

# Coupled multi-physics simulation of chloride diffusion in saturated and unsaturated concrete

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## Abstract

Chloride-induced corrosion of steel reinforcement is one of the major long-term deterioration mechanisms for reinforced concrete infrastructures. Chloride transport through cement-based materials is a complex chemo-physical process involving ionic diffusion in concentrated solution, pore structure, chemistry, membrane permeability of the matrix, cracking, and the variation of the internal and external environmental conditions. Although in the literature there are plenty of both simplistic phenomenological models and sophisticated models, in this study, a new model is developed taking aim at capturing the fundamental physics and, at the same time, having a formulation as simple as possible that it can be effectively calibrated and validated using available limited experimental data. The model couples the ionic diffusion process with the concrete micro-structure evolution due to continued hydration accounting for hygro-thermal variations and their effects on both the diffusion and hydration processes. The formulation is implemented in a semi-discrete conduit transport network that mimics the internal heterogeneity of the cementitious material by connecting the matrix space between coarse aggregate pieces. This allows the model to replicate naturally the meso-scale tortuosity effect which is an important feature towards representing realistically the heterogeneity-induced variations of chloride concentration within the concrete. The limited model parameters are carefully calibrated and the formulation is validated by simulating multiple experiments ranging from diffusion through pastes to large concrete cylinders. The results of numerical simulations show the ability of the model to describe spatial and temporal evolution of the chloride concentration within the samples under varying chloride concentrations and temperature boundary conditions within both saturated and

unsaturated concrete.

*Keywords:* Chloride transport, Concrete pore structure, Aging and deterioration, Multi-physics modeling

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## 1 INTRODUCTION

Chloride penetration in concrete is one of the major causes of long-term corrosion of steel reinforcement in reinforced concrete structures and, particularly in infrastructure exposed to chloride rich environments, such as marine structures and roadways subjected to deicing salts [1]. In many studies, to predict service life of reinforced concrete structures, such as bridges, the penetration depth of chloride is utilized as measurement of long-term corrosion time-to-failure [2, 3]. The evaluation of chloride diffusion in concrete is also important in order to develop new durable concrete and to assess the durability of structures especially under extremely aggressive environments; for instance, this is the key activity of the project ReSHEALience ([www.uhdc.eu](http://www.uhdc.eu)) [4].

In past years, chloride transport in concrete has drawn much attention and many methods for determining chloride diffusivity in both saturated and non-saturated conditions have been developed [5, 6]. The early attempts to simulate chloride penetration into concrete were focused on describing the ion diffusion in concentrated solution, such as Chatterji that firstly proposed the fundamental equations of diffusion by coupling Fick's laws, Nernst and Nernst-Planck equations together [7, 8, 9]. Bažant [10] applied Maxwell's equations of electrostatics to consider the balance of electric charge. Then Zhang and Gjørv [11] introduced the effects of ionic species activity by expressing the driving diffusion force based on chemical potentials but not on the species concentration. Samson and Marchand [12] showed that the total membrane potential is two times larger when considering the chemical activity by analyzing the numerical solution of Extended Nernst-Planck Model and, therefore, its effect needs to be also considered as a diffusion driving force.

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22 These early studies performed thorough analysis on the influence of the concentrated solution  
23 chemistry on the diffusion of ionic species. Based on that, later studies moved forward to explore  
24 the effect of the complex concrete micro-structure and its evolution since chloride transport in  
25 concrete pore solution differs from that in concentrated solution and pore structure and chemical  
26 reactions have significant influence on the diffusion process. Tang [13, 14] studied the concentra-  
27 tion dependence of diffusion and migration of chloride ions in pore solution by considering the  
28 effect of surrounding ions and membrane potential. Masi et al. [15] simulated the diffusion pro-  
29 cess by means of the percolation concepts. System porosity and the adsorption parameter were  
30 included in the model. Starting from Fick's law, Xi and Bažant [16] deduced a general expres-  
31 sion for chloride diffusion including a series of factors, such as adsorption isotherm, temperature  
32 influence, aggregate effects and concentration dependence. Johannesson et al. [17] modelled  
33 the multi-species ionic diffusion in concrete with account to interaction between ions in the pore  
34 solution and the cement hydrates. Nguyen and Amiri investigated the electrical double layer  
35 (EDL) effects on chloride transport and found that the EDL is strong in concrete containing slag,  
36 while relatively weak in regular concrete [18, 19]. Li et al. [20] proposed a multi-phase model  
37 for predicting the effective coefficient of chlorides in concrete and discussed the effect of ag-  
38 gregates, showing that the size and shape of aggregate have small influence on the diffusion of  
39 chloride. Marchand et al. proposed a phenomenological model considering the change of poros-  
40 ity over time [21]. This model was later improved by considering the effect of temperature on  
41 ionic transport in cementitious materials through energy balance [22, 20].

42 In recent years, a few advanced models have been proposed, aiming at capturing the features  
43 of chloride transport in complex and variable exposure conditions. Based on the experimental  
44 results, Isteita and Xi studied the coupling effect between chloride penetration and temperature  
45 gradient and proposed a coupling parameter to consider the effect of temperature variation on  
46 chloride penetration [23]. Similarly, a fitting parameter coupling moisture transport and chloride  
47 penetration is presented in [24]. Ožbolt et al proposed a 3D chemo-hygro-thermo mechanical  
48 model for continuum that is able to simulate physical processes before [25, 26] and after [27]  
49 depassivation of steel reinforcement. Song et al proposed the concept of "contact duration" to

50 consider the time dependence of chloride binding capacity [28]. Conciatori et al. performed  
51 sensitivity analysis to quantify the influence of parameter variation [29]. The results showed  
52 that chloride ingress is very sensitive to many parameters including porosity, temperature, ionic  
53 diffusion coefficient, water permeability etc., and exhibits high variability at the early period of  
54 the ingress. This indicates that modelling chloride penetration with too many parameters is very  
55 challenging in calibration and might results in unsuccessful fitting.

56 As it can be seen from this short review, phenomenological models are not accurate enough  
57 and are limited to the range of data to which they were fitted and thus are not effectively pre-  
58 dictive. Simple theoretical models consider a subset of the main governing processes that affect  
59 chloride penetration and thus, can not be generalized over a wide range of exposure conditions.  
60 Other sophisticated models consider a large number of parameters which are hard to calibrate  
61 uniquely using limited experimental data. In this paper, a new model is developed with the aim  
62 to strike a sensitive balance between capturing the fundamental physics, but at the same time,  
63 having a formulation as simple as possible without compromising its versatility and generality  
64 to achieve effective calibration and successful validation. Moreover, the proposed formulation  
65 is based on a discrete approach that considers many significant features presented in the next  
66 section, such as accounting for the heterogeneity induced by coarse aggregate through the use of  
67 a discrete lattice system that represents the flow within the meso-scale structure.

## 68 **2. Significance of the proposed research**

69 This model is formulated by considering five major chemo-physical phenomena governing  
70 chloride ion diffusion in cementitious materials, namely, 1) effects of chemical activity and mem-  
71 brane potential on ion transport in concentrated solutions in porous media, 2) effects of pore  
72 structure evolution (pore volume and tortuosity) on diffusivity, 3) effects of surrounding ions  
73 that make the diffusivity concentration-dependent, 4) the thermal effects on diffusivity, chloride  
74 binding capacity, and micro-structure change as reflected by cementitious material hydration re-  
75 actions, and 5) effects of advection due to moisture transport in unsaturated conditions. During  
76 the development of this model, the authors decided not to explicitly model the phenomena that

77 are hard to measure experimentally, controversial or have very limited experimental data that  
78 represent it. Instead, for such phenomena, simplifying assumptions broadly supported in liter-  
79 ature were adopted. This approach is the key in striking the balance between simplicity and  
80 representation of chemo-physical phenomena in this model. For example, the model does not  
81 represent explicitly the diffusion of all ionic species present in the pore solution. Instead, it rep-  
82 resents their effects on chloride diffusion following simplified counter ion effects formulations  
83 with very limited parameters. Theoretically, one could model the diffusion of all existing species  
84 in the solution and impose electric charge balance. Yet practically, this means that experimental  
85 data relevant to rapid chloride penetration tests will not be sufficient to calibrate the various dif-  
86 fusing species and the concentrations of these species have to be explicitly monitored to correctly  
87 identify their diffusion parameters. If such comprehensive experimental data is not available,  
88 model parameters relevant to all other diffusing species will be assumed and correspondingly,  
89 their effects on the chloride diffusion modeling will be high. In this case, while there should  
90 be some additional benefits from modeling the various diffusion processes, the biased parameter  
91 identification would reduce the model robustness and increase its sensitivity. Additionally, the  
92 model neglects the time dependence of the chloride binding process because evaluating its rate  
93 requires modeling of phenomena at the level of material gel microstructure which is much finer  
94 than the scale at which the model is formulated, and it is also much finer than the scale at which  
95 the chloride concentrations are determined in the experiments used for calibration and validation.  
96 Therefore, chloride binding to the matrix is considered including the effects of temperature on  
97 the binding capacity, but the local variation of the binding capacity over time is ignored.

98 As a result, model free parameters are limited yet, the modeled chemo-physical processes  
99 are comprehensive enough to represent a wide range of experimental results. In addition, the  
100 model is readily extendable to multi-ionic diffusion with full charge balance if comprehensive  
101 experimental data are made available as it is implemented within a fully coupled multi-physics  
102 framework that accounts for moisture and heat diffusion along with the typical cementitious  
103 material chemical reactions.

104 Geometrically speaking, one of the main advantages of the proposed model is that it is imple-

105 mented in a discrete lattice system that represents flow through the concrete internal structure.  
106 Again, when experimental data is made available in which, the chloride concentration in the  
107 cementitious matrix is separated from that of the aggregate within it, this model can better rep-  
108 resent the variations of concentration due to the heterogeneity of the concrete internal structure  
109 considering the cement matrix as shortcut for flow as compared to aggregate locations. Never-  
110 theless, given the fact that this model advances the flow in between the matrix zones inside the  
111 concrete structure, it naturally captures the meso-scale tortuosity. This is a very important aspect  
112 when dealing with the formation of micro-cell corrosion, i.e. position of anodic and cathodic  
113 sites. Chloride ions ingress in a tortuous way that avoids aggregate as it is hard to penetrate,  
114 leading to a non-uniform distribution of chloride concentration at any depth. Given the fact that  
115 the formation of micro-cell corrosion depends on local concentration rather than average con-  
116 centration, as predicted by most existing models, it is of great importance to characterize the  
117 meso-scale tortuosity when modeling the chloride-induced corrosion in concrete. This feature  
118 is beyond the reach of any macroscopic continuum model since it inherently homogenizes the  
119 concrete internal structure. Furthermore, this discrete nature makes the model readily extendable  
120 to meso-structural cracking effects necessary to model the two-way coupling between cracking  
121 on diffusivity and cracking evolution under corrosion progression. This two-way coupling has  
122 been already employed in modeling concrete spalling at elevated temperatures [30] and moisture  
123 diffusion behavior of self-healing concrete [31].

124 Certainly, the benefits of the meso-scale discrete discretization approach must be paid with an  
125 additional computational cost. However, the proposed approach does not add a very significant  
126 computational cost when compared to its continuum counterparts. The reason for this is twofold:  
127 (1) continuum meshes for diffusion problems must have very fine discretization meshes at the  
128 boundaries to capture the high gradients with an acceptable accuracy; (2) continuum meshes  
129 would discretize all the space around and within the aggregates with nearly the same density. For  
130 these reasons, the discrete approaches are more effective compared to continuum approaches, yet  
131 of course they are more computationally demanding. Based on the authors experience in using  
132 both the discrete (1D conduit) scheme and the FE continuum (3D tetrahedral elements) scheme

133 in many previous research applications concerning aging, creep, shrinkage and Alkali Silica  
134 Reaction (ASR) problems [32, 33, 34, 35, 36], they noticed that the discrete mesh requires no  
135 more than 50% of computational time compared to continuum mesh with similar refinement.  
136 This difference has not been quantitatively evaluated but the authors have consistently observed  
137 it in their work.

