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6 **An analytical solution for chloride diffusion in concrete with**
7 **considering binding effect**

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14 **ABSTRACT**

15 This paper presents a novel analytical solution for the chloride diffusion problem in
16 concrete when chloride binding is taken into account. The analytical solution is
17 obtained by splitting bound chlorides into chemically-bound and physically-bound
18 chlorides. The former is treated as moving particles that are trapped in randomly
19 distributed immobile holes. The latter is modelled using a linear binding isotherm.
20 Under this assumption the original problem of diffusion with binding can be
21 transformed to the problem of diffusion with a moving boundary for which an analytical
22 solution can be developed. The present solution is validated using existing experimental
23 data.

24

25 **Keywords:** Chloride diffusion; binding; concrete; moving boundary; analytical
26 solution.

27

28 **1. Introduction**

29 Chloride-induced reinforcing steel corrosion is a major problem for the reinforced
30 concrete structures that are exposed to marine environment. In order to protect the
31 reinforcing steel from corrosion one has to understand how chlorides penetrate in
32 concrete and how the individual components used in concrete mixture affect the
33 chloride penetration. In early studies chloride ingress in concrete was approximated as
34 a diffusion process [1,2,3,4,5,6], in which only parameters used to describe the chloride
35 penetration in concrete are the surface concentration and diffusion coefficient of
36 chlorides. However, concrete is a porous material the transport of chlorides in porous
37 materials is significantly different from that in ideal solutions. Besides, chloride
38 penetration in concrete involves not only the diffusion of chloride ions in pore solution
39 of the concrete but also the physical and chemical interactions between chloride ions
40 and pore surfaces within the cement matrix [7,8,9,10]. To accurately describe the
41 chloride ingress in concrete, attempts were made to modify the diffusion model by
42 including chloride binding [11,12,13,14,15,16,17,18,19], in which the total chlorides
43 were divided into two parts; namely the free and bound chlorides. It was assumed that
44 the transport of the free chlorides in concrete could follow the Fick's second law;
45 whereas the bound chlorides in concrete were absorbed physically and/or chemically
46 by the cement matrix of concrete. Experimental studies on chloride binding in different

47 types of concrete have shown that the use of supplementary cementitious materials in
48 concrete can have significant influence on chloride binding and thus also on the
49 transport of chlorides in the concrete [20,21].

50

51 The incorporation of chloride binding into chloride transport model can more
52 accurately predict the chloride ingress as well as quantify the influence of binder
53 materials on chloride penetration in concrete. However, it also complicates the problem.
54 For the classical diffusion problem one can find an analytical solution using error
55 function. When the chloride binding is involved in the diffusion equation, however, the
56 related parabolic partial differential equation involves a concentration-dependent
57 coefficient, which makes it difficult to obtain an analytical solution. Currently, only
58 numerical solutions are available for the diffusion problems when chloride binding is
59 also considered [14,15,16,17,18,19]. In this paper, we have managed to develop an
60 analytical solution for chloride transport in concrete when its binding is also considered.
61 This is achieved by splitting the bound chlorides into chemically-bound and physically-
62 bound chlorides. The former is treated as moving particles that are trapped in randomly
63 distributed immobile holes. The latter is modelled using a linear binding isotherm. The
64 analytical solution developed is validated using existing experimental results.

65

66 **2. Chloride diffusion with considering chloride binding**

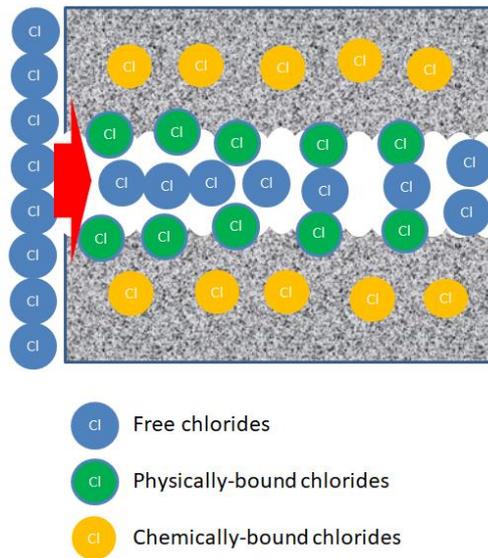
67 Consider the transport of chlorides in concrete. The mass change of the total
68 chlorides in a unit volume of concrete in a time interval dt can be expressed as follows,

