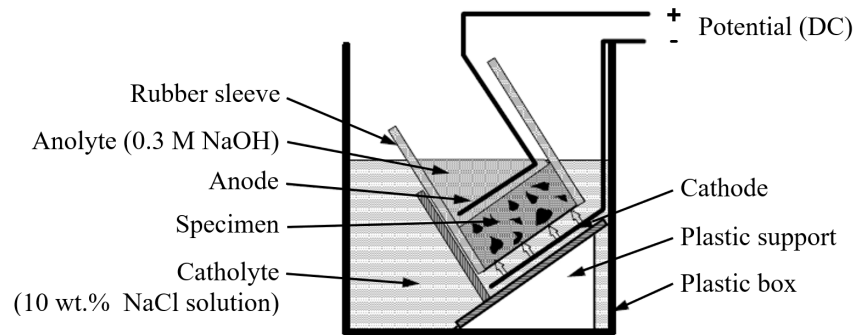
255 The non-steady-state migration coefficient of the saturated mortar specimens, noted as  
 256  $D_{\text{Sat}}$  [ $\times 10^{-12} \text{ m}^2/\text{s}$ ], is calculated with the following equation:

$$D_{\text{Sat}} = \frac{0.0239(237 + T)L}{(U - 2)t} \left( x_d - 0.0238 \sqrt{\frac{(237 + T)Lx_d}{U - 2}} \right) \quad (5)$$

257 where  $U$  [V] is the absolute value of the applied voltage;  $T$  [ $^{\circ}\text{C}$ ] is the average value of the  
 258 initial and final temperatures in the anolyte solution;  $L$  [mm] is the thickness of the specimen;  
 259  $x_d$  [mm] is the average value of the penetration depths;  $t$  [h] is the test duration.

260 The measured  $D_{\text{Sat}}$  -value is commonly used to indicate the capacity of saturated  
 261 cementitious materials to resist chloride penetration.

262



263

264 Fig. 4 Set-up for rapid chloride migration test (after NT Build 492 [34]).

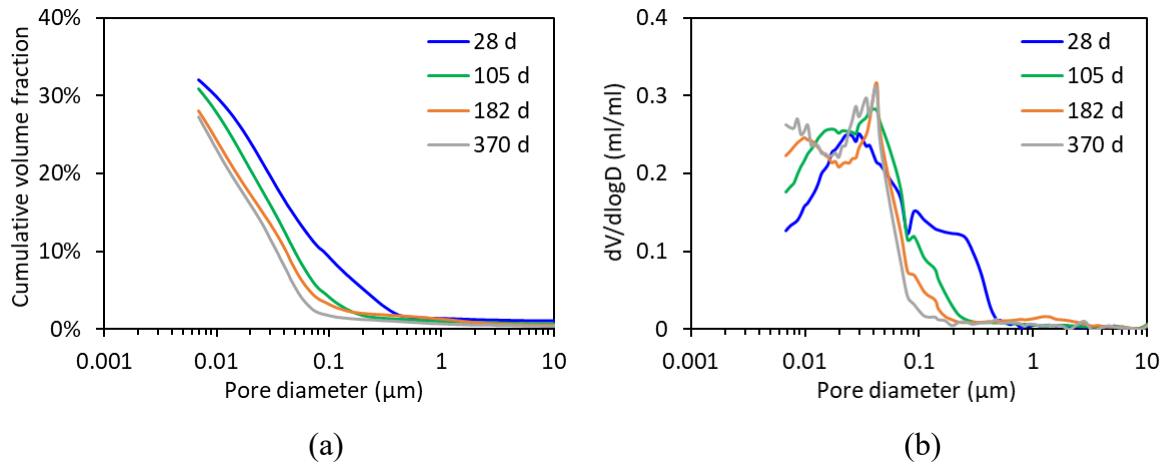
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## 266 4. Results and discussion

### 267 4.1 Evolution of pore structure

268 The pore size distributions of the six paste mixtures as shown in Table 1 were determined  
 269 by MIP measurements and using the Washburn equation. The results of the FA-blended  
 270 mixture MF5, as a representative, are presented in Figs. 5 (a) and (b). The total porosity is as

271 expected decreased with age. A slight decrease of the porosity is found from 182 to 370 days,  
 272 as shown in Fig. 5a. With a higher age from 28 to 370 days, the pores shift towards a finer  
 273 distribution. The amount of the large capillary pores ( $0.08 \sim 0.5 \mu\text{m}$ ) is considerably reduced  
 274 while the amount of the gel pores ( $< 0.01 \mu\text{m}$ ) is increased, as indicated in Fig. 5b. Between  
 275 182 and 370 days, the patterns of the pore size distribution are quite similar (Fig. 5b).  
 276