138 Finally, in this model, aging as well as heat and moisture transport processes are introduced  
139 by using a comprehensive hygro-thermo-chemical model with which the new chloride diffusion  
140 model is fully coupled. As a result, the effects of the changes in water to cement ratio ( $w/c$ ),  
141 change in porosity over time, presence of thermal gradients or temperature variations, and diffu-  
142 sion in unsaturated concrete are naturally captured without introducing additional fitting param-  
143 eters. While it is true that aging and hygro-thermal variations may not be of significant effect on  
144 chloride diffusion in some field applications where structures are old enough and hygro-thermal  
145 conditions are nearly constant, the importance of considering these features stems from the need  
146 to use accelerated experimental data in which all or part of these aging and hygro-thermal ef-  
147 fects are very significant. Without their proper considerations, model predictions of real-world  
148 situations that are based on accelerated lab testing can be considerably inaccurate.

### 149 **3. Multi-physics formulation**

150 Many factors influence the ionic transport in cementitious materials. However, since it is  
151 mainly taking place within the liquid water in the pore structure, the physics of ionic transport  
152 can start from considering the diffusion of ions in concentrated solutions (liquid pore solution)  
153 and then account for the effects of the pore structure. These main effects can be summarized as

- 154 (1) Geometrical effect, i.e. pore size distribution and its connectivity.
- 155 (2) Chemical reactions effect, since the pore walls are chemically active, part of the moving  
156 ions tend to bind with the pore walls.
- 157 (3) Electric potential effect, since the pore walls are not neutral but in general negatively  
158 charged, a membrane potential is generated and affects the diffusion of ionic species.

159 It is also important to consider that the internal pore structure of a cementitious material ages  
 160 and changes in time. As a result of the chemical reactions, including hydration, polymerization  
 161 and gel densification [37], the pore structure densifies, and, in turn, results in time-dependent  
 162 decreasing porosity and increasing tortuosity. In addition, if the ionic solution is not in ther-  
 163 modynamic equilibrium (i.e. there is moisture gradient within the pores), then advection of the  
 164 dissolved ions has to be also considered. Moreover, all the processes mentioned above are af-  
 165 fected by thermal conditions, i.e. as temperature increases, ionic mobility, moisture diffusivity,  
 166 chemical reactions rates and binding capacities usually increase too.

167 To predict accurately the transport of an ionic species in a cementitious material one has to  
 168 consider all the above mentioned phenomena. However, as discussed earlier in Sec. 2, the ap-  
 169 proach used here in developing the proposed formulation accounts for the most relevant electro-  
 170 chemo-physical phenomena encountered during chloride penetration using the minimum amount  
 171 of free parameters that can be calibrated from standard tests at the macro-scale.

172 In the following sections, the formulation of a chloride diffusion model will be detailed. Since  
 173 the model depends on temperature and moisture variations, as well as, on material aging, these  
 174 phenomena are here modeled using the Hygro-thermo-chemical (HTC) model by Di Luzio and  
 175 Cusatis [38, 39] which will be briefly reviewed and the coupling between the chloride diffusion  
 176 model and the HTC model will be also presented.

### 177 3.1. Formulation of chloride diffusion

178 The macroscopic equation for the transport of ionic species can be based on the extended  
 179 Nernst–Planck equation with an advection term [40, 41, 42, 43]. The mass balance equation  
 180 (continuity equation) of chloride ions can be written as

$$\frac{\partial}{\partial t} \left( \frac{w_{cap}}{\rho_w} C + w_s C_b \right) = -\nabla \cdot J_c + \frac{w_{cap}}{\rho_w} \dot{r} \quad (1)$$

181 where  $C$  is the concentration of the ionic species in the pore solution ( $\text{mol}/\text{m}^3$ ),  $w_{cap}$  is the mass  
 182 of capillary water content ( $\text{kg}/\text{m}^3$ ),  $\rho_w$  is the water density ( $\text{kg}/\text{m}^3$ ),  $w_{cap}/\rho_w$  is the volumetric  
 183 water content ( $\text{m}^3/\text{m}^3$ ),  $w_s$  is the volumetric solid content ( $\text{m}^3/\text{m}^3$ ),  $C_b$  is the concentration of



184 the species bound in the solid content ( $\text{mol/m}^3$ ),  $J_c$  is the ionic flux ( $\text{mol/m}^2/\text{s}$ ) in cementitious  
 185 materials,  $\dot{r}$  stands for chemical reaction rate and  $\frac{w_{cap}}{\rho_w} \dot{r}$  is a source/sink term accounting for the  
 186 creation/consumption of the ions in solution as a result of chemical reactions ( $\text{mol/m}^3/\text{s}$ ). It  
 187 should be noted here that chloride ions are assumed to move only within the capillary pores  
 188 occupied by capillary water  $w_{cap}$  in this formulation. As it will be explained later, the HTC  
 189 model differentiates between capillary and physically bound (adsorbed) water which together  
 190 form the non-evaporable water. This assumption is very reasonable since the physically bound  
 191 water is adsorbed in the the C-S-H gel structure and is nearly immobile. As will be shown in  
 192 the simulation results, this assumption will be validated by modeling diffusion in unsaturated  
 193 conditions with calibrated model parameters using saturated conditions only.

194 There are two different types of chemical reactions: the reactions occurring solely in the  
 195 aqueous phase (i.e. formation or dissociation of acids) and the reactions that involve more than  
 196 one phase, such as surface or classical reactions. The adsorption of ions, i.e. the capture of  
 197 ions by the surface of the solid as a result of electrostatic forces, is a surface reaction, whereas  
 198 dissolution or precipitation reactions belong to the classical category of chemical reactions. In  
 199 Eq. 1, the second term in the LHS corresponds to the surface or classical chemical reactions, on  
 200 the contrary the last term in the RHS considers reactions occurring solely in the aqueous phase.  
 201 However, since the hydrated cement paste has a highly reactive nature, we can assume that the  
 202 surface or classical reactions are much more significant than reactions occurring solely in the  
 203 aqueous phase. Expanding Eq. 1 and neglecting the chemical reactions in the aqueous phase  
 204 ( $\dot{r} = 0$ ) one gets

$$\frac{C}{\rho_w} \frac{\partial w_{cap}}{\partial t} + \frac{w_{cap}}{\rho_w} \frac{\partial C}{\partial t} + w_s \frac{\partial C_b}{\partial t} + C_b \frac{\partial w_s}{\partial t} = -\nabla \cdot J_c \quad (2)$$

205 where only dissolution/precipitation reactions are taken into account.

206 The so-called chloride binding isotherm provides the relationship between the free and the  
 207 bound chloride concentration at a given temperature. In the literature four types of adsorption  
 208 isotherm (linear, Langmuir, Freundlich and BET binding isotherm) have been proposed [44] and  
 209 among them the Freundlich isotherm appears to fit the experimental results very well [16, 44, 45,

210 46]. Therefore, the Freundlich isotherm is adopted in this study and has the following expression

$$\log(C'_b) = A_0 \log(C) + B_0 \quad (3)$$

211 where  $C'_b$  is the mass of bound chlorides per gram of solid gel (mg/g),  $A_0$  and  $B_0$  are two material  
212 parameters.

213 Because the relationship between  $C'_b$  and  $C_b$  can be expressed as  $C'_b = 1000M_{Cl}C_b/\rho_s$ , where  
214  $M_{Cl}$  is the molar mass of chloride,  $\rho_s$  is the density of solid content(kg/m<sup>3</sup>), the Freundlich  
215 isotherm in Eq. 3 can be rewritten as

$$C_b = \frac{C^{A_0} 10^{B_0} \rho_s}{1000M_{Cl}} \quad (4)$$

216 The binding process is also influenced by the temperature through different mechanisms.  
217 There are two main types of binding processes: (1) the physical binding that is caused by the  
218 adsorption of chloride ions on the C-S-H surface; (2) the chemical binding that leads to the  
219 formation of Friedel's salt [44]. Temperature variation affects these two binding processes dif-  
220 ferently. As temperature increases, the physical binding process slows down because of higher  
221 thermal energy of ions. On the contrary, higher temperature accelerates the chemical binding  
222 process [47], although the increased temperature increases the solubility of Friedel's salt [48].  
223 For temperature variations between 0 ~ 50° and for low chloride concentration ( $\leq 1\text{mol/L}$ ),  
224 a significant increase of bound chloride is observed in experimental data as temperature rises  
225 [49, 50, 51]. Other experiments report that there is no noticeable increase of the Friedel's salt  
226 solubility [52] and the concentration of bound chloride shows slight differences as temperature  
227 varies [48, 51, 53]. Consequently, in this study, to describe the effects of temperature on chloride  
228 binding, only the effect of chemical binding is considered using an exponential temperature-  
229 dependent coefficient

$$C_b = \frac{C^{A_0} 10^{B_0} \rho_s}{1000M_{Cl}} \exp \left[ \frac{U_b}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (5)$$

230 where  $U_b$  is a coefficient that characterized the temperature effect on the adsorption process,  $A_0$

231 and  $B_0$  are both determined at the reference temperature  $T_0$ . The temporal derivative of the bound  
 232 chloride from Eq. 5 can be expressed as

$$\frac{\partial C_b}{\partial t} = \frac{\partial C_b}{\partial C} \frac{\partial C}{\partial t} + \frac{\partial C_b}{\partial T} \frac{\partial T}{\partial t} = \frac{A_0 C_b}{C} \frac{\partial C}{\partial t} + \frac{U_b C_b}{RT^2} \frac{\partial T}{\partial t} \quad (6)$$

233 The sorption isotherm law is needed to determine the capillary water content,  $w_{cap}$ , as a function  
 234 of the relative humidity and aging. In the HTC model  $w_{cap}$  is formulated using an improved  
 235 version of the original expression proposed by Norling Mjornell [54]. Based on this sorption  
 236 isotherm formulation, the capillary water in concrete can be expressed as a function of relative  
 237 humidity,  $h$ , and hydration degree  $\alpha_c$ . The volumetric solid content,  $w_s$ , can be calculated as  
 238  $(c\alpha_c + w_n)/\rho_s$ , where  $c$  is the mass of cement content ( $\text{kg}/\text{m}^3$ ),  $\alpha_c$  is the hydration degree,  $w_n$  is  
 239 the non-evaporable water content ( $\text{kg}/\text{m}^3$ ). The temporal derivative of  $w_{cap}$  and  $w_s$  can be written  
 240 as

$$\frac{\partial w_{cap}}{\partial t} = \frac{\partial w_{cap}}{\partial h} \frac{\partial h}{\partial t} + \frac{\partial w_{cap}}{\partial \alpha_c} \dot{\alpha}_c \quad \text{and} \quad \frac{\partial w_s}{\partial t} = (c\dot{\alpha}_c + \dot{w}_n)/\rho_s \quad (7)$$

241 Substituting Eqs. 6-7 into Eq. 2, the LHS of Eq. 2 can be expressed as

$$\begin{aligned} \frac{C}{\rho_w} \frac{\partial w_{cap}}{\partial t} + \frac{w_{cap}}{\rho_w} \frac{\partial C}{\partial t} + w_s \frac{\partial C_b}{\partial t} + C_b \frac{\partial w_s}{\partial t} &= \left( \frac{w_{cap}}{\rho_w} + \frac{w_s A_0 C_b}{C} \right) \frac{\partial C}{\partial t} + \\ &+ (c\dot{\alpha}_c + \dot{w}_n) \frac{C_b}{\rho_s} + \frac{C \dot{\alpha}_c}{\rho_w} \left( \frac{\partial w_{cap}}{\partial \alpha_c} \right) + \frac{w_s U_b C_b}{RT^2} \frac{\partial T}{\partial t} + \frac{C}{\rho_w} \frac{\partial w_{cap}}{\partial h} \frac{\partial h}{\partial t} \end{aligned} \quad (8)$$

242 For fully saturated conditions with  $h = 1$ , the last term in Eq. 8 is equal to zero. The various  
 243 quantities,  $w_{cap}$ ,  $w_n$ ,  $\alpha_c$ , and  $h$  can be obtained by coupling Eq. 2 with the HTC model [38, 39]  
 244 (see Section 4).