69
$$\frac{\partial C_T}{\partial t} = -\nabla \cdot J \quad (1)$$

70 where C_T is the content of total chlorides in concrete, t is the time, and J is the flux of
 71 chlorides. In order to consider chloride binding, the total chlorides are divided into free
 72 and bound chlorides [22,23,24]; whereas the bound chlorides are further split into
 73 chemically-bound and physically-bound chlorides [15,25], as follows,

74
$$C_T = C_f + S_c + S_p \quad (2)$$

75 where C_f is the content of free chlorides, S_c is the content of chemically-bound
 76 chlorides, and S_p is the content of physically-bound chlorides (see Fig.1).



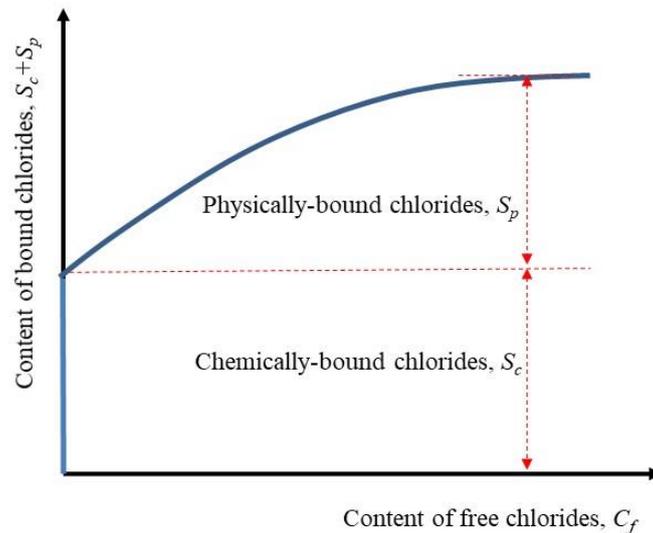
77
 78 **Fig.1.** A schematic description of chloride transport in concrete.

79 The chemical binding of chlorides herein is assumed to be irreversible and the
 80 corresponding binding process can be treated as the diffusion problem of particles
 81 which are trapped in randomly distributed immobile holes. The physical binding of
 82 chlorides is assumed to be reversible and the physically-bound chlorides can be treated

83 as immobile “free chlorides”, which can be modelled using a chloride binding isotherm
 84 (see Fig.2). The flux of chlorides in Eq.(1) is contributed only by the free chlorides and
 85 can be expressed in terms of the contents of free and physically-bound chlorides as
 86 follows [25],

$$87 \quad J = -\frac{D_e}{\varepsilon} \frac{C_f}{C_f + S_p} \nabla(C_f + S_p) \quad (3)$$

88 where D_e is the effective diffusion coefficient of chloride ions and ε is the porosity of
 89 concrete.



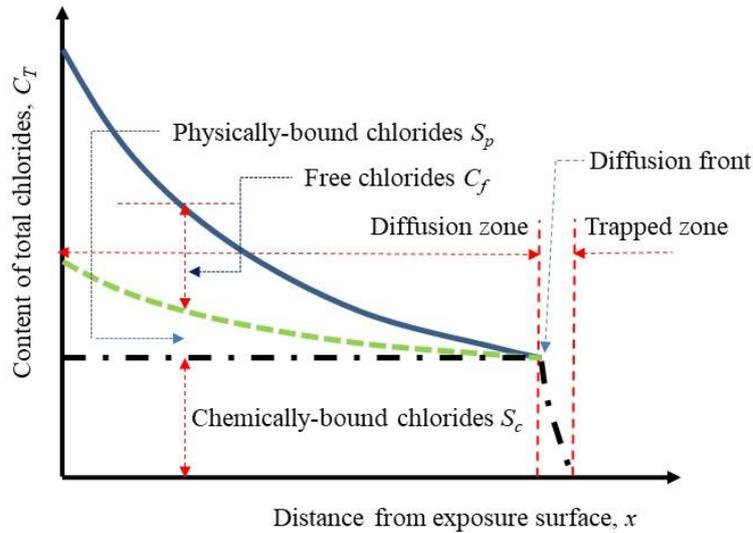
90

91 **Fig.2.** Illustration of chemically-bound (S_c) and physically-bound (S_p) chlorides.