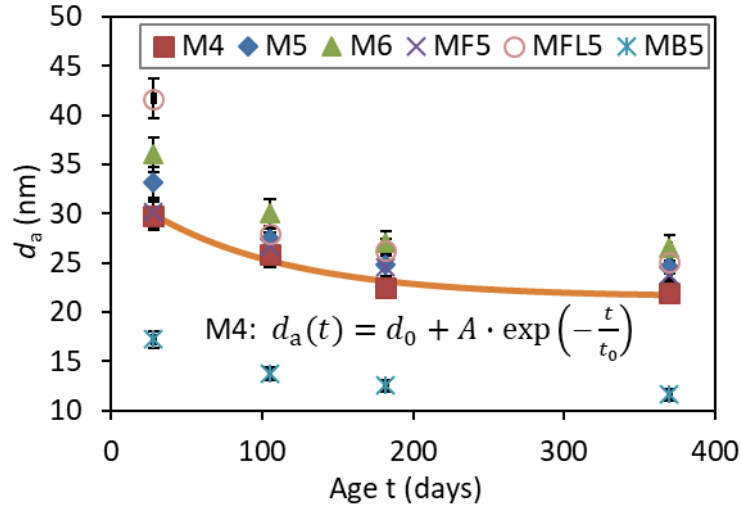
277  
 278 (a) (b)  
 279 Fig. 5 Evolution of (a) cumulative pore volume and (b) differential curve with age for FA-  
 280 blended pastes MF5 (w/b = 0.5).  
 281

282 The average pore diameter  $d_a$ , representing the pore size fineness and often-adopted to  
 283 simplify an arbitrary porous system as a transport tube [3], was determined according to the  
 284 pore size distribution results and using Eq. (4). Fig. 6 shows the evolution of the  $d_a$  value in  
 285 cementitious paste specimens with age. Each value was determined based on at least three  
 286 replicates and the standard deviation was within 5.1% for all binders. At 28 days the ternary  
 287 binder MFL5 has the largest  $d_a$  value while the binary binder MB5 has the smallest  $d_a$  value.  
 288 Compared with the reference OPC binder M5, the FA-blended binder MF5 has a lower  $d_a$  at  
 289 28 days, but shows a similar  $d_a$  after 105 days. The binder MFL5 exhibits a larger  $d_a$  at 28  
 290 days but a slightly smaller  $d_a$  after 105 days as compared to the binder M6. It appears that the  
 291 differences of the  $d_a$  between various binders are diminished with age from 28 to 370 days.  
 292 As can be deduced from Fig. 6, changes of the  $d_a$  are very small after one year. This holds  
 293 for all the binders under study. From regression analysis on experimental data, the evolution  
 294 of the average pore diameter  $d_a(t)$  can be described with an exponential decay function as  
 295 shown in Eq. (6).

$$d_a(t) = d_0 + A \cdot \exp\left(-\frac{t}{t_0}\right) \quad (t \geq 28 \text{ days}) \quad (6)$$

296 where  $d_0$ ,  $A$  and  $t_0$  are fitting parameters.

297



298

299 Fig. 6 Evolution of the average pore diameter  $d_a$  with age obtained from MIP tests. Mixtures:

300 M4 (OPC, w/b = 0.4), M5 (OPC, w/b = 0.5), M6 (OPC, w/b = 0.6), MF5 (FA 30%, w/b =

301 0.5), MB5 (BFS 70%, w/b = 0.5), MFL5 (FA 30% + LP 5%, w/b = 0.5).

302

#### 303 4.2 Evolution of chloride diffusion coefficient

304 The chloride diffusion coefficients of cementitious mortars at saturated state,  $D_{Sat}$ , were

305 derived from RCM tests. Fig. 7 shows the changes of the  $D_{Sat}$  with age from 28 days up to 2

306 years in saturated mortar specimens. Each  $D_{Sat}$  value was the average of three parallel

307 measurements, with a maximum standard deviation of 6.9% for all binders. The roles of w/b

308 ratio and SCMs are under study. In general, the  $D_{Sat}$ -value is decreasing in the first 105 days.

309 Particularly for the mortars containing 30% FA (MF5, MFL5), the  $D_{Sat}$  drops drastically

310 during this period and their values at 105 days are almost five times smaller than those at 28

311 days. The mortar containing 70% BFS (MB5) exhibits a high chloride resistance, with the

312  $D_{Sat}$ -value at 28 days approximately four times smaller than that of OPC mortar (M5).

313 For OPC mortars the  $D_{Sat}$ -values show a slight increasing trend after 182 days, while

314 decreasing slowly again from one year onward. The reason for the increase of the  $D_{Sat}$ -value

315 remains a pending issue. One possible explanation is the delayed ettringite formation (DEF)

316 [38]. It is worthwhile to note that all the mortar specimens were cured in a humid climate

317 (RH > 98%). Under such circumstances leaching of the alkali hydroxide from the mortar

318 specimens into the surrounding water can take place and, subsequently, reduces the alkali  
 319 hydroxide concentration of the mortar pore solutions. The DEF process can be triggered as a  
 320 consequence of such alkali leaching effect [54,55].

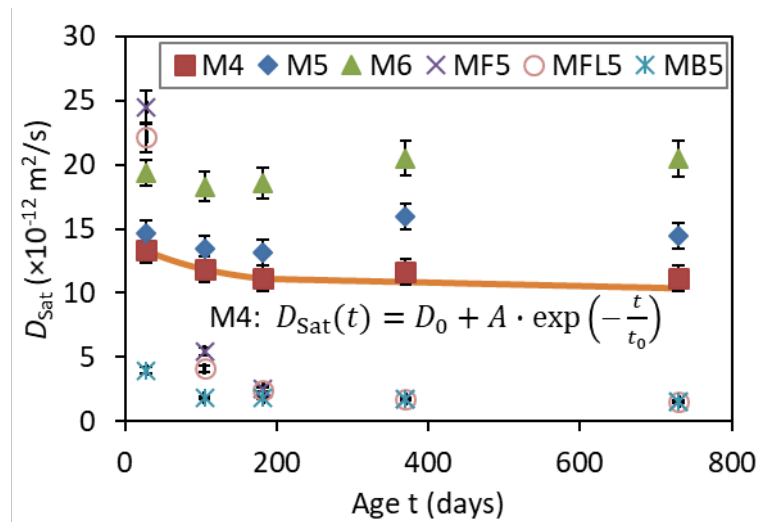
321 For all blended mortars the  $D_{Sat}$ -values decrease slowly after 182 days. After one year the  
 322 mortars blended with 30% FA (MF5) or with 70% BFS (MB5) have an almost equal  
 323 resistance to chloride penetration. By comparing the  $D_{Sat}$ -values in LP-filled ternary mortar  
 324 (MFL5) and LP-free binary mortar (MF5), it is found that the presence of 5% LP slightly  
 325 decreases the  $D_{Sat}$ -value in the period from 28 days to 2 years.