245 In the RHS of Eq. 2, we need now to specify the term,  $J_c$ , which represents the flux of chloride  
 246 ions in the cementitious material. In the transport of charged ions through a porous media like  
 247 concrete, its pore structure, characterized by porosity, pores shape and spatial distribution, con-  
 248 nectivity, tortuosity, as well as, the interfacial transition zone (ITZ), plays an important role [55].

249 For partially saturated conditions, moisture movement occurs, leading to the motion of water  
 250 from higher saturated pores toward less saturated pores. This means that ionic species can also  
 251 be transported along with the fluid by advection. Therefore, the flux of ionic species in concrete  
 252 pore solution can be expressed as

$$J_c = f_\phi J_s + vC \quad \text{with} \quad J_s = f_\gamma f_\psi f_s f_T J_0 \quad (9)$$

253 where  $J_s$  is the flux of ionic species in concentrated solution of a porous material,  $f_\phi$  is the  
 254 function that considers the effect of pore structure and  $v$  is the fluid mass velocity. For fully  
 255 saturated conditions, moisture inside concrete is in static equilibrium and thus no moisture mass  
 256 transport occurs (i.e.  $v = 0$ ). The flux of ionic species in concentrated solution is very different  
 257 from the flux in dilute solution due to the interactions of surrounding ions and the existence of  
 258 an electro-chemical potential. The flux in dilute solution can be expressed with the first Fick's  
 259 law as  $J_0 = -D_0 \nabla C$ , in which  $D_0$  is the diffusivity coefficient in dilute solution. The flux  
 260 of concentrated solution,  $J_s$ , can be related to  $J_0$  through a set of coefficients:  $f_\gamma$ ,  $f_\psi$ ,  $f_s$  and  
 261  $f_T$ , which account for the different chemo-physical phenomena encountered in the diffusion  
 262 process of a concentrated solution with respect to a dilute solution. These phenomena, and the  
 263 corresponding coefficients that represent them, are explained hereafter.

### 264 3.2. *Effect of pore solution chemistry*

265 Since the pore solution of a cement paste is very rich in ions with an initially very high  
 266 alkaline concentration [56], the transport of ionic species is driven by the gradient of electro-  
 267 chemical potential [57], which can be written as

$$u = u_0 + RT \ln(\gamma C) + zF\psi \quad (10)$$

268 where  $u$  is the electro-chemical potential of a species (J/mol),  $u_0$  is the chemical potential in  
 269 the standard state,  $\gamma$  is the activity coefficient (-),  $z$  is the valency of the ion,  $F$  is the Faraday  
 270 constant (96485.33 C/mol),  $R$  is the ideal gas constant (8.3143 J/mol/K),  $T$  is the temperature  
 271 of the material (K), and  $\psi$  is the electrical potential (V). In pore solution, the electrical potential

272  $\psi$  consists of two components. The first represents the formed counter-electrical potential  $\psi_0$   
 273 between the moving chloride ions and the surrounding moving cations. The second is called  
 274 a membrane-electrical potential  $\psi_m$  and is caused by membrane effects of cement paste. Both  
 275 electrical potentials produce an opposite force and are combined together to form the overall  
 276 electro-chemical potential.

277 The counter-electrical potential,  $\psi_0$ , is the result of the difference in drift velocities between  
 278 cations and anions [13] and can be expressed as

$$\psi_0 = -\frac{RT}{F}(\tau_{+0} - \tau_{-0}) \ln(\gamma C) = -\frac{RT}{F} K_{\tau 0} \ln(\gamma C) \quad (11)$$

279 where  $\tau_{+0}$  and  $\tau_{-0}$  are the transference number of cations and anions, and the symbol  $K_{\tau 0}$  de-  
 280 notes the difference in transference number or drift velocity in the pure solution. For a spe-  
 281 cific electrolytic solution, it can be regarded as constant, e.g. for sodium chloride solution,  
 282  $K_{\tau 0} = -0.207$  [14].

283 The membrane-electrical potential,  $\psi_m$ , is induced by moving within the C-S-H gel porous  
 284 structure which has a negatively charged surface that behaves as an electro-negative membrane:  
 285 accelerating cations and decelerating anions. As a result, there is a selective permeability which  
 286 increases the difference in mobility between cations and anions. The  $\psi_m$  can be expressed as  
 287 [13, 58]

$$\psi_m = -\frac{RT}{F} K_{\tau m} \ln(\gamma C) \quad (12)$$

288 where  $K_{\tau m}$  denotes the difference in mobility caused by the membrane-electrical potential. The  
 289 resulting electrical potential in pore solution,  $\psi = \psi_0 + \psi_m$ , can be substituted in Eq. 10 which  
 290 gives the total electro-chemical potential as:

$$u = u_0 + RT f_\psi \ln(\gamma C) \quad \text{with} \quad f_\psi = 1 - zK_{\tau 0} - zK_{\tau m} \quad (13)$$

291 Then, the gradient of the total electro-chemical potential is calculated as:

$$\nabla u = \frac{RT}{C} f_\psi \left( 1 + \frac{\partial \ln(\gamma)}{\partial \ln(C)} \right) \nabla C + R f_\psi \ln(\gamma C) \nabla T = \frac{RT}{C} f_\psi f_\gamma \left( 1 + \frac{C}{T f_\gamma} \ln(\gamma C) \frac{\partial T}{\partial C} \right) \nabla C \quad (14)$$

with  $f_\gamma = 1 + \frac{\partial \ln(\gamma)}{\partial \ln(C)}$

292 The second term in the RHS of Eq. 14 represents the coupling effect between temperature  
 293 and chloride concentration on the electro-chemical potential gradient. In this study, the room  
 294 temperature is 296 K,  $C$  is between 0 ~ 1 mol/L,  $\gamma$  is between 0.6 ~ 1,  $f_\gamma$  is between 0.95 ~  
 295 1.21 [14]. Since the maximum temperature difference considered in this research is 25 K and  
 296 assuming that  $\partial T / \partial C \approx \Delta T / \Delta C = 25 \text{ K L} / \text{mol}$ , which means that the absolute value of the  
 297 coupling term is less than 0.053 which is negligible as compared to 1. Therefore,  $\nabla u$  can be  
 298 simplified as:

$$\nabla u = \frac{RT}{C} f_\psi f_\gamma \nabla C \quad (15)$$

299 The presented gradient of the electro-chemical potential in Eq. 15 is now related to the con-  
 300 centration gradient using  $f_\psi$  which represents the effect of the overall electrical potential (see  
 301 Eq. 13), and  $f_\gamma$  which represents the effect of ionic activity, that is equal to 1 for an ideal (very  
 302 dilute) solution. The activity coefficient accounts for the interactions of the different types of  
 303 ions, such as ion-solvent interaction (electrophoretic effect) and ion-ion interaction (relaxation  
 304 effect), that take place in a real solution [59]. As reported in literature [12], the chemical activity  
 305 has a significant effect on the chemical potential and various formulations have been proposed  
 306 to model it. In this work the Extended Debye-Hückel equation [60, 61] is used to describe the  
 307 relationship between activity coefficient and concentration and it reads as

$$\frac{\partial \ln(\gamma)}{\partial \ln(C)} = -2.302 I \left[ \frac{A_\gamma |z_+ z_-|}{2 \sqrt{I} (1 + B_\gamma a' \sqrt{I})^2} - B^* \right] \quad (16)$$

308 where  $A_\gamma$ ,  $B_\gamma$  are parameters related to temperature. However, experimental results show that  
 309 the dependence of activity coefficient on temperature is very weak [62, 63]. Therefore,  $A_\gamma$ ,  $B_\gamma$

310 are assumed to be constant in this research and the values at 25°C reported in [61] are adopted  
 311 hereafter, i.e.  $A_\gamma = 0.509 \text{ dm}^{1/2}/\text{mol}^{1/2}$  and  $B_\gamma = 3.286 \text{ dm}^{1/2}/(\text{mol}^{1/2} \cdot \text{nm})$ . The coefficient  
 312  $a'$  is a constant corresponding to the radius of the ion and  $B^*$  is a model parameter. The term  
 313  $I$  represents the ionic strength,  $I = (n_+z_+^2 + n_-z_-^2)C/2$ , in which  $z_+$  and  $z_-$  are charge number  
 314 of cations and anions, respectively,  $n_+$  and  $n_-$  are the ion identification number of cations and  
 315 anions, respectively. Thus, the effect of chemical activity of pore solution on the electro-chemical  
 316 potential is given by the coefficient  $f_\gamma$  that has the following expression

$$f_\gamma = 1 - 2.302 I \left[ \frac{A_\gamma |z_+ z_-|}{2 \sqrt{I} (1 + B_\gamma a' \sqrt{I})^2} - B^* \right] \quad (17)$$

### 317 3.3. Effect of solution concentration

318 Chloride diffusion coefficients of concrete determined from the conventional diffusion or mi-  
 319 gration tests are not constant but are strongly dependent on the concentration [13, 64, 65, 66, 67,  
 320 68]. The flux of ionic species in concentrated solution is different from a flux in dilute solution  
 321 because ions are very close to each other and that creates mechanical interactions or frictional  
 322 effects between the moving ions. As the concentration increases, these effects become more  
 323 important to consider. For a concentrated electrolytic solution the multi-component diffusion  
 324 equation can be expressed as [13, 69]

$$C_i \nabla u_i = \sum_j K_{ij} (v_j - v_i) = RT \sum_j \frac{C_i C_j}{(\sum_i C_i) \mathcal{D}_{ij}} (v_j - v_i) \quad (18)$$

325 where  $u_i$  is the electro-chemical potential of species  $i$ ,  $K_{ij}$  is friction coefficient of species  $i$   
 326 with respect to the species  $j$ ,  $v_i$  is the average velocity of species  $i$ ,  $\mathcal{D}_{ij}$  is a diffusion coefficient  
 327 describing the interaction between the  $i$  and  $j$  species. Again, while this potential can be theoreti-  
 328 cally represented, concrete pore solution is rich in multiple ionic species and their concentrations  
 329 have to be explicitly monitored so that the different ionic diffusion parameters can be calibrated.  
 330 Thus as a reasonable simplification, a binary solution is only considered here. For a binary elec-  
 331 trolytic solution composed of anions, cations, and solvent, the Eq. 18 can be written for anions  
 332 (ions with negative charge) as

$$\begin{aligned}
C_- \nabla u_- &= K_{0-}(v_0 - v_-) + K_{+-}(v_+ - v_-) = \\
&= RT \frac{C_- C_+}{(C_- + C_+ + C_0) \mathcal{D}_{-+}} (v_+ - v_-) + RT \frac{C_- C_0}{(C_- + C_+ + C_0) \mathcal{D}_{-0}} (v_0 - v_-)
\end{aligned} \tag{19}$$

333 Here the subscript indices “-”, “+” and “0” are used to refer to anions, cations and solvent respec-  
334 tively. So  $v_-$ ,  $v_+$  and  $v_0$  are the velocities and  $C_-$ ,  $C_+$  and  $C_0$  are the concentration of the anions,  
335 cations and solvent, respectively,  $\mathcal{D}_{-0}$  represents the diffusion coefficient of the anion in dilute  
336 solution. Setting  $\beta_v = v_+/v_-$  and  $f = \mathcal{D}_{-0}/\mathcal{D}_{-+}$ , considering a neutral NaCl salt solution, i.e.  
337  $C_- = C_+ = C$ ,  $v_-$  being the velocity of chloride ions  $v_{Cl}$ , and  $\mathcal{D}_{-0}$  being the diffusion coefficient  
338 of chloride in dilute solution  $D_0$  and also considering fully saturated situation ( $v_0 = 0$ ), the Eq. 19  
339 can be simplified as

$$C \nabla u = -RT \frac{C f (1 - \beta_v) + C_0}{(2C + C_0) D_0} (C v_{Cl}) \tag{20}$$