92

93 When the chlorides diffuse into concrete, they will first react with the cement
 94 matrix of concrete to form chemically-bound chlorides. As soon as the chemically-
 95 bound chlorides are saturated at a place, the free chloride ions move forward. During
 96 the forward movement of free chlorides, part of them is absorbed on the pore surface
 97 to form physically-bound chlorides. Hence, the transport of chlorides in the concrete

98 with uniformly distributed porosity can be defined separately in two different zones.
 99 One is the diffusion zone in which the chemically-bound chlorides are already
 100 saturated. There is no chemical binding taking place in that zone. The other is the
 101 trapped zone in which the chemically-bound chlorides are not saturated. Any free
 102 chlorides diffusing into that zone will be trapped by chemical binding. The boundary
 103 between the two zones is defined by the diffusion front of free chlorides or the
 104 saturation front of chemically-bound chlorides. Fig.3 schematically describes the
 105 variations of the free, physically-bound, and chemically-bound chlorides in the two
 106 zones. Substituting Eqs.(2) and (3) into (1) and noting S_c is constant in the diffusion
 107 zone, it yields,



108

109 **Fig.3.** Schematic distribution profiles of chlorides in concrete.

110

111
$$\frac{\partial(C_f+S_p)}{\partial t} = \nabla \left[\frac{D_e}{\varepsilon} \frac{C_f}{C_f+S_p} \nabla(C_f + S_p) \right] \quad 0 < x < \xi(t) \quad (4)$$

112 The initial and boundary conditions of free chlorides $C_f(t,x)$ can be expressed as
113 follows,

$$114 \quad C_f(0, x) = 0 \quad (5)$$

$$115 \quad C_f(t, 0) = C_s \text{ and } C_f(t, \xi) = 0 \quad (6)$$

116 where ξ is the time-dependent coordinate representing the depth of the diffusion front,
117 which moves forward when time increases and C_s is the content of free chlorides on the
118 concrete exposure surface. For a given binding isotherm the content of physically-
119 bound chlorides can be expressed in terms of the content of free chlorides. Thus,
120 Eqs.(4)-(6) represent the diffusion problem with a moving boundary. It is obvious that
121 the solution of Eqs.(4)-(6) also depends on the binding isotherm function of $S_p = f(C_f)$.
122 For a linear binding isotherm of $S_p = \alpha C_f$ where α is a constant Eq.(4) becomes a linear
123 parabolic partial differential equation and can be simplified as follows,

$$124 \quad \frac{\partial C_f}{\partial t} = \nabla \left(\frac{D_e}{\varepsilon(1+\alpha)} \nabla C_f \right) \quad 0 < x < \xi(t) \quad (7)$$

125 For the diffusion problem governed by Eq.(7), the depth of the diffusion front is
126 proportional to square root of the diffusing time [26]. Thus, the following expression
127 can be assumed for $\xi(t)$,

$$128 \quad \xi(t) = k_\xi \sqrt{Dt} \quad (8)$$

129 where $D = D_e / [\varepsilon(1+\alpha)]$ and k_ξ is a constant to be determined. The solution of Eq.(7) with
130 the initial and boundary conditions defined by Eqs.(5) and (6) can be expressed as
131 follows [26],

132
$$C_f(t, x) = C_s \left(1 - \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}{\operatorname{erf}\left(\frac{k_\xi}{2}\right)} \right) \quad 0 \leq x \leq \xi(t) \quad (9)$$

133 where $\operatorname{erf}(\cdot)$ is the error function. It is obvious from Eq.(9) that if k_ξ is known then the
 134 solution (9) for $C_f(t, x)$ is completely defined. In order to determine k_ξ an additional mass
 135 conservation equation needs to be developed at the point of the diffusion front, which
 136 can be expressed as follows,

137
$$-\frac{D_e}{\varepsilon} \frac{\partial C_f}{\partial x} = S_c \frac{d\xi}{dt} \quad \text{at } x = \xi(t) \quad (10)$$

138 Physically, the left-hand-side of Eq.(10) represents the diffusion flux from the
 139 diffusion zone into the trapped zone; whereas the right-hand-side of Eq.(10) represents
 140 the flux required in order that the diffusion front can advance by a distance of $d\xi$ in the
 141 time interval of dt . Substituting Eqs.(8) and (9) into (10), it yields,

