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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**

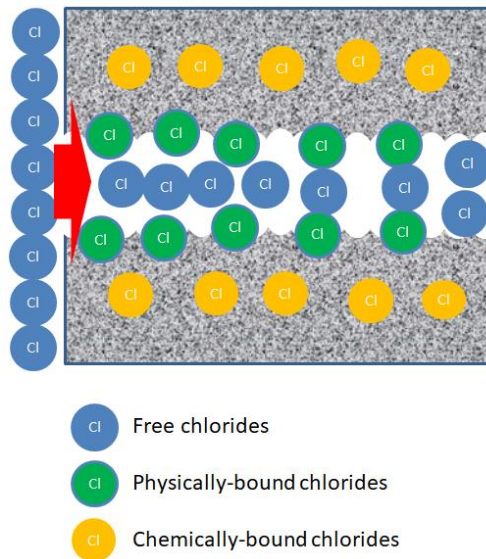
67 Consider the transport of chlorides in concrete. The mass change of the total  
68 chlorides in a unit volume of concrete in a time interval  $dt$  can be expressed as follows,

69 
$$\frac{\partial C_T}{\partial t} = -\nabla \cdot J \tag{1}$$

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 
$$C_T = C_f + S_c + S_p \tag{2}$$

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).



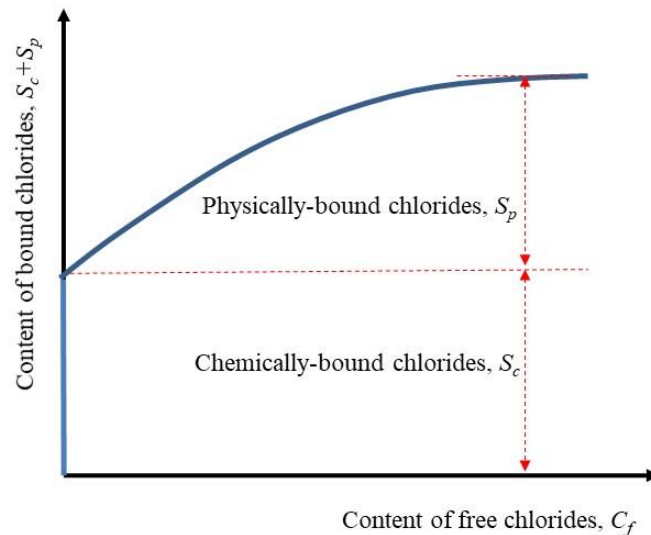
77  
 78 **Fig.1.** A schematic description of chloride transport in concrete.

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],

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

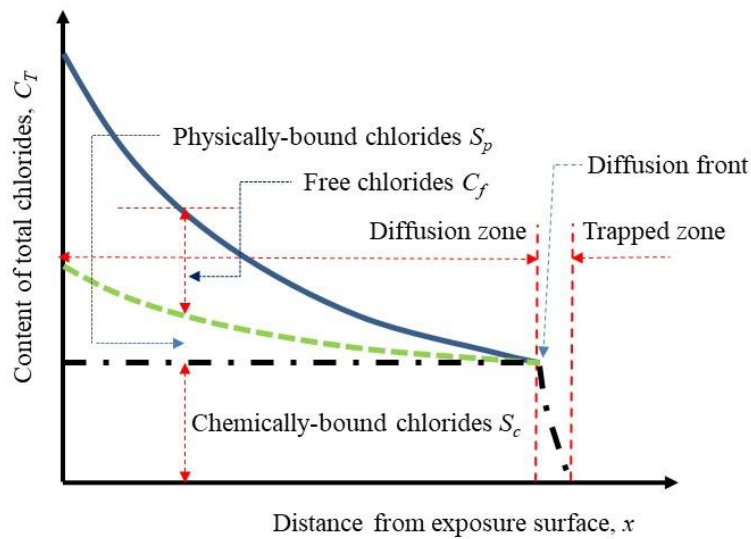
88 where  $D_e$  is the effective diffusion coefficient of chloride ions and  $\varepsilon$  is the porosity of  
 89 concrete.



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  $\xi$  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  $\alpha$  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  $k_\xi$  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  $k_\xi$  is known then the  
 134 solution (9) for  $C_f(t,x)$  is completely defined. In order to determine  $k_\xi$  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  $k_\xi$ , which can be used to determine  $k_\xi$   
 144 for a given ratio of  $(1+\alpha)C_s/S_c$ . After  $k_\xi$  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/m<sup>3</sup> and 1050 kg/m<sup>3</sup>, respectively.  
161 The proportion of OPC used was 480, 420, 370 and 325 kg/m<sup>3</sup> 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/m<sup>3</sup> 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  $\rho_{con}$  in  $\text{kg/m}^3$  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  $\alpha$  describing the physically-bound chlorides are assumed as follows, which  
 176 is based on the binding isotherm provided in [27],

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

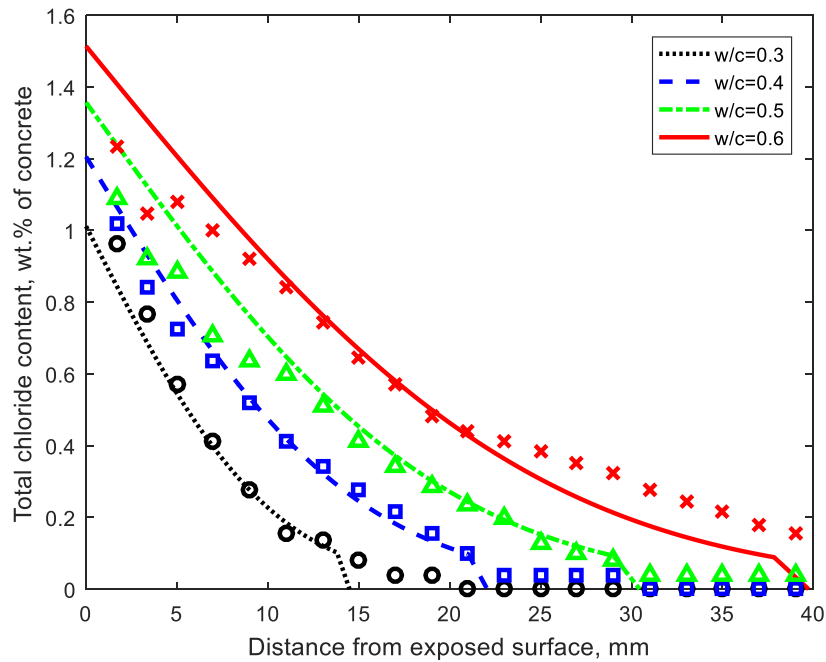
$$178 \quad \alpha = 0.255 \quad (14)$$

179 where  $\rho_{cem}$  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

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