340 Since  $J_s = C v_{Cl}$  by definition, then Eq .20 can be rearranged as

$$J_s = -f_s \frac{D_0}{RT} C \nabla u \quad \text{with} \quad f_s = \frac{2C + C_0}{C f_v + C_0} \quad \text{and} \quad f_v = f(1 - \beta_v) \tag{21}$$

341 where  $f_s$  represents the effect of solution concentration and  $f_v$  is the friction coefficient which is  
342 usually much greater than 2 [14]. Substituting Eq. 15 into Eq. 21 one gets the relation between  
343 the flux in the concentrated pore solution and the concentration gradient as

$$J_s = -f_\psi f_\gamma f_s D_0 \nabla C = -D_s \nabla C, \quad \text{with} \quad D_s = f_\gamma f_\psi f_s D_0 \tag{22}$$

#### 344 3.4. Effect of age-dependent pore structure

345 The overall diffusion coefficient of chloride,  $D_c$ , in a cementitious material is also governed  
346 by porosity and pore characteristics such as shape, size, orientation, spatial distribution, connec-  
347 tivity, and size variation [55]. Moreover, the pore structure is not constant but changes as the  
348 material ages. To consider these features, the diffusion of chloride in the pore solution of porous



349 materials can be expressed as  $D_c = f_\phi D_s$ , which implies that the flux of chloride in a cementitious  
 350 material can be formulated as  $J_c = (J_0 f_s f_\gamma f_\psi) f_\phi$ , in which  $f_\phi$  is a coefficient that accounts for the  
 351 porosity and its characteristics [5, 70] as

$$f_\phi = \frac{w_{cap}}{\rho_w} \frac{\delta}{\tau^2} q(\phi) = \frac{w_{cap}}{\rho_w} \tau_a q(\phi) \quad (23)$$

352 As shown in Fig. 1a,  $\tau$  is the tortuosity factor which is defined as the ratio of the effective length,  
 353  $L_{eff}$ , which is the shortest path that connect two points in the pore structure, to the length of the  
 354 straight line that connects the two points [55];  $\delta$  is the constrictivity factor which represents a  
 355 measure of the presence of bottlenecks in the pores path by relating the minimum pore diameter  
 356 to the maximum pore diameter. If the cross section of pores is constant, then the constrictivity  
 357 factor,  $\delta$  is equal to 1. If the pore structure becomes narrow at some point, then  $0 < \delta < 1$  or if  
 358 the pores are not connected, then  $\delta = 0$  [70], see Fig.1b. The coefficient  $\tau_a = \delta/\tau^2$  is the apparent  
 359 tortuosity factor and is assumed to be a free model parameter which lumps together the effect of  
 360 tortuosity and constrictivity since it is extremely difficult to identify separately the effect of  $\delta$  and  
 361  $\tau$ . In addition to that the pore volume has its own effect which is accounted for by introducing  
 362 the function  $q(\phi)$  based on Kozeny-Carman model [71] as

$$q(\phi) = \left( \frac{\phi}{\phi_0} \right)^3 \left( \frac{1 - \phi_0}{1 - \phi} \right)^2 \quad (24)$$

363 where  $\phi$  is the current porosity that changes over time and  $\phi_0$  is the initial porosity at the initial  
 364 setting of the material. The effect of porosity is very important when trying to use accelerated  
 365 lab experiments to predict long term behavior because concrete continues to hydrate and its pore  
 366 structure densifies and becomes more tortuous.

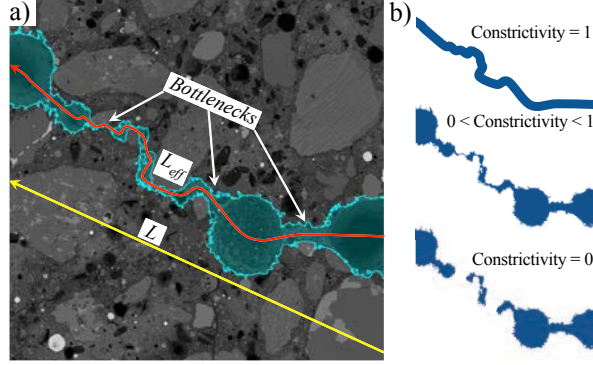


Figure 1: Concrete porous microstructure showing a) tortuous path through pores, and b) different constrictivity conditions

367 As concrete ages, its internal structure changes due to many chemical and physical reac-  
 368 tions that are also influenced by the curing conditions. In the presented model, the evolution of  
 369 porosity and cement hydration is also obtained by employing the HTC model that, once the mix  
 370 composition is given, provides the hydration degree  $\alpha_c$ , capillary water  $w_{cap}$  and non-evaporable  
 371 water  $w_n$  at a specific time. The porosity can be calculated using capillary water content at full  
 372 saturation as  $\phi = w_{cap}^{sat}/\rho_w$ , in which  $w_{cap}^{sat}$  is calculated with  $h = 1$ .

### 373 3.5. Effect of temperature

374 It is well known from thermodynamics that temperature plays a significant role in the diffu-  
 375 sion process. Consequently, the diffusivity of ionic species in pure water varies under different  
 376 temperatures. For this reason, the diffusivity is modified as  $f_T D_0$  to consider the effect of vari-  
 377 able temperature, in which  $D_0$  is determined at the reference temperature  $T_0$  and  $f_T$  is a factor  
 378 expressed as

$$f_T = \exp\left[\frac{U}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \quad (25)$$

379 where  $U$  is the activation energy of the diffusion process.

380 Considering the effect of temperature, the diffusion flux of chloride ions and its divergence  
 381 in a cementitious material in saturated conditions (where the fluid mass is stationary  $v = 0$ ) can  
 382 be written as

$$J_c = f_\phi f_\gamma f_\psi f_s f_T J_0 \quad \text{and} \quad \nabla \cdot J_c = -f_\phi f_\gamma f_\psi f_s f_T D_0 \nabla^2 C = -D_c \nabla^2 C \quad (26)$$

383 where  $D_c$  is the diffusivity coefficient of chloride in concrete,  $D_c = f_s f_\phi f_\gamma f_\psi f_T D_0$ . Combining  
 384 Eqs. 2, 8, and 26, the transport of chloride in saturated conditions ( $\partial h / \partial t = 0$ ) is governed by the  
 385 following equation

$$\left( \frac{w_{cap}}{\rho_w} + \frac{w_s A_0 C_b}{C} \right) \frac{\partial C}{\partial t} + \frac{w_s U_b C_b}{RT^2} \frac{\partial T}{\partial t} = D_c \nabla^2 C - \frac{C \dot{\alpha}_c}{\rho_w} \frac{\partial w_{cap}}{\partial \alpha_c} - (c \dot{\alpha}_c + \dot{w}_n) \frac{C_b}{\rho_s} \quad (27)$$

386 For unsaturated condition the advection term must be considered in  $J_c$  (see Eq. 9). The fluid  
 387 mass velocity,  $v$ , can be expressed as  $v = -J_w / \rho_w$  where  $J_w$  is the flux of water mass per unit  
 388 volume. Following Di Luzio and Cusatis [38],  $J_w$  is proportional to the spatial gradient of  $h$ , thus  
 389 one can write  $J_w = -D_h \nabla h$ , in which  $D_h$  is the moisture permeability that is a nonlinear function  
 390 of  $T$  and  $h$  [38]. This gives  $v = -D_h \nabla h / \rho_w$  and consequently  $J_c = -D_c \nabla C - CD_h \nabla h / \rho_w$ . Then  
 391 the previous Eq. 27 can be generalized for unsaturated conditions as

$$\left( \frac{w_{cap}}{\rho_w} + \frac{w_s A_0 C_b}{C} \right) \frac{\partial C}{\partial t} + \frac{w_s U_b C_b}{RT^2} \frac{\partial T}{\partial t} + \frac{C}{\rho_w} \frac{\partial w_{cap}}{\partial h} \frac{\partial h}{\partial t} = D_c \nabla^2 C + C \frac{D_h}{\rho_w} \nabla^2 h - \frac{C \dot{\alpha}_c}{\rho_w} \frac{\partial w_{cap}}{\partial \alpha_c} - (c \dot{\alpha}_c + \dot{w}_n) \frac{C_b}{\rho_s} \quad (28)$$

#### 392 4. Coupling with the HTC model

393 The spacial and temporal distributions of temperature,  $T$ , relative humidity,  $h$ , and the hydra-  
 394 tion degree,  $\alpha_c$ , are needed for the chloride diffusion model to define both environmental effects  
 395 and concrete aging. These fields are obtained by employing the Hygro-Thermo-Chemical (HTC)  
 396 model by Di Luzio and Cusatis [38, 39], which simulates the coupled heat and moisture transport  
 397 with a good prediction of cement hydration process and its effects on generating heat sources and  
 398 consuming moisture. Following [38, 39] the moisture mass and enthalpy balance equations read:

$$\nabla \cdot (D_h \nabla h) - \frac{\partial w_e}{\partial h} \frac{\partial h}{\partial t} - \frac{\partial w_e}{\partial \alpha_c} \dot{\alpha}_c - \dot{w}_n = 0 \quad (29)$$

$$\nabla \cdot (\lambda_t \nabla T) - \rho c_t \frac{\partial T}{\partial t} + \dot{\alpha}_c c \tilde{Q}_c^\infty = 0 \quad (30)$$

399 where  $D_h$  is moisture permeability,  $w_e$  is evaporable water,  $\dot{w}_n = 0.253\dot{\alpha}_c c$  is rate of non-  
 400 evaporable water,  $\rho$  is the mass density of concrete,  $c_t$  is the isobaric heat capacity (specific  
 401 heat),  $\lambda_t$  is the heat conductivity,  $\tilde{Q}_c^\infty \approx 450$  kJ/kg is the hydration enthalpy.

402 The moisture permeability is dependent on relative humidity  $h$  and temperature  $T$ , as

$$D_h(h, T) = \exp\left(\frac{E_{ad}}{RT_0} - \frac{E_{ad}}{RT}\right) D_{h1} \left[1 + \left(\frac{D_{h1}}{D_{h0}} - 1\right)(1-h)^n\right]^{-1} \quad (31)$$

403 where  $T_0 = 296$  K,  $E_{ad}/R \approx 2700$  K [38, 39],  $D_{h0}$  and  $D_{h1}$  represent moisture permeability for a  
 404 completely dry situation ( $h = 0$ ) and completely saturated situation ( $h = 1$ ). The evaporable wa-  
 405 ter content (the so-called sorption isotherm) can be assumed to be a function of relative humidity  
 406 and degree of hydration [54, 38] as

$$w_e(h, \alpha_c) = k_{vg}^c \alpha_c c \left[1 - \frac{1}{e^{10(g_1 \alpha_c^\infty - \alpha_c)h}}\right] + K_1(\alpha_c) \left[e^{10(g_1 \alpha_c^\infty - \alpha_c)h} - 1\right] \quad (32)$$

407 where the first term represents the gel water (physically bound) whereas the second term rep-  
 408 represents the capillary water  $w_{cap}$ , and  $\alpha_c^\infty$  is the asymptotic degree of hydration. The coefficient  
 409  $K_1(\alpha_c)$  is given by

$$K_1(\alpha_c) = \frac{w_0 - 0.188\alpha_c c - k_{vg}^c \alpha_c c \left[1 - e^{-10(g_1 \alpha_c^\infty - \alpha_c)}\right]}{e^{10(g_1 \alpha_c^\infty - \alpha_c)} - 1} \quad (33)$$

410 The material parameters are  $g_1$  and  $k_{vg}^c$  to be calibrated from experimental data or from multi-  
 411 scale analysis [72]. The moisture capacity is given by  $\partial w_e / \partial h$  (derivative of the sorption isotherm  
 412 to respect to  $h$  that is needed in the first equation in Eq. 29.