142
$$\frac{k_\xi}{2} \operatorname{erf}\left(\frac{k_\xi}{2}\right) \exp\left(\frac{k_\xi^2}{4}\right) = \frac{(1+\alpha)C_s}{\sqrt{\pi}S_c} \quad (11)$$

143 Eq.(11) is a nonlinear algebraic equation about k_ξ , which can be used to determine k_ξ
 144 for a given ratio of $(1+\alpha)C_s/S_c$. After k_ξ is determined it can be substituted into Eq.(8)
 145 for calculating the depth of diffusion front $\xi(t)$ and Eq.(9) for calculating the
 146 concentration profile $C_f(t, x)$ of free chlorides directly. The content of the total chlorides
 147 can be calculated using Eq.(2).

148 Note that, in the trapped zone there are no free chlorides and the content of
 149 chemically-bound chlorides could be any value between 0 and S_c , indicating that the
 150 solution in the trapped zone is of singularity. Also, since the chemically-bound
 151 chlorides are not able to transport the trapped zone is in fact infinitely small. In other

152 words, both the fronts of the diffusion zone and trapped zone move forward at the same
153 time.

154

155 **3. Experimental validation of analytical solution**

156 The analytical solution described above is now used to simulate the chloride
157 diffusion experiments (ponding tests) reported by Qiao et al. [27]. In the diffusion
158 experiments, ordinary Portland cement (OPC) concrete specimens with water-to-
159 cement ratios of 0.3, 0.4, 0.5 and 0.6 were mixed, in which the proportions of sand and
160 gravel were kept unchanged with the values of 616 kg/m³ and 1050 kg/m³, respectively.
161 The proportion of OPC used was 480, 420, 370 and 325 kg/m³ for 0.3, 0.4, 0.5 and 0.6
162 water-to-cement ratio concrete. The density of the concrete calculated based on the
163 mixing proportion is 2449, 2413, 2380 and 2345 kg/m³ for 0.3, 0.4, 0.5 and 0.6 water-
164 to-cement ratio concrete. The porosities of the concretes with water-to-cement ratio of
165 0.3, 0.4, 0.5 and 0.6 are assumed to be 0.10, 0.12, 0.135 and 0.15, respectively. The
166 specimens were immersed in the solution of chloride concentration 5 mole/l for four
167 months. After then powder samples were taken at different depths from the tested
168 specimens, from which the total chloride contents were determined.

169 In the analytical solution, the surface concentration of free chlorides, C_s , in the
170 unit of wt.% of concrete is calculated as follows,

$$171 \quad C_s = \frac{5 \times 35.5 \times 100 \times \varepsilon}{\rho_{con}} \quad (12)$$

172 where ρ_{con} in kg/m^3 is the density of the concrete and the number of 35.5 in the right
 173 hand side of Eq.(12) is the molar mass of chloride molecule. The concentration of
 174 chemically-bound chlorides, S_c , in the unit of wt.% of concrete and the dimensionless
 175 parameter α describing the physically-bound chlorides are assumed as follows, which
 176 is based on the binding isotherm provided in [27],