326 Based on regression analysis, and considering the basic evolution of microstructure  
 327 [38,44], an exponential decay function as shown in Eq. (7) can be used to describe the  
 328 experimental data of the time-dependent diffusion coefficient  $D_{Sat}(t)$ .

$$D_{Sat}(t) = D_0 + A \cdot \exp\left(-\frac{t}{t_0}\right) \quad (t \geq 28 \text{ days}) \quad (7)$$

329 where  $D_0$ ,  $A$  and  $t_0$  are fitting parameters.

330



331

332 Fig. 7 Evolution of the chloride diffusion coefficient  $D_{Sat}$  with age obtained from RCM tests.

333 M4 (OPC, w/b = 0.4), M5 (OPC, w/b = 0.5), M6 (OPC, w/b = 0.6), MF5 (FA 30%, w/b =  
 334 0.5), MB5 (BFS 70%, w/b = 0.5), MFL5 (FA 30% + LP 5%, w/b = 0.5).

335

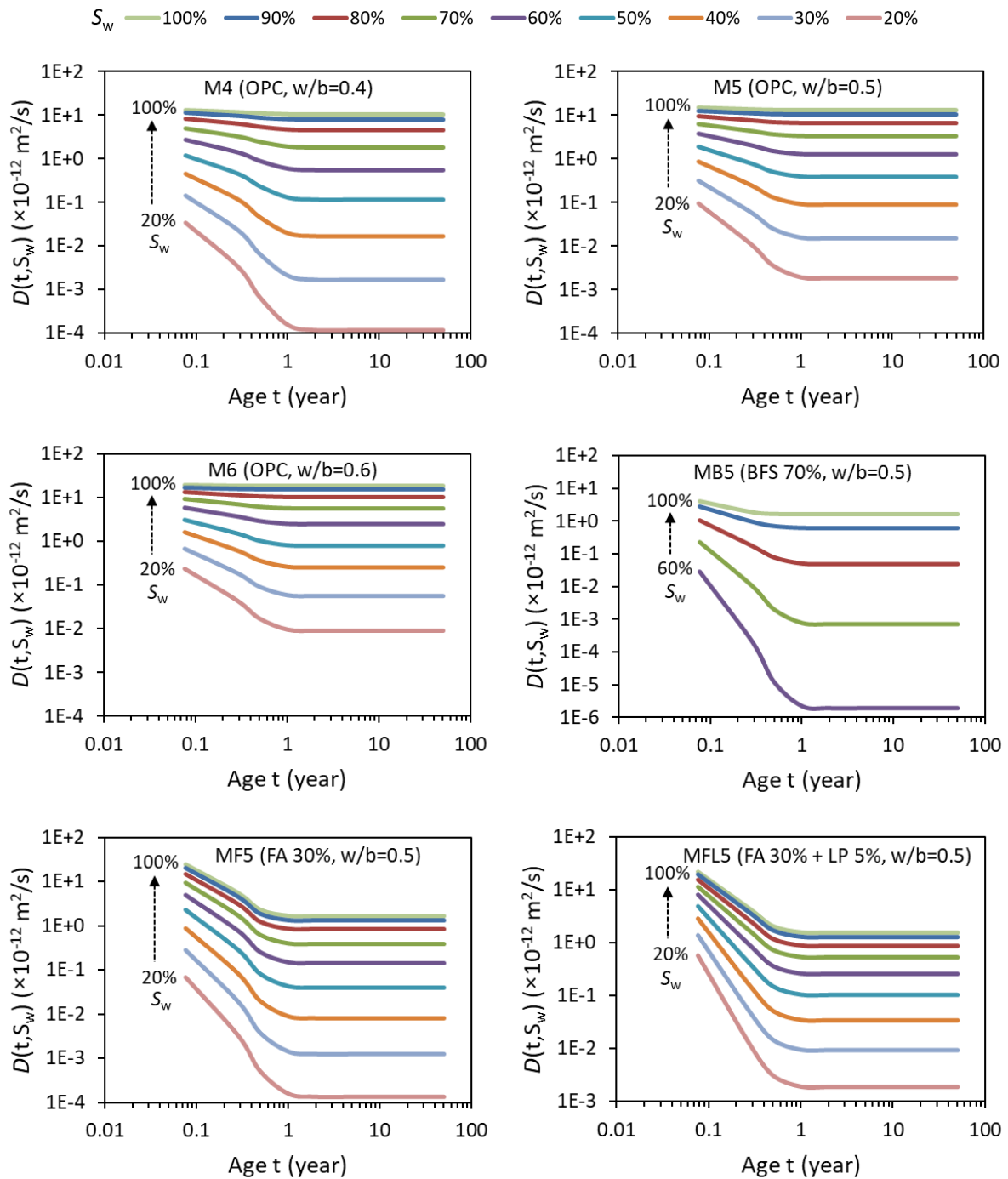
### 336 4.3 Evolution of unsaturated chloride diffusion coefficient