413 The hydration degree,  $\alpha_c$ , that represents the fraction of Portland clinker fully reacted with  
 414 water is used to characterize cement hydration [38, 73, 74, 75] and its evolution is expressed as

$$\dot{\alpha}_c = \frac{A_{c1} e^{-\eta_c \alpha_c / \alpha_c^\infty} e^{-E_{ac}/R(T-T_0)}}{1 + (5.5 - 5.5h)^4} \left(\frac{A_{c2}}{\alpha_c^\infty} + \alpha_c\right) (\alpha_c^\infty - \alpha_c) \quad (34)$$

415 where  $E_{ac}/R \approx 5000$  K,  $T_0 = 296$  K,  $\eta_c$ ,  $A_{c1}$ ,  $A_{c2}$  are material parameters to be calibrated  
416 from experimental data or from multi-scale analysis [72]. For details on the calibration and  
417 validation of this theory see [39]. This model was coupled in many research works with LDPM  
418 to successfully represent and predict concrete long term behavior under coupled shrinkage, creep,  
419 ASR degradation [76, 77, 34, 35, 36, 78, 79, 32, 33].

## 420 **5. Numerical implementation**

### 421 *5.1. mesh generation*

422 The proposed model for chloride transport in cementitious materials is implemented into a  
423 discrete conduit network generated from the meso-scale geometry of the Lattice Discrete Par-  
424 ticle Modeling (LDPM) [80, 81] that constructs the discrete mesh considering the geometrical  
425 characterization of concrete heterogeneity. As shown in Fig. 2, the coarse aggregates in con-  
426 crete are assumed to be spherical and then placed through try-and-reject random procedure into  
427 the volume. Based on the Delaunay tetrahedralization from the centers of the considered aggre-  
428 gates a system of polyhedral cells (see Fig. 2) is created using a tessellation procedure. The  
429 surfaces between polyhedral cells are located where the cement paste is likely to be and where  
430 the diffusion/transport phenomena take place.

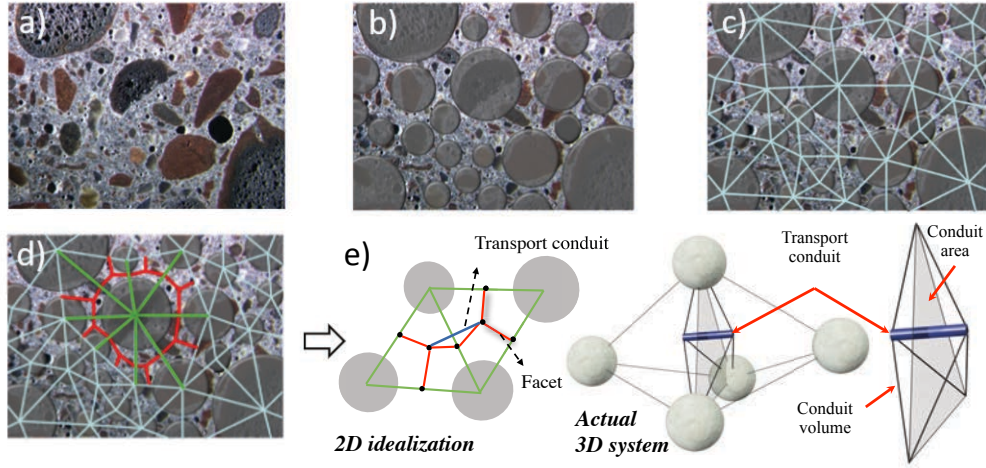


Figure 2: Mesh generation: (a) Concrete material; (b) Supporting particles for grain generation; (c) Delaunay tetrahedralization (d) Tessellation (e) 2D idealization and 3D visualization of the conduit element connecting the centers of two tetrahedrons

431 These preferential diffusion paths are identified by the interconnected tetrahedrons (triangles  
 432 in 2D) that create the transport lattice network, whose nodes coincide with the tessellation points  
 433 and their connection generates the 1D transport conduits, see Fig. 2e. This network of 1D  
 434 transport conduits previously presented by [82], is adopted here to simulate the transport of heat,  
 435 moisture and chloride ions.

436 Compared with standard continuous finite element approaches, the advantage of the discrete  
 437 diffusion network is that it can simulate the transport process anchored in the heterogeneous  
 438 meso-scale structure of the material leading to transport paths of chloride ions that are neither  
 439 straightforward nor homogeneous even at the same depth from the side exposed to the chloride  
 440 solution. Thus the model can capture naturally the tortuosity at the meso-scale that is generated  
 441 by aggregate grain size distribution. However, the tortuosity at finer scales is then captured by  
 442 the apparent tortuosity parameter  $\tau_a$  introduced earlier in Sec. 3.4. Following our main idea  
 443 of keeping the formulation as simple as possible yet capturing as much physics with available  
 444 experimental data, in this study, due to the lack of information about the percentage concentra-  
 445 tions of chlorides within the matrix and aggregate, the conduits represent their volume-averaged  
 446 properties. Nevertheless, the modeling framework is already capable of representing the more

447 complex and realistic conditions if experimental data become available.

448 The computational cost of the proposed diffusion network on a single processor is propor-  
 449 tional to the number of adopted particles due to the explicit integration scheme. For example,  
 450 considering a cylinder of 200 mm high, 75 mm in radius, a discretization with 1934 particles  
 451 (coarse aggregate pieces) ends up with 30468 nodes, while a finer discretization of the same ge-  
 452 ometry containing 4,549 particles will require 70,089 diffusion nodes. Consequently, the com-  
 453 putational process becomes very time-consuming when a large number of particles are present.  
 454 This means that the particle size distribution should be carefully selected so as to achieve a bal-  
 455 ance between computational cost and the geometrical representation of the meso-structure. The  
 456 particles size distribution depends on three parameters, maximum particle size, fuller coefficient,  
 457 and minimum particle size. The first can be obtained directly from the mix design and the sec-  
 458 ond can be identified by fitting the concrete sieve curve. As for the last one, although a small  
 459 minimum particle size characterizes better the heterogeneity of the material, in the meanwhile  
 460 it leads to expensive computational cost. Hence in this study, as specified later in each studied  
 461 case, the minimum particle size is chosen as small as possible while keeping the computational  
 462 cost reasonable.

## 463 5.2. Numerical solution

464 To clarify the numerical solution of the proposed model it is worth rewriting the governing  
 465 differential equation system for 1D case in the following general form

$$\begin{aligned}
 a_{11} \frac{\partial h}{\partial t} + a_{12} \frac{\partial T}{\partial t} + a_{13} \frac{\partial C}{\partial t} &= \frac{\partial}{\partial x} \left( d_{11} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial x} \left( d_{12} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial x} \left( d_{13} \frac{\partial C}{\partial x} \right) + \kappa_1 \\
 a_{21} \frac{\partial h}{\partial t} + a_{22} \frac{\partial T}{\partial t} + a_{23} \frac{\partial C}{\partial t} &= \frac{\partial}{\partial x} \left( d_{21} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial x} \left( d_{22} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial x} \left( d_{23} \frac{\partial C}{\partial x} \right) + \kappa_2 \\
 a_{31} \frac{\partial h}{\partial t} + a_{32} \frac{\partial T}{\partial t} + a_{33} \frac{\partial C}{\partial t} &= \frac{\partial}{\partial x} \left( d_{31} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial x} \left( d_{32} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial x} \left( d_{33} \frac{\partial C}{\partial x} \right) + \kappa_3
 \end{aligned} \tag{35}$$

466 Since the governing equations presented in the proposed model are not fully coupled, some  
 467 of the coefficients in the previous Eq. 35 are null, i.e.  $a_{12} = a_{13} = a_{21} = a_{23} = 0$  and  $d_{12} =$   
 468  $d_{13} = d_{21} = d_{23} = d_{32} = 0$ . The expressions of the other coefficients are  $a_{11} = \partial w_e / \partial h$ ,  $a_{22} = \rho c_t$ ,  
 469  $a_{31} = C / \rho_w (\partial w_{cap} / \partial h)$ ,  $a_{32} = w_s U_b C_b / R T^2$ ,  $a_{33} = w_{cap} / \rho_w + w_s A_0 C_b / C$ ,  $d_{11} = D_h$ ,  $d_{22} = \lambda_t$ ,

470  $d_{31} = CD_h/\rho_w$ ,  $d_{33} = D_c$ ,  $\kappa_1 = -(\partial w_e/\partial \alpha_c)\dot{\alpha}_c - \dot{w}_n$ ,  $\kappa_2 = \dot{\alpha}_c C \tilde{Q}_c^\infty$ ,  $\kappa_3 = -C\dot{\alpha}_c/\rho_w(\partial w_{cap}/\partial \alpha_c) -$   
471  $(c\dot{\alpha}_c + \dot{w}_n)C_b/\rho_s$ . Considering a 1D transport conduit, using the classical Galerkin method to  
472 obtain the weak formulation of the differential problem and a finite element approximation of  
473 the primary variables,  $T(x, t) \cong \sum_i^N T_i(t)N_i(x)$ ,  $h(x, t) \cong \sum_i^N h_i(t)N_i(x)$ , and  $C(x, t) \cong \sum_i^N C_i(t)N_i(x)$   
474 ( $N_i(x)$  are linear 1D shape functions), and assembling the total element level matrices, one can  
475 obtain the global equation as following

$$\mathbf{M}\dot{\mathbf{u}} + \mathbf{K}\mathbf{u} = \mathbf{F} \quad (36)$$

476 where  $\mathbf{u}$  is the vector of nodal quantities  $\{h \ T \ C\}^T$ , the dot over  $\mathbf{u}$  indicates temporal derivative,  
477 the matrices  $\mathbf{M}$ ,  $\mathbf{K}$ , and the vector  $\mathbf{F}$  are obtained by the global assemblage of element level  
478 matrices given by

$$\mathbf{M}^{el} = \frac{A_e l_e}{6\delta} \begin{bmatrix} 2a_{11} & 0 & 0 & -a_{11} & 0 & 0 \\ 0 & 2a_{22} & 0 & 0 & -a_{22} & 0 \\ 2a_{31} & 2a_{32} & 2a_{33} & -a_{31} & -a_{32} & -a_{33} \\ -a_{11} & 0 & 0 & 2a_{11} & 0 & 0 \\ 0 & -a_{22} & 0 & 0 & 2a_{22} & 0 \\ -a_{31} & -a_{32} & -a_{33} & 2a_{31} & 2a_{32} & 2a_{33} \end{bmatrix} \quad (37)$$

$$\mathbf{K}^{el} = \frac{A_e}{l_e} \begin{bmatrix} d_{11} & 0 & 0 & -d_{11} & 0 & 0 \\ 0 & d_{22} & 0 & 0 & -d_{22} & 0 \\ d_{31} & 0 & d_{33} & -d_{31} & 0 & -d_{33} \\ -d_{11} & 0 & 0 & d_{11} & 0 & 0 \\ 0 & -d_{22} & 0 & 0 & d_{22} & 0 \\ -d_{31} & 0 & -d_{33} & d_{31} & 0 & d_{33} \end{bmatrix} \quad (38)$$

$$\mathbf{F}^{el} = \frac{A_e l_e}{2\delta} [\kappa_1 \ \kappa_2 \ \kappa_3 \ \kappa_1 \ \kappa_2 \ \kappa_3 ]^T \quad (39)$$

479 where  $l_e$  is the conduit length,  $A_e$  is the conduit area at the interface between the two interacting



480 tetrahedrons (projection of the shaded area along the direction of  $l_e$ ). Since the conduit represents  
 481 a volume defined by double pyramids (see Fig. 2e),  $\delta = 3$  is used to represent the correct element  
 482 volume.