$$177 \quad S_c = 0.4\rho_{cem} \quad (13)$$

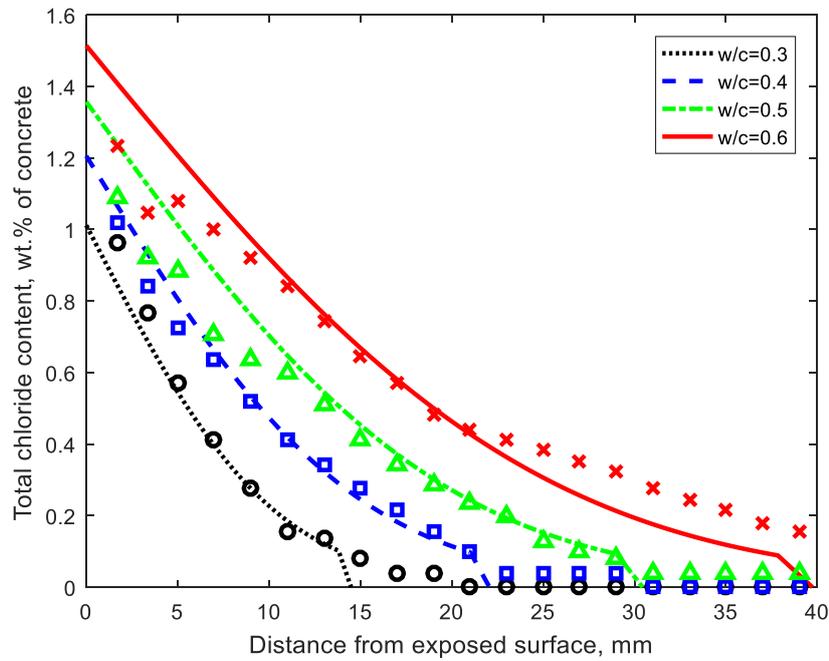
$$178 \quad \alpha = 0.255 \quad (14)$$

179 where ρ_{cem} is the relative weight of cement product (cement plus water) in concrete.

180 The effective diffusion coefficient of chloride ions is assumed as follows,

$$181 \quad D_e = 8.27 \times 10^{-11} w^{2.55} \varepsilon \quad (15)$$

182



183

184

185 **Fig.4.** Experimental validation of present analytical solutions (data points are
186 experimental results from [27]).

187

188 where w is the water-to-cement ratio. The comparison between the simulated total
189 chlorides and experimentally obtained total chlorides is shown in Fig.4. It can be seen
190 from the figure that the predicted total chloride distribution profiles for concrete
191 specimens with different water-to-cement ratios are all in reasonably good agreement
192 with the experimental data. Note that the experimental data are the average of the two
193 samples. In the original data [27], there were big variations for the samples with high
194 water-to-cement ratios (0.5 and 0.6) and close to the exposed surface (less than 10 mm).
195 Thus, although the predicted curves shown in Fig.4 for samples with water-to-cement
196 ratio 0.5 and 0.6 are slightly higher than the experimental data, they are still in the
197 variation ranges of the experimental results. This indicates that the present model is
198 able to represent the main transport features of chlorides in concrete.

199

200 **4. Conclusions**

201 In this paper, we have presented a novel analytical solution for chloride diffusion
202 in concrete, which takes account the effect of chloride binding. By splitting the bound
203 chlorides into chemically-bound and physically-bound chlorides, the original problem
204 of diffusion with chloride binding is transformed to the problem of diffusion with a
205 moving boundary for which an analytical solution can be developed. The present
206 solution has been validated by using the experimental data published in literature. The

207 comparison of the distribution profiles of total chlorides predicted by using the present
208 analytical solution and those measured in experiments has demonstrated the capability
209 and rationality of the present analytical model.

210

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217

218 **References**

- 219 [1] A. Atkinson, A.K. Nickerson, The diffusion of ions through water-saturated cement.
220 Journal of Materials Science 19(9) (1984) 3068-3078.
- 221 [2] H.G. Midgely, J.M. Illston, The penetration of chlorides into hardened cement
222 pastes. Cement and Concrete Research 14(4) (1984) 546-558.
- 223 [3] R.A. de Medeiros-Junior, M.G. de Lima, P.C. de Brito, M.H.F. de Medeiros,
224 Chloride penetration into concrete in an offshore platform-analysis of exposure
225 conditions. Ocean Engineering 103 (2015) 78-87.

- 226 [4] I. Othmen, S. Bonnet, F. Schoefs, Statistical investigation of different analysis
227 methods for chloride profiles within a real structure in a marine environment.
228 Ocean Engineering 157 (2018) 96-107.
- 229 [5] J.Z. Zhang, I.M. McLoughlin, N.R. Buenfeld, Modelling of chloride diffusion into
230 surface-treated concrete. Cement and Concrete Composites 20(4) (1998) 253-
231 261.
- 232 [6] A. Costa, J. Appleton, Chloride penetration into concrete in marine environment –
233 Part II: prediction of long-term chloride penetration. Materials and
234 Structures 32(219) (1999) 354-359.
- 235 [7] H.W. Song, C.H. Lee, K.Y. Ann, Factors influencing chloride transport in concrete
236 structures exposed to marine environments. Cement and Concrete Composites
237 30(2) (2008) 113-121.
- 238 [8] W.Q. Jiang, X.H. Shen, S.X. Hong, Z.Y. Wu, Q.F. Liu, Binding capacity and
239 diffusivity of concrete subjected to freeze-thaw and chloride attack: A numerical
240 study. Ocean Engineering 186 (2019) 106093.
- 241 [9] J.P. Li, W. Shao, The effect of chloride binding on the predicted service life of RC
242 pipe piles exposed to marine environments. Ocean Engineering 88 (2014) 55-62.
- 243 [10] C. Arya, N.R. Buenfeld, J.R. Newman, Factors influencing chloride-binding in
244 concrete. Cement and Concrete Research 20(2) (1990) 291-300.
- 245 [11] A. Boddy, E. Bentz, M.D.A. Thomas, R.D. Hooton, An overview and sensitivity
246 study of a multimechanistic chloride transport model. Cement and Concrete
247 Research 29(6) (1999) 827-837.