337 The evolution of the chloride diffusion coefficient  $D(t, S_w)$  with age (28 days  $\rightarrow$  50 years)  
 338 at various degrees of water saturation  $S_w$  was predicted by Eq. (3), with  $d_a(t)$  and  $D_{Sat}(t)$

339 according to Eqs. (6) and (7), respectively. Note that for a particular age the  $D(t, S_w)$  values  
 340 at various saturation levels  $S_w$  were obtained based on the same pore structure, i.e. same  
 341 average pore diameter  $d_a$  was adopted. The obtained  $D(t, S_w)$  values for different mortar  
 342 mixtures are given in Fig. 8.

343

344



345

346

347

348 Fig. 8 Evolution of the chloride diffusion coefficient  $D(t, S_w)$  with age (28 days  $\rightarrow$  50 years)  
 349 in the cementitious mortars at various degrees of water saturation  $S_w$ .

350

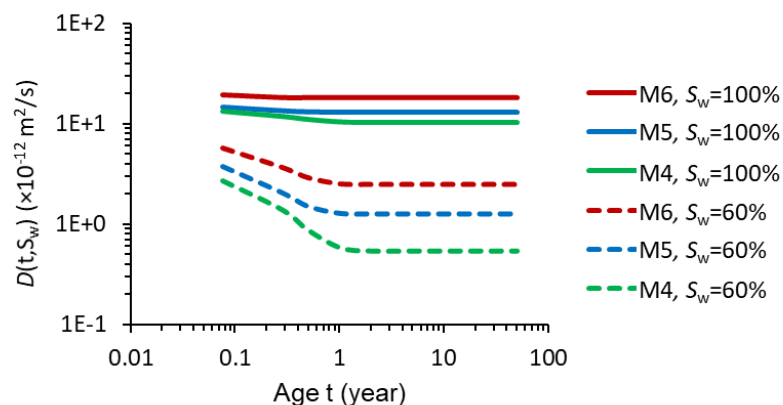
351 For all binders, similar characteristics can be observed in Fig. 8. The chloride diffusion  
 352 coefficient  $D$  generally decreases with age, especially in the first year. At saturated state ( $S_w$   
 353 = 100%) the diffusion coefficient  $D$  exhibits a relatively small decrease with age. The  
 354 decrease of the diffusion coefficient  $D$ , however, becomes increasingly pronounced with  
 355 decreasing saturation level  $S_w$ . It is well known that as hydration proceeds there is a  
 356 concomitant reduction in water content because the pore water is progressively combined as  
 357 components of solid hydrates. Hence at longer ages the saturation level  $S_w$  will play an  
 358 increasingly important role in the diffusion coefficient  $D$ .

#### 359 4.3.1 Effect of w/b ratio on $D(t, S_w)$

360 Fig. 9 presents the chloride diffusion coefficient  $D(t, S_w)$  in the OPC mortars with w/b  
 361 ratios of 0.4, 0.5 and 0.6. The data are taken from Fig. 8. At saturated state ( $S_w = 100\%$ ) the  
 362 diffusion coefficient  $D$  decreases slightly with age after 28 days, whereas at unsaturated state  
 363 ( $S_w = 60\%$ ) the diffusion coefficient  $D$  drops rapidly until the end of the first year. It is  
 364 revealed that the time-dependency of the  $D$ -value is influenced substantially by the saturation  
 365 level  $S_w$ . Such time-dependency is stronger for a lower  $S_w$ .

366 A higher w/b ratio results in a higher diffusion coefficient  $D$ , regardless of the degree of  
 367 water saturation  $S_w$ . The effect of the w/b ratio on the  $D$  value, however, is much more  
 368 significant in unsaturated mortars ( $S_w = 60\%$ ) than in saturated mortars ( $S_w = 100\%$ ). By  
 369 increasing the w/b ratio from 0.4 (M4) to 0.6 (M6), the diffusion coefficient  $D$  is  
 370 approximately 1.7 times higher for  $S_w = 100\%$ , compared to 4.3 times for  $S_w = 60\%$ .

371



372

373 Fig. 9 Chloride diffusion coefficient  $D(t, S_w)$  in the saturated ( $S_w = 100\%$ ) and unsaturated  
 374 ( $S_w = 60\%$ ) OPC mortars with w/b ratios of 0.4 (M4), 0.5 (M5) and 0.6 (M6).