483 Temporal integration of Eq. 36 is performed by applying Crank-Nicolson method (a central  
 484 difference method) which has been widely used as a numerical solution for partial differential  
 485 equations due to its unconditional stability (for constant coefficients). For each time step, from  
 486  $t_n$  to  $t_{n+1} = t_n + \Delta t$ , Eq. 36 is solved using the Crank-Nicolson method as

$$\left( \mathbf{M}_{n+1/2} - \frac{1}{2} \Delta t \mathbf{K}_{n+1/2} \right) \mathbf{u}_{n+1}^i = \left( \mathbf{M}_{n+1/2} + \frac{1}{2} \Delta t \mathbf{K}_{n+1/2} \right) \mathbf{u}_n + \Delta t \mathbf{F}_{n+1/2} \quad (40)$$

487 This calculation is repeated updating the coefficients,  $\mathbf{M}_{n+1/2}$ ,  $\mathbf{K}_{n+1/2}$ , and  $\mathbf{F}_{n+1/2}$  using the mid  
 488 time-step value,  $(\mathbf{u}_{n+1}^{i+1} + \mathbf{u}_{n+1}^i)/2$ , until the convergence is achieved, i.e. the Euclidean norm of the  
 489 difference of nodal values between two iterations is satisfactorily small,  $\|\mathbf{u}_{n+1}^{i+1} - \mathbf{u}_{n+1}^i\| < 10^{-4}$ .

490 Finally, the numerical calculation of the proposed formulation requires, at each discrete el-  
 491 ement, the time integration of the internal variables, such as the hydration degree. Express-  
 492 ing an internal variable as  $y$  the time-dependent evolution law can be generally written as  $\dot{y} =$   
 493  $f(y, h, T, C)$ . It can be effectively integrated using the second order Runge-Kutta formula (mid-  
 494 point method), in this way the value of the internal variable  $y_{n+1}$  at time  $t_{n+1}$  is evaluated as  
 495  $y_{n+1} \approx y_n + \Delta t_n f(y_{n+1/2}, h_{n+1/2}, T_{n+1/2}, C_{n+1/2})$ , in which  $y_n$  is the value of the internal vari-  
 496 able at time  $t_n$ ,  $\Delta t_n$  is the time increment,  $y_{n+1/2} = (y_{n+1} + y_n)/2$ ,  $h_{n+1/2} = (h_{n+1} + h_n)/2$ , and  
 497  $T_{n+1/2} = (T_{n+1} + T_n)/2$ .

498 The proposed formulation is implemented in Mars, a multi-purpose computational software  
 499 for the explicit dynamic simulation of structural performance [83].

## 500 6. Identification of model parameters

501 As explained before, the model accounts for multiple physical phenomena yet, it uses lit-  
 502 erature published data regarding many of the physical quantities involved in representing such  
 503 phenomena. Note that the chloride diffusion model also depends on the HTC model. To sum-  
 504 marize all these model parameters (both the chloride diffusion and the HTC model parameters),

505 Table 1 enlists each group of parameters that are used to represent a specific phenomenon. In  
506 the table, values and sources are listed for all independently measured or reasonably assumed  
507 parameters.

Table 1: Known or independently identified parameters used in different modeled phenomena

Modeled Phenomena	Parameter (unit)	Value [source]	Parameter (unit)	Value [source]
Cement hydration	$E_{ac}/R$ (K)	5000 [74]	$A_{c1}$ ( $\text{h}^{-1}$ )	$1.50 \times 10^7$ [39]
	$A_{c2}$ (-)	$1.0 \times 10^{-4}$ [39]	$\eta_c$ (-)	5.5 [39]
Sorption isotherm	$k_{vg}^c$ (-)	0.2 [39]	$g_1$ (-)	1.25 [39]
Moisture diffusion and heat transfer	$E_{ad}/R$ (K)	2700 [84]	$\lambda_t$ (W/m °C)	2.3 [85]
	$c_t$ (J/kg/K)	1100 [86]	$Q_c^\infty$ (kJ/kg)	450 [36]
	$T_0$ (K)	296 [defined]		
Concrete compo- nents densities	$\rho$ ( $\text{kg}/\text{m}^3$ )	2400 [86]	$\rho_c$ ( $\text{kg}/\text{m}^3$ )	1800 [86]
	$\rho_s$ ( $\text{kg}/\text{m}^3$ )	2340 [87]		
Chloride chemical activity	$A_\gamma$ ( $\text{dm}^{0.5}/\text{mol}^{0.5}$ )	0.509 [61]	$a'$ (nm)	0.4 [61]
	$B_\gamma$ ( $\text{dm}^{0.5}/(\text{mol}^{0.5} \cdot \text{nm})$ )	3.286 [61]	$B^*$ (dm/mol)	0.045 [61]
Pore solution chemistry	$K_{r0}$ (-)	-0.207 [14]	$K_{rm}$ (-)	-0.402 [14]
	$D_0$ ( $\text{m}^2/\text{s}$ )	$2.03 \times 10^{-9}$ [14]	$C_0$ ( $\text{mol}/\text{m}^3$ )	55000 [calculated]
Charge and ion identification	$z_+$	+1 [60]	$z_-$	-1 [60]
	$n_+$	1 [60]	$n_-$	1 [60]

508 The rest of the model parameters need to be calibrated using specific experimental data rele-  
509 vant to them. Typically, there are two sets of parameters to be calibrated. The first set is relevant  
510 to the HTC model and is based on the concrete mix design, curing conditions and ageing. Since  
511 the chloride penetration model depends on  $\alpha_c$ ,  $h$ , and  $T$  to capture various microstructural effects  
512 as well as thermal and hygral effects, HTC model parameters must be determined first so that  
513 their calibration process does not affect the robustness of the calibration of the chloride diffusion  
514 parameters. This condition is followed in all calibrations performed in this work. In some cases

515 though, chloride penetration tests are performed on samples that have already reach a significant  
516 degree of hydration (old enough) and the tests are performed under isothermal and fully saturated  
517 conditions. For such cases, the pore structure characteristics are fixed and no heat or moisture  
518 sources/sinks are present. As a result, the pore structure effect is not changing. This means that  
519 even if not enough data is present about the exact composition of the material, chloride penetra-  
520 tion parameters can be still calibrated after choosing appropriate values of the HTC parameters  
521 from literature. In this case, one must notice that the identified parameter values will be sensitive  
522 to the difference between assumed HTC parameters and the ones representing the actual material.  
523 Yet, this is an acceptable approximation if experimental data to evaluate the hydration degree and  
524 other HTC related phenomena are lacking. The detailed procedure regarding the calibration of  
525 HTC parameters and the needed experiments to perform the calibration are described in [39] to  
526 which the reader is directed for additional information.

527       Regarding the proposed chloride penetration model, the presented formulation has only four  
528 basic free parameters under isothermal conditions that need to be identified from experimental  
529 results: apparent tortuosity factor  $\tau_a$ , the friction coefficient  $f_v$ , and two material parameters re-  
530 lated to binding capacity,  $A_0$  and  $B_0$ . Typically, all parameters can be calibrated using chloride  
531 penetration profiles data. The apparent tortuosity factor  $\tau_a$  plays an important role in the chloride  
532 penetration depth. Parameters  $A_0$  and  $B_0$  determine the binding capacity and can be identified  
533 by fitting the bound or total chloride concentration at the boundary, where the free chloride con-  
534 centration is always equal to the chloride concentration in the external solution. The friction  
535 coefficient  $f_v$  represents the concentration dependence of chloride diffusion, and it influences the  
536 curvature of the concentration-depth profile. Therefore, ideal identification of the four param-  
537 eters can be achieved using two chloride concentration-depth profiles relevant to two different  
538 boundary concentrations. First,  $A_0$  and  $B_0$  are identified by matching the chloride concentration  
539 at the surface, then  $\tau_a$  is calibrated by matching the chloride penetration depth, and finally  $f_v$   
540 is calibrated by fitting the curvature. Of course, due to experimental data scatter and the slight  
541 dependence of the concentration-depth profile on each of the parameters, fine tuning is typically  
542 inevitable but based on the calibrations performed in this work, fine tuning is very minimal if

Table 2: Chloride diffusion model calibrated free parameters

Parameter	Symbol (unit)	Sec. 7.1	Sec. 7.2	Sec. 7.3	Sec. 7.4
Apparent tortuosity	$\tau_a$ (-)	0.054	0.11	0.4	0.06
Material parameter for chloride binding	$A_0$ (-)	0.45	0.55	0.7	0.5
Material parameter for chloride binding	$B_0$ (-)	1.0	1.46	1.9	1.25
Friction coefficient	$f_v$ (-)	400	600	600	500
Activation energy for chloride diffusion	$U$ (J/mol)	-	22450	40000	-
Activation energy for chloride binding	$U_b$ (J/mol)	-	5810	33200	-

543 two experimental curves are used. Note that all of these four parameters have to be identified at  
544 the same reference temperature  $T_0$  (typically room temperature).

545 To consider the effect of temperature variation, two additional parameters need to be cali-  
546 brated by fitting an additional chloride concentration-depth profile at a different temperature  $T$ :  
547 the activation energy of the diffusion process  $U$  and the activation energy for the binding process  
548  $U_b$ . The parameter  $U$  considers the effect of temperature on the diffusivity, so it can be calibrated  
549 by matching the change in maximum penetration depth.  $U_b$  considers the effect of temperature  
550 on binding capacity, so it can be calibrated by matching the bound or total concentration at the  
551 boundary. Thus, for cases with thermal changes, a minimum of three chloride concentration-  
552 depth profiles are needed, two of them relevant to two different boundary concentrations and  
553 one of them is at the same boundary concentration of either of the first two but at a different  
554 temperature.

555 It is important to say that the aforementioned calibration procedure represents an ideal case  
556 in which, all the needed experimental data are available. For cases where parts of the data are not  
557 available, or if data is very scattered, one can slightly deviate from this procedure yet all efforts  
558 have to be made to follow it as closely as possible.

## 559 7. Numerical simulations of experimental literature

560 The three-dimensional diffusion network, shown in Fig. 2e and presented in the previous sec-  
561 tion, is hereafter used to simulate chlorides diffusion in cementitious materials. The capability  
562 of the proposed model is verified through the numerical simulations on both cement paste and  
563 concrete. The numerical simulations are performed with reference to four experimental data sets

564 taken from the literature. The data were chosen to represent simple to complex cases, starting  
565 with tests on cement paste at constant [88] and different temperatures [22], then tests on concrete  
566 samples with different temperature and chloride concentration combinations [23]. These three  
567 different tests cover all model functionality under fully saturated conditions. The last set of exper-  
568 iments is relevant to testing chloride penetration in partially saturated concrete [24] which attests  
569 to effectiveness of the model since it does not postulate any phenomenological assumptions to  
570 account for non-saturated flow conditions and it just covers it through the coupling between the  
571 different physical processes.

### 572 *7.1. Diffusion in saturated cement paste: Effect of exposure duration*

573 The first experimental investigation considered in this study is reported in [88] in which they  
574 adopted X-ray scanning to measure iodide ions instead of chloride ions to quantify the chloride  
575 transport, based on the fact that although iodide and chloride ions have similar penetration depth  
576 the latter is much more convenient to detect. With a mixture proportion that comprised 850 g  
577 cement (US ASTM C150 Type I) and 340 g water, samples were cast and cured for 35 days  
578 immersed in water. All samples are 9.5 mm in diameter and 30 mm in height.

579 Later the samples were sealed at room temperature (23 °C) for 50 days. Following that,  
580 the top end of the sample was covered with 0.6 mol/L potassium iodide solution up to 14 days.  
581 The curing conditions and the experimental procedure are accurately modelled in the numerical  
582 analyses.