- 248 [12] O.M. Jensen, P.F. Hansen, A.M. Coats, F.P. Glasser, Chloride ingress in cement
249 paste and mortar. *Cement and Concrete Research* 29(9) (1999) 1497-1504.
- 250 [13] B. Martín-Pérez, H. Zibara, R.D. Hooton, M.D.A. Thomas, A study of the effect
251 of chloride binding on service life predictions. *Cement and Concrete Research*
252 30(8) (2000) 1215-1223.
- 253 [14] G.K. Glass, N.R. Buenfeld, The influence of chloride binding on the chloride
254 induced corrosion risk in reinforced concrete. *Corrosion Science* 42(2) (2000)
255 329-344.
- 256 [15] V. Baroghel-Bouny V, X. Wang, M. Thiery, M. Saillio, F. Barberon, Prediction of
257 chloride binding isotherms of cementitious materials by analytical model or
258 numerical inverse analysis. *Cement and Concrete Research* 42(9) (2012) 1207-
259 1224.
- 260 [16] L.P. Tang, Engineering expression of the ClinConc model for prediction of free
261 and total chloride ingress in submerged marine concrete. *Cement and Concrete*
262 *Research* 38(8-9) (2008) 1092-1097.
- 263 [17] L.Y. Li, C.L. Page, Modelling of electrochemical chloride extraction from
264 concrete: influence of ionic activity coefficients. *Computational Materials*
265 *Science* 9(3-4) (1998) 303-308.
- 266 [18] L.Y. Li, C.L. Page, Finite element modelling of chloride removal from concrete
267 by an electrochemical method. *Corrosion Science* 42(12) (2000) 2145-2165.

- 268 [19] L.Y. Li, D. Easterbrook, J. Xia, W.L. Jin, Numerical simulation of chloride
269 penetration in concrete in rapid chloride migration tests. *Cement and Concrete*
270 *Composites* 63 (2015) 113-121.
- 271 [20] J.Z. Zhang, J. Guo, D.H. Li, Y.R. Zhang, F. Bian, Z.F. Fang, The influence of
272 admixture on chloride time-varying diffusivity and microstructure of concrete by
273 low-field NMR. *Ocean Engineering* 142 (2017) 94-101.
- 274 [21] C.L. Page, O. Vennesland, Pore solution composition and chloride binding
275 capacity of silica fume cement pastes. *Materials and Structures* 16(1) (1983) 19-
276 25.
- 277 [22] G.K. Glass, G.M. Stevenson, N.R. Buenfeld, Chloride-binding isotherms from the
278 diffusion cell test. *Cement and Concrete Research* 28(7) (1998) 939-945.
- 279 [23] L.P. Tang, L.O. Nilsson, Chloride binding capacity and binding isotherms of OPC
280 pastes and mortars. *Cement and Concrete Research* 23(2) (1993) 247-253.
- 281 [24] P. Sandberg, Studies of chloride binding in concrete exposed in a marine
282 environment. *Cement and Concrete Research* 29(4) (1999) 473-477.
- 283 [25] D.W. Li, L.Y. Li, X.F. Wang, Chloride diffusion model in concrete in marine
284 environment with considering binding effect. *Marine Structures* 66 (2019) 44-
285 51.
- 286 [26] J. Crank, *The Mathematics of Diffusion* (2nd Edition). Clarendon Press, Oxford,
287 1975.

288 [27] C.Y. Qiao, W. Ni, Q.H. Wang, J. Weiss, Chloride diffusion and wicking in
289 concrete exposed to NaCl and MgCl₂ solutions. *Journal of Materials in Civil*
290 *Engineering* 30(3) (2018) 04018015.