375

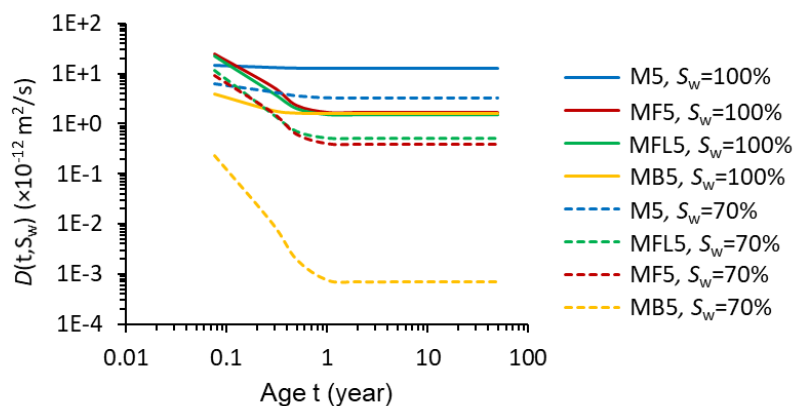


376 4.3.2 Effect of SCMs on  $D(t, S_w)$

377 Fig. 10 shows the effect of SCMs on the chloride diffusion coefficient  $D(t, S_w)$  for  
 378 saturated ( $S_w = 100\%$ ) and unsaturated ( $S_w = 70\%$ ) mortar specimens. The data come from  
 379 Fig. 8. Regardless of the binders, a longer term and sharper decrease of the diffusion  
 380 coefficient  $D$  with age is found for  $S_w = 70\%$  than for  $S_w = 100\%$ , a similar finding as  
 381 already drawn from Fig. 9.

382 For a given water content, either saturated or unsaturated, the blended mortars (MF5,  
 383 MB5 and MFL5) exhibit lower diffusion coefficient  $D$  than the OPC mortar (M5) after 1 year.  
 384 At saturated state ( $S_w = 100\%$ ) the addition of 30% FA (MF5) or 70% BFS (MB5) results in  
 385 almost the same diffusion coefficient  $D$  at an age of 1 year. At unsaturated state ( $S_w = 70\%$ ),  
 386 however, the diffusion coefficients  $D$  between MF5 and MB5 differ significantly. Compared  
 387 to binary mortar MF5, the ternary mortar MFL5 shows slightly lower diffusion coefficient  $D$   
 388 at  $S_w = 100\%$  (regardless of the age) but obviously higher diffusion coefficient  $D$  at  $S_w = 70\%$   
 389 (after 1 year). These observations make it reasonable to consider that in the process of  
 390 durability design the selection of cementitious materials based on  $D$ -values at saturated state  
 391 can be very different from that based on  $D$ -values at non-saturated state. Since onsite  
 392 cementitious materials are often unsaturated, it is highly advised to examine the unsaturated  
 393 chloride diffusion coefficient when comparing the durability of structures made with different  
 394 cementitious materials.

395

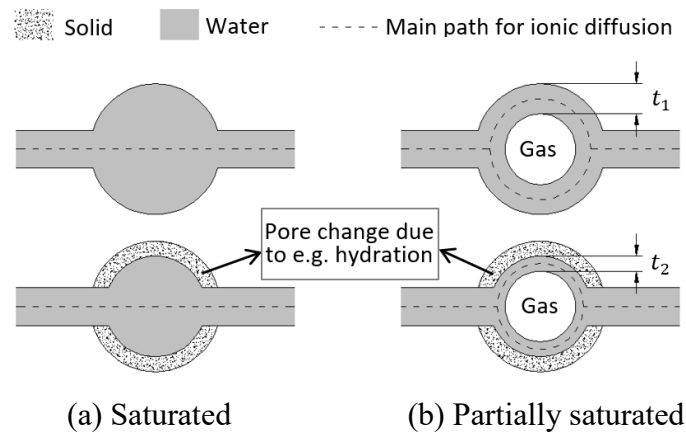


396

397 Fig. 10 Chloride diffusion coefficient  $D(t, S_w)$  in saturated ( $S_w = 100\%$ ) and unsaturated ( $S_w$   
 398  $= 70\%$ ) blended mortars. M5 (OPC, w/b = 0.5), MF5 (FA 30%, w/b = 0.5), MB5 (BFS 70%,  
 399 w/b = 0.5), MFL5 (FA 30% + LP 5%, w/b = 0.5).

400

401 Both Figs. 9 and 10 reveal that for a particular pore structure change, due to either  
 402 hydration or varying w/b ratio or addition of SCMs, changes of the diffusion coefficient  
 403  $D(t, S_w)$  are more pronounced at unsaturated state ( $S_w < 100\%$ ) than at saturated state ( $S_w =$   
 404  $100\%$ ). This is acceptable in view of the main path for ionic diffusion in pore systems. When  
 405 a slight change of pore structure (due to e.g. hydration) occurs in the saturated pore system  
 406 (Fig. 11a), the main path for ionic diffusion changes slightly, resulting in a slight change of  
 407 the diffusion coefficient  $D$ . However, when a slight change of pore structure occurs in the  
 408 partially saturated pore system (Fig. 11b), the rate of ionic diffusion can be impaired  
 409 significantly because of the decreased thickness (from  $t_1$  to  $t_2$ ) of the layers of capillary  
 410 water adsorbed on the partially water-filled pores (or channels). Note that the large pore, as  
 411 depicted in Fig. 11, can be a large channel in 3D microstructure.  
 412



413  
 414 (a) Saturated (b) Partially saturated  
 415 Fig. 11 Schematic illustrations on the effect of a minor pore structure change on ionic  
 416 diffusion in (a) saturated and (b) partially saturated pore systems.  
 417

418 The observation that the dependence of chloride diffusion on pore structure is more  
 419 pronounced in non-saturated pore system than in saturated pore system can be supported as  
 420 well by a recent experimental study [56]. There, it has been found that for cementitious  
 421 systems hydrated beyond 28 days the w/b ratio and SCMs influence the pore connectivity  
 422 mainly by altering the connectivity of small capillary pores while the connectivity of large  
 423 capillary pores is not influenced much. Under saturated state, the large capillary pores can  
 424 have a great contribution to ionic transport. With decrease of saturation level  $S_w$ , the role of  
 425 the small capillary pores in ionic transport becomes increasingly prominent and, subsequently,  
 426 the pore structures made with different w/b ratios or SCMs can exhibit even larger  
 427 differences in the diffusion coefficient  $D$ .