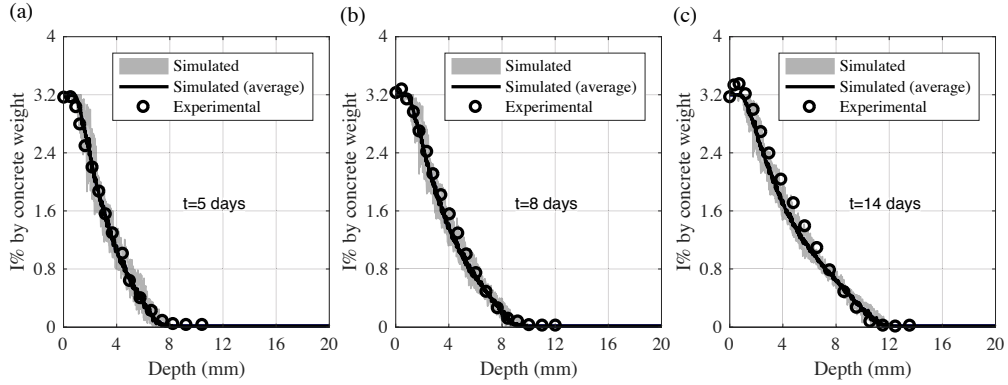


Figure 3: Experimental [88] and numerical results of iodine penetration for different ponding durations: a) 5 days; b) 8 days; c) 14 days

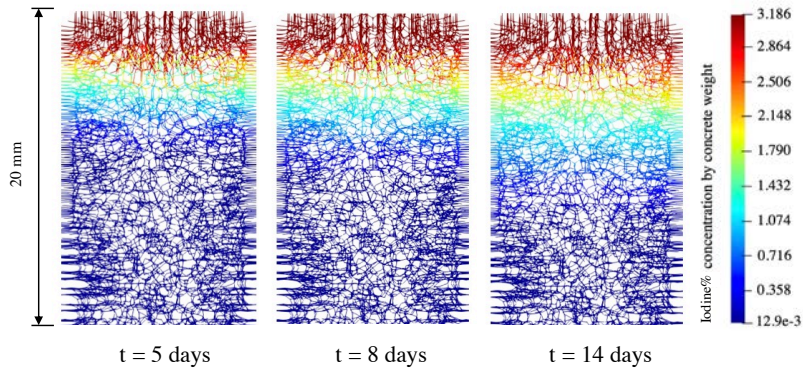


Figure 4: Contour of iodine concentration for different ponding durations

583 The test results after 14-day ponding are used for calibration (see Fig. 3c). In performing  
 584 the calibrations, since only one chloride concentration is used, the ideal calibration procedure  
 585 couldn't be followed. Nevertheless, by assuming an initial reasonable value for  $A_0$  and  $B_0$ , they  
 586 were easily fine tuned by matching the surface concentration at 14 days (Fig. 3c). Next, the extent  
 587 was matched by calibrating  $\tau_a$  and then the curvature was matched by calibrating  $f_v$  following  
 588 the ideal calibration procedure.

589 The calibrated parameters values are shown in Table 2 (column 1). It should be noted that,  
 590 although KI solution was used in the experiment the calibration is based on NaCl since the anions  
 591 in the two solutions have similar diffusion coefficient in concrete [88, 89] and the experiment

592 used iodide ions to study chloride diffusion because Iodine has higher fluorescence and thus,  
593 easier to measure using X-ray techniques. So, by using the calibrated parameters, simulations  
594 of the profiles at 5 and 8 days are used as validations (see Fig. 3a and Fig. 3b). By examining  
595 the surface concentrations at 5 and 8 days, it is clear that the chosen values for  $A_0$  and  $B_0$  seem  
596 reasonable since the surface concentrations match exactly the same surface concentration at 14  
597 days.

598 Note that due to the discrete heterogeneous geometry of the diffusion network, the numerical  
599 value of the chloride concentration varies even at the same cutting section. Therefore, in all the  
600 plots in Fig. 3, the simulated scatter is reported (grey area) together with the average value of the  
601 numerical chloride concentration results that can be compared with the experimental data. This  
602 comparison shows a very good match since the numerical simulations capture pretty well the  
603 growth of the chloride concentration as the ponding time increases. It is important to notice here  
604 that the mesh used was generated using a fictitious aggregate size distribution with a maximum  
605 aggregate size of 0.9 mm and a minimum of 0.45 mm with 0.6 Fuller coefficient. This guarantees  
606 simulating 34% of the coarse aggregate as typically recommended in LDPM literature [80, 81,  
607 90, 91]. The maximum aggregate size was chosen to be no more than 10% of the minimum  
608 sample dimension (9.5 mm) in order to reduce the scatter. Nevertheless, due to the discrete nature  
609 of the model, there will always be a small scatter but to keep the computational cost reasonable,  
610 the chosen maximum aggregate size was slightly lower than 10% of the minimum dimension.  
611 Yet, our preliminary simulations show that if a coarser mesh is used, the scatter will increase but  
612 the average line stays almost the same which validates the acquired results and proves that the  
613 scatter is not an artifact but it represents a meso-scale measure of heterogeneity. The resulting  
614 conduit transport networks are shown in Fig. 4 and are colored based on the weight percentage  
615 of iodine in the cement paste.

## 616 7.2. Diffusion in saturated cement paste: Effect of ponding temperature

617 The second experimental investigation considered is described in [22]. They casted cylin-  
618 drical specimens with ordinary Canadian Type 10 portland cement (diameter= 70 mm, height  
619 = 200 mm, cement content = 380 kg/m<sup>3</sup>,  $w/c = 0.6$  ). After three months of curing in 100%

620 relative humidity fog room, the samples were cut into 50-mm disks and were sealed on the bot-  
621 tom and on the lateral surface and then immersed for 100 days in 0.5 mol/L NaCl solution at  
622 different temperatures, 4 °C, 23 °C and 38 °C. Similarly here, only the profiles relevant to a  
623 single chloride concentration are available, thus, the same procedure as specified in the previous  
624 section is used. First, the chloride penetration profile at room temperature, 23 °C, is used to cal-  
625 ibrate the 4 basic parameters, and then the experimental results at 4 °C are used to calibrate the  
626 two activation energies,  $U$  and  $U_b$ . All the calibrated parameters values are reported in Table 2  
627 (column 2). Figure 5 shows the comparisons between numerical solutions and experimental data,  
628 in which the agreement is very good. As temperature grows from 4 °C to 23 °C, the chloride  
629 concentration increases and is captured by the model. Nevertheless, at 38 °C, the concentration  
630 of chloride ions near the top end is slightly lower than the concentration for 23 °C, contrary to  
631 what one would expect. Despite this small inconsistency in the experimental data, the numerical  
632 values of the chloride concentration present the expected trend near the top end and match pretty  
633 well the experimental data at deeper depth. It is important to note here that the provided experi-  
634 mental data represents an average value of chloride contents determined using ASTM C1556  
635 [92] layer-by-layer acid dissolution procedure at 2–3 mm depth increments. Therefore, experi-  
636 mental scatter and resolution inaccuracy is expected, and thus, the observed slight deviation of  
637 the expected increasing trend of chloride concentration at the surface with increased temperature  
638 is very well acceptable. Similarly, here also, the conduit transport network is generated using  
639 an aggregate size range of 3 mm to 6 mm with the maximum aggregate size slightly lower than  
640 10% of the minimum dimension (70 mm). Again, the gray area representing simulation scatter  
641 is also very narrow. The distribution of chloride ions within the transport network in the three  
642 concrete samples is presented in Fig. 6 at the different exposure temperatures. Note that in all  
643 figures since the chloride ions did not diffuse through the whole depth, only the active part is  
644 shown.



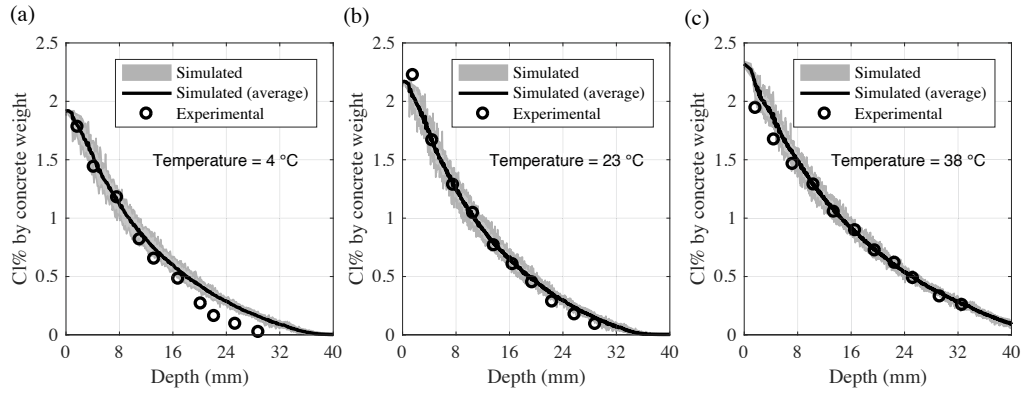


Figure 5: Experimental [22] and numerical results of chloride penetration at different temperatures: a) 4 °C; b) 23 °C; c) 38 °C

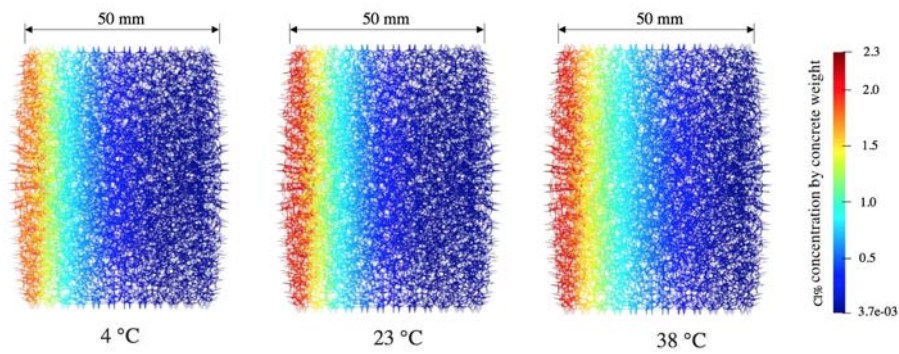


Figure 6: Contour of chloride concentration at different temperatures from simulation

### 645 7.3. Diffusion in saturated concrete

646 Ordinary concrete is a multi-phase composite material in which the aggregate pieces are  
 647 relatively impermeable and any diffusion process takes place mostly in the cement paste and  
 648 interfacial transition zone. Many researchers [16, 20, 93] investigated the influence of aggregate  
 649 content on chloride ingress and concluded that the addition of aggregate does influence chloride  
 650 diffusion due to the different overall porosity of concrete as compared to that of cement paste.  
 651 In the proposed model the porosity of concrete  $\phi$  is analyzed based on the HTC model and the  
 652 influence of aggregate on the diffusion path of chloride is considered by tortuosity parameter  $\tau_a$   
 653 in Eq. 23.