428 Therefore, it is reasonable to conclude that the non-saturated state tends to promote a  
 429 longer term and sharper decrease of the diffusion coefficient  $D$  than the saturated state.

## 430 5. Comparative study

431 A comparison on evolutions of the unsaturated chloride diffusion coefficient with age is  
 432 made between the present approach (Eq. (3)) and the DuraCrete approach [33]. The  
 433 comparative study highlights the significance of the degree of water saturation in the service  
 434 life prediction of concrete structures in chloride-laden environments. In the following the  
 435 impact of moisture transport on ionic diffusion phenomenon is not considered in the  
 436 calculations of *long-term* chloride penetration [31,41,42].

### 437 5.1 Specimens and exposure condition

438 For the sake of simplification, the study concerns two cementitious mortars exposed to  
 439 atmospheric marine condition. Table 2 shows the mixtures and properties of the two mortars.  
 440 The relative humidity RH of the atmospheric marine condition changes in the range of 65~90%  
 441 within each year, with an average annual RH of 77.5% [11].

442  
 443 Table 2 Details of two mortar mixtures;  $D_{\text{Sat},28\text{days}}$  is the chloride diffusion coefficient  
 444 obtained from RCM tests of 28-day-old saturated mortar specimens.

Mortars	Binders	w/b	$D_{\text{Sat},28\text{days}} (\times 10^{-12} \text{ m}^2/\text{s})$
M5	OPC	0.5	14.71
MB5	OPC 30% + BFS 70%		3.97

445

### 446 5.2 $D(t)$ by DuraCrete approach

447 In DuraCrete [33] the service life of marine concrete structures relies on Eq. (8), which  
 448 describes the changes of chloride diffusion coefficient  $D(t)$  with age  $t$ .

$$D(t) = D_0 \cdot k_c \cdot k_e \cdot \left(\frac{t_0}{t}\right)^n \quad (8)$$

449 where  $D_0$  [ $\text{m}^2/\text{s}$ ] is the chloride diffusion coefficient at a reference age  $t_0$ ;  $k_c$  is the curing  
 450 factor ( $k_c = 0.79$  when  $t_0 = 28$  days);  $n$  is the ageing factor;  $k_e$  is the environment factor,  
 451 which depends on environment class  $k_{e,0}$  and type of cement  $k_{e,c}$ :

$$k_e = k_{e,0} \cdot k_{e,c} \quad (9)$$

452 The values of the ageing factor  $n$  and the sub-factors ( $k_{e,0}$  and  $k_{e,c}$ ) are presented in Table  
 453 3. DuraCrete follows a probabilistic method as well as partial factors to calculate the  
 454 probabilities of failure. The details are out of the scope and will not be presented.

455

456 Table 3 Characteristic values of the ageing factor  $n$  and the environment factor ( $k_{e,0}$  and  $k_{e,c}$ )  
 457 [33].

	Condition	Characteristic values
Ageing factor $n$	OPC, Submerged	0.30
	OPC, Tidal and splash	0.37
	OPC, Atmospheric	0.65
	BFS, Submerged	0.71
	BFS, Tidal and splash	0.60
	BFS, Atmospheric	0.85
$k_{e,0}$ for environment class	Submerged	1.32
	Tidal zone	0.92
	Splash zone	0.27
	Atmospheric	0.68
$k_{e,c}$ for type of cement	OPC	1.0
	BFS	2.9

458

### 459 5.3 $D(t, S_w)$ by present approach

460 In the present approach the evolution of the unsaturated chloride diffusion coefficient  
 461  $D(t, S_w)$  with age is determined by Eq. (3), with the values of  $d_a(t)$  and  $D_{\text{Sat}}(t)$  according to  
 462 Eqs. (6) and (7), respectively. The degree of water saturation  $S_w$  is supposed to change with  
 463 time  $t$  when the mortars are exposed to atmospheric marine condition. Assuming a service  
 464 life of 50 years, Eqs. 10 (a) (b) (c) are introduced to describe the time-related saturation level  
 465  $S_w(t)$ :

466 1) In the first 28 days the mortar specimens are saturated ( $S_w = 100\%$ ) (Eq. (10a)).

467 2) In the service period (28 days  $\rightarrow$  50 years), the saturation level  $S_w$  of the mortar  
 468 specimens decreases with time (Eq. (10b)). Eq. (10b) is given following the power  
 469 expression of Eq. (1).

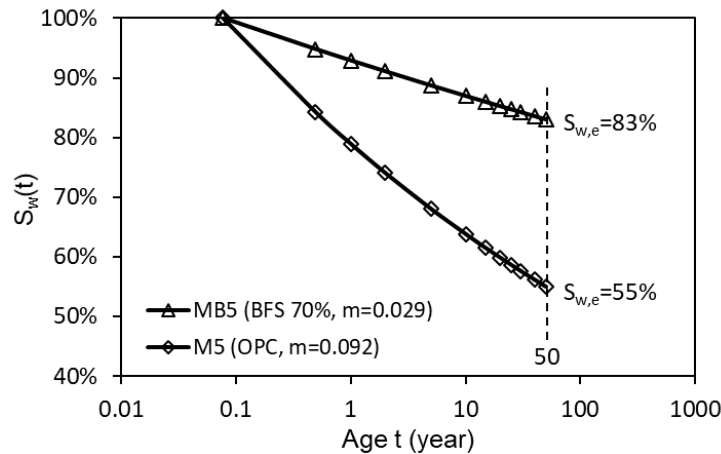
470 3) At the age of 50 years, each mortar specimen reaches its equilibrium saturation level,  
 471  $S_{w,e}$ , which corresponds to the equilibrium humidity level approximately the same as  
 472 the average annual RH of the atmospheric air, i.e. 77.5% RH. At this RH level the  $S_{w,e}$   
 473 can be estimated from the water vapor desorption isotherm (WVDI) of each mortar.  
 474 The WVDI results can be referred to a previous study reported in Ref. [57], where the  
 475  $S_{w,e}$  values are 55% and 83% for mortars M5 and MB5, respectively.

$$S_w(t) = 100\% \quad 0 \leq t \leq 0.0767 \text{ year (28 days)} \quad (10a)$$

$$S_w(t) = S_{w,t=0.0767} \cdot \left(\frac{0.0767}{t}\right)^m \quad 0.0767 < t < 50 \text{ years} \quad (10b)$$

$$S_w(t) = S_{w,e} \quad t = 50 \text{ years} \quad (10c)$$

476 where  $m$  is a constant. By combining Eq. (10c) with Eq. (10b), the  $m$ -values are determined  
 477 as 0.092 and 0.029 for mortars M5 and MB5, respectively. Fig. 12 shows the time-related  
 478 saturation level  $S_w(t)$  obtained with Eqs. 10 (a) (b) (c) for OPC and BFS-blended mortars.  
 479



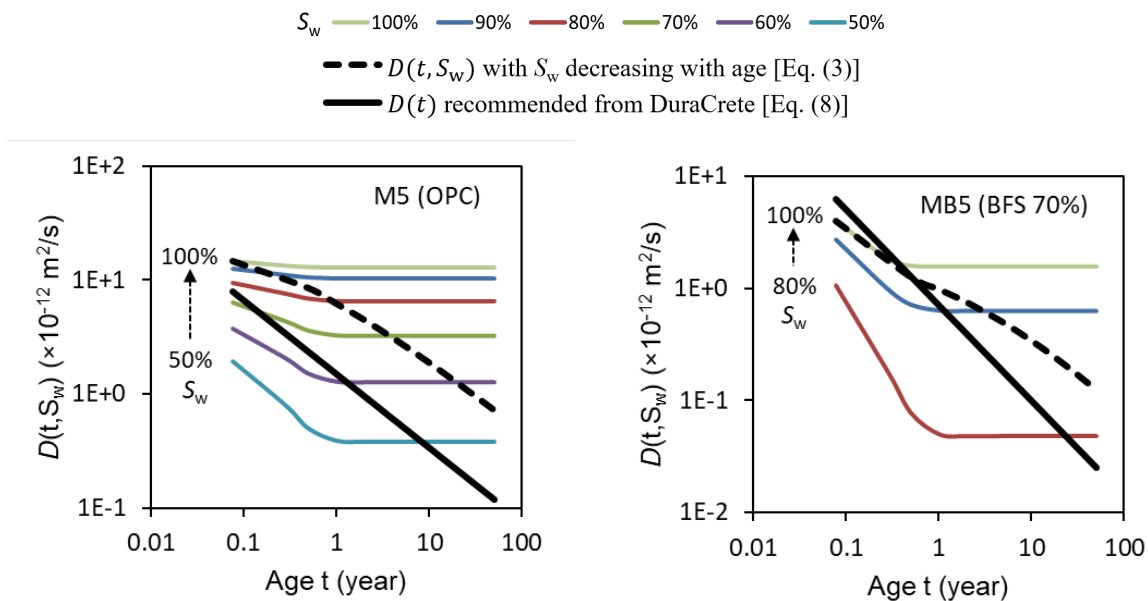
480  
 481 Fig. 12 Time-related degree of water saturation  $S_w(t)$  for atmospheric OPC and BFS-blended  
 482 mortars following Eqs. 10 (a) (b) (c).  
 483

484 Figs. 13 (a) and (b) present the chloride diffusion coefficient  $D(t, S_w)$  at different  
 485 saturation levels  $S_w$  for OPC mortar M5 and BFS-blended mortar MB5, respectively. The  
 486 data come from Fig. 8. In the cases when the saturation level  $S_w$  decreases with time by  
 487 following Eqs. 10 (a) (b) (c), the evolution of  $D(t, S_w)$  is replotted in Figs. 13 (a) and (b) with

488 the dotted black lines. It is shown that the  $D(t, S_w)$  value, with the  $S_w$  decreasing with age  
 489 (corresponding to lower  $S_w$  with depth as indicated in Fig. 2), drops much more significantly  
 490 with age compared to that obtained based on saturated mortars ( $S_w = 100\%$ ).

491 For a comparative study the time-dependent chloride diffusion coefficient  $D(t)$   
 492 recommended in DuraCrete (Eq. (8)) is also presented in Figs. 13 (a) and (b) with the solid  
 493 black lines. At any particular age the  $D(t)$  value from Eq. (8) is in the same order of  
 494 magnitude as that determined from Eq. (3). This holds for both OPC and BFS-blended  
 495 binders. The significant influence of the degree of water saturation on chloride diffusion,  
 496 hidden behind but not explicitly addressed in DuraCrete, can therefore be clearly  
 497 demonstrated by Eq. (3) proposed in the present work.

498  
 499  
 500



501  
 502 Fig. 13 Evolution of unsaturated chloride diffusion coefficient  $D(t, S_w)$  in neat OPC mortar  
 503 (M5) and BFS-blended mortar (MB5).  
 504

505 Debates have been reported with respect to the ageing factor  $n$ . One of the most popular  
 506 mentioned is that the ageing factor  $n$ , as recommended in the DuraCrete, can result in the  
 507 chloride diffusion coefficient  $D$  to become extremely small at long ages and, accordingly,  
 508 tend to produce a much longer predicted service life than those actually achievable [58].  
 509 Based on the comparative study as indicated in Fig. 13, the very small  $D$ -value at long ages  
 510 may be achieved in the sense that the internal part of the onsite concrete is partially saturated.  
 511 A number of field studies have proved very small diffusion coefficient,  $D = 0.9 \times 10^{-12} \text{ m}^2/\text{s}$  for  
 512 cement concrete after 24-year service in Gothenburg harbor [59]. Much larger values of the

513 ageing factor  $n$  have been reported based on field studies, e.g. ageing factor up to 0.7 based  
514 on chloride profiles for coastal bridges in service up to 37 years [60], than those reported  
515 based on RCM tests of laboratory saturated concretes, e.g. ageing factors up to 0.24 [38].

## 516 **6. Applications and limitations of the proposed approach**

517 The formula of time-dependent unsaturated chloride diffusion coefficient developed in  
518 this work, viz. Eq. (3), provides a tool for durability assessment of reinforced concrete  
519 structures, even for those of old structures with unknown mixtures. After a reference age  $t_{\text{ref}}$ ,  
520 the degree of hydration  $\alpha(t)$  changes limited (Fig. 3). The values of  $D_{\text{Sat}}(t)$  and  $d_a(t)$ , as  
521 indicated in Eq. (3), will change limited accordingly. The long-term chloride diffusion  
522 coefficient will, therefore, primarily rely on the time-dependent degree of water saturation  
523  $S_w(t)$ .

524 Field investigations have revealed that the influential depth of water permeation, caused  
525 by water storage or wetting-drying cycles, is limited to the outermost few centimeters of the  
526 cover concrete and the internal concrete still relies on self-desiccation. Chloride ingress in  
527 the surface concrete is fast while that in the internal concrete (which has a low water content)  
528 is quite slow. The chloride penetration period required to initiate reinforcement corrosion  
529 highly depends on the slow chloride diffusion in the internal unsaturated concrete. Such slow  
530 chloride diffusion can be evaluated by Eq. (3), where the values of  $S_w$  and  $d_a$ , both changing  
531 with age due to self-desiccation, can be estimated from laboratory measurements.

532 There is a need for long-term inspections and field measurements to capture the moisture  
533 profile and its evolution with age in cover concrete under marine environment, in order to  
534 accurately predict the chloride transport in the surface part of the concrete, i.e. Zone I as  
535 illustrated in Fig. 2. Moreover, existing works such as those presented here need to be  
536 continued accounting for the impact of water permeation on chloride diffusion. Accumulation  
537 of the chloride ions in surface concrete, owing to e.g. wetting-drying cycles, can take place  
538 and its effect on unsaturated chloride diffusion is well worth studying.

## 539 **7. Conclusions**

540 A formula for predicting the evolution of chloride diffusion coefficient in unsaturated  
541 cementitious materials is proposed. The significant influence of the degree of water saturation  
542  $S_w$  on long-term chloride diffusion, hidden behind but not explicitly addressed in DuraCrete,  
543 has been substantiated. One of the lessons to be gained from this study is that the  $S_w$  should

544 be taken into account when engineers make a final specification for concrete mixes. The  
545 effect of the  $S_w$  on chloride diffusion is of greater importance than perhaps is commonly  
546 considered. The non-saturated state enables to promote a longer term and sharper decrease of  
547 chloride diffusion, compared with saturated state. The ageing factor  $n$  is significantly  
548 influenced by the  $S_w$ .

549 The effects of factors, such as w/b ratio and SCMs, on chloride diffusion coefficient  
550 become increasingly pronounced with decreasing  $S_w$ . At saturated state the mortars including  
551 70% slag or 30% fly ash, cured after 1 year, have almost equal resistance to chloride  
552 diffusion. At non-saturated state, however, the mortar with 70% slag shows obviously smaller  
553 chloride diffusion than the mortar with 30% fly ash. Compared to the binary mortar (70%  
554 OPC + 30% fly ash), the ternary mortar (65% OPC + 30% fly ash + 5 % limestone powder)  
555 shows slightly smaller chloride diffusion at saturated state but obviously larger chloride  
556 diffusion at non-saturated state (e.g.  $S_w = 70\%$ ).

557 The results call into question the use of the chloride diffusion coefficient of saturated  
558 concretes, obtained from current standard diffusion/migration tests, when onsite concretes are  
559 actually partially saturated. A continuation of this work will consider the effect of water  
560 permeation on chloride transport. Within the scope of this work, an accurate service life  
561 prediction is not expected. The present work has the intension to emphasize the significance  
562 of the degree of water saturation in determinations of the ageing factor  $n$  and long-term  
563 transport properties in marine concrete.

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