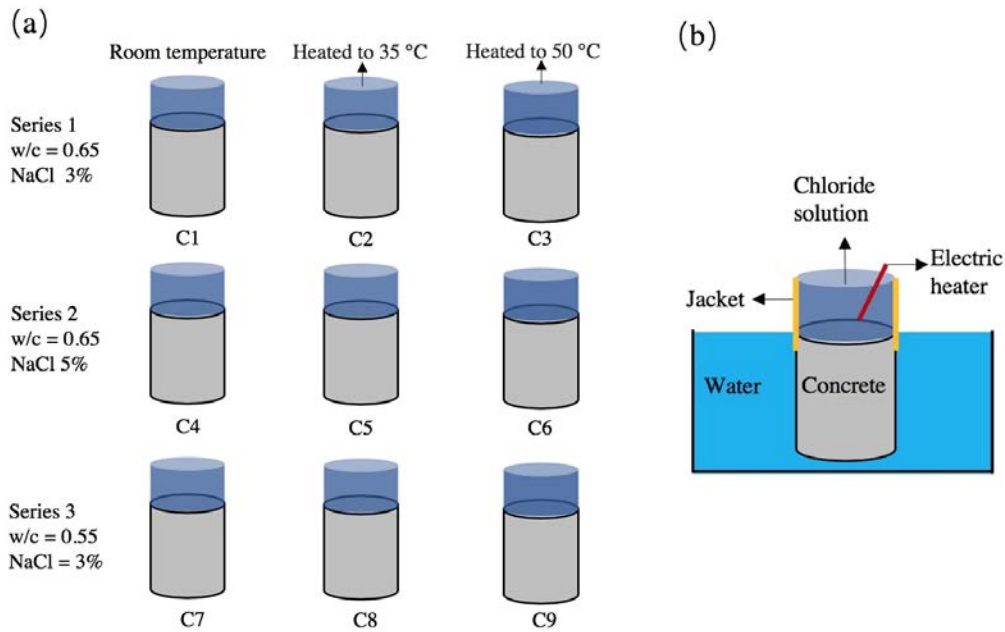


Figure 7: Experimental investigation from [23] (a) Testing series and experimental parameters (b) Experimental setup

654 In the previous sections, the effect of aggregate is not considered since the numerical analyses  
 655 concern only cement paste. Herein the effectiveness of the model in simulating concrete is  
 656 analyzed with reference to a complete experimental study conducted by Isteita and Xi [23].  
 657 They performed ponding tests, summarized in Figure 7a, that comprised three series exposed to  
 658 different temperature gradients and chloride concentrations. There were three specimens of the  
 659 same mix in all three series and all of them were cylinders with 150 mm in diameter and 200  
 660 mm in height. The first and second series used a mix that contains  $356 \text{ kg/m}^3$  of cement (ASTM  
 661 C150 Type I) with 0.65  $w/c$  and 5.28 aggregate to cement ratio. The third series used a mix that  
 662 contains  $380 \text{ kg/m}^3$  of cement (ASTM C150 Type I) with 0.55  $w/c$  and 4.24 aggregate to cement  
 663 ratio. For both mixes, aggregate size distribution data was not reported so, a maximum aggregate  
 664 size of 19 mm, a minimum aggregate size of 5 mm, and a fuller coefficient of 0.5 are assumed in  
 665 the simulation for such a typical concrete mixture. Using these data one can construct the LDPM  
 666 mesh and then create the conduit mesh as explained before. Note here that all coarse aggregate  
 667 volume was represented since the chosen minimum aggregate size is the typical limit between

668 coarse and fine aggregate. This guarantees that the generated conduit network is rich enough so  
669 that the conduits are passing throughout mortar only.

670 After twenty-eight-day curing all samples were immersed in distilled water (see Fig.7b) and  
671 ponding tests were performed from the top ends with a solution of 3%, 5% and 3% chloride  
672 concentration (mass fraction) for the three series, respectively, at three constant temperatures  
673 of 23 °C, 35 °C and 50 °C in each series. The chloride concentration at different depths was  
674 evaluated for five different durations of ponding: 3 days, 6 days, 12 days, 24 days, and 48 days.  
675 Since the temperature of the distilled water is relatively constant, 20 °C, the ponding tests were  
676 thus performed under a temperature gradient. More details on the experimental investigation can  
677 be found in [23].

678 In the numerical simulation to accurately impose the temperature boundary conditions, the  
679 temperature of the top surface of the specimen is set as the corresponding temperature of the  
680 chloride solution whereas the temperature of the other external surfaces is set at the initial en-  
681 vironmental temperature of 20 °C and then kept constant. Different from previous experimen-  
682 tal investigations which are strictly 1-D transport, the setup in this experiment might cause a  
683 non-uniform transport of chloride ions along a cross-section due to the temperature difference  
684 between the side surface and the inside core. As the penetration goes on, a temperature gradient  
685 along the cross section of the cylinder is created. Chloride ions near the core concrete transport  
686 faster due to a higher temperature, compared with those near the side surface. As the ponding test  
687 continues, the differences accumulate gradually, resulting in a non-uniform chloride distribution  
688 along the cross section. To visualize this profile, the chloride concentration field was interpolated  
689 from the diffusion network on a tetrahedral mesh sharing the same diffusion network nodes and  
690 then the volume was colored by the field values as shown in Fig. 8. One can see the slice taken  
691 at 13 mm depth showing clearly the higher chloride concentrations in the middle. Note also the  
692 ability of the model to scatter the concentrations across the specimen. As opposed to any other  
693 continuum model, while there is an obvious concentration gradient from the center towards the  
694 edge (See Fig. 8a), the gradient is not axisymmetric but rather shows irregular variations. These  
695 variations are due to the scatter of the diffusion network around the aggregate. It is also impor-

696 tant to mention that in the experiments, concrete powder was collected by drilling a small hole  
 697 at the center of the sample then, this powder was used to determine the chloride concentration  
 698 using ASTM C1152/C1152M-04(2012) [92]. To mimic the experiments numerically, only the  
 699 numerical results within an inner core with one third of the original radius are considered when  
 700 analyzing the chloride concentration profile. The one third value was chosen by best guess since  
 701 the drilling diameter was not reported in the experiments.

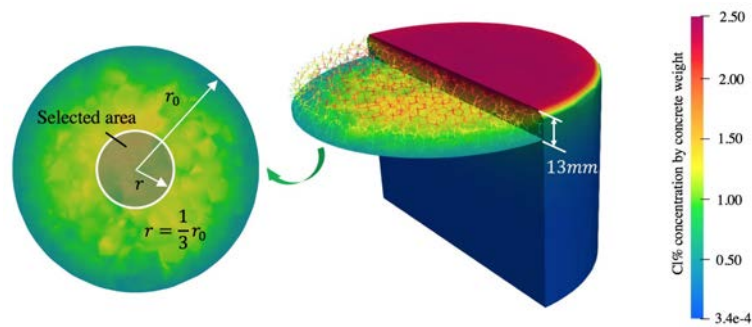


Figure 8: Numerical results of chloride distribution of sample C3 after 48-day ponding. cross section at depth = 13 mm, vertical section along central axis.

702 To perform a more accurate calibration, the four basic parameters  $\tau_a$ ,  $A_0$ ,  $B_0$  and  $f_v$  were  
 703 calibrated by fitting the 3-day and the 48-day ponding curves obtained under room temperature,  
 704 23 °C, in series 1 and 2 (with 3% and 5% chloride concentrations, respectively). The corre-  
 705 sponding best fitting plots are shown in Figs. 9a and 9e and Figs. 10a and 10e. Then activation  
 706 energy  $U$  and  $U_b$  are calibrated by fitting the 48-day experimental data under temperature of  
 707 35 °C in series 1, as shown in Fig. 9e. In this calibration, five curves were used instead of the  
 708 ideal three curves mentioned in the calibration procedure. This was because of the large scatter  
 709 of the experimental data.

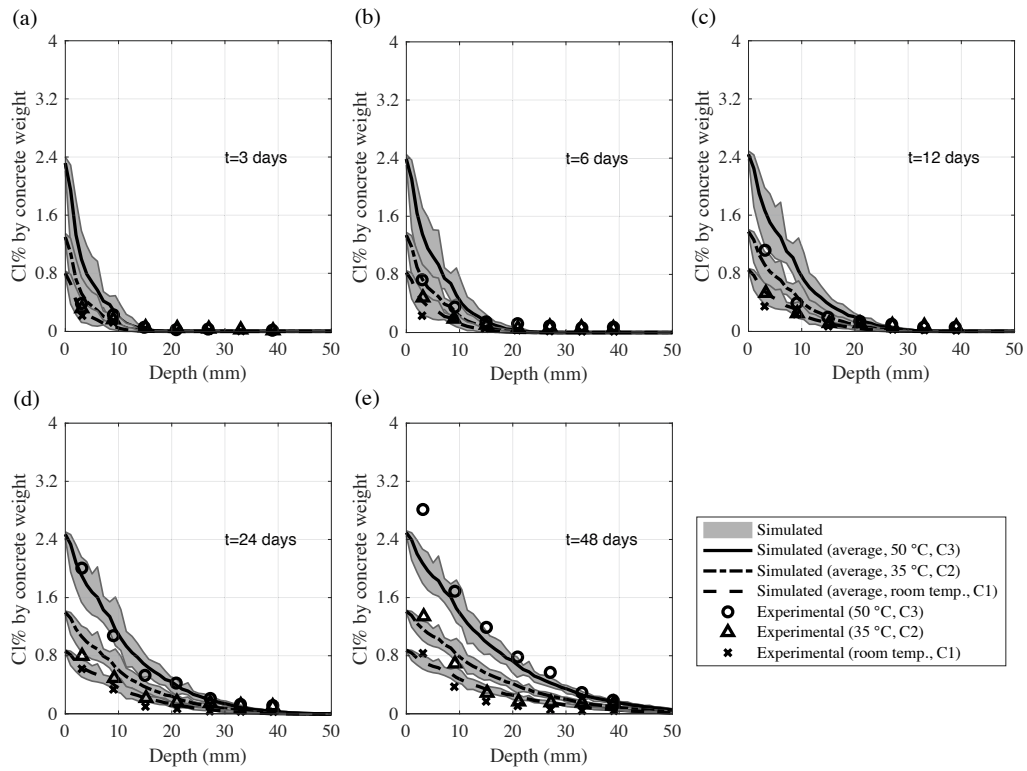


Figure 9: C1 ~ C3 experimental [23] and numerically simulated chloride penetration for different ponding durations,  $w/c = 0.65$ , NaCl concentration = 3%: (a) 3 days; (b) 6 days; (c) 12 days; (d) 24 days; (e) 48 days.

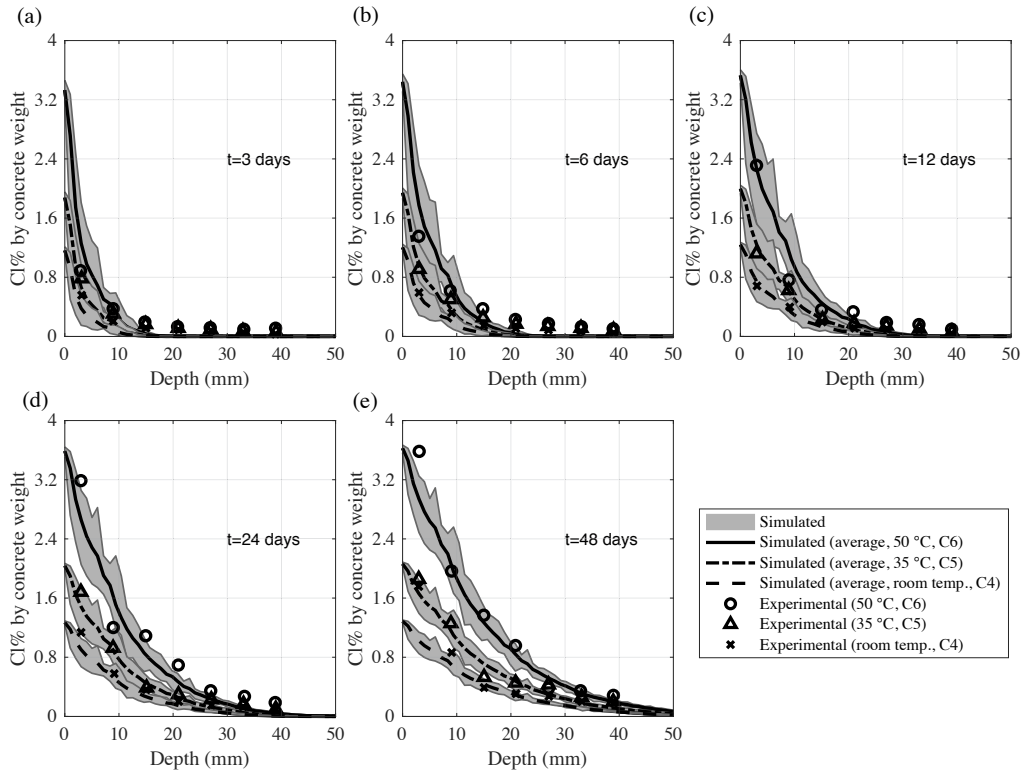


Figure 10: C4 ~ C6 experimental [23] and numerically simulated chloride penetration for different ponding durations,  $w/c = 0.65$ , NaCl concentration = 3%: (a) 3 days; (b) 6 days; (c) 12 days; (d) 24 days; (e) 48 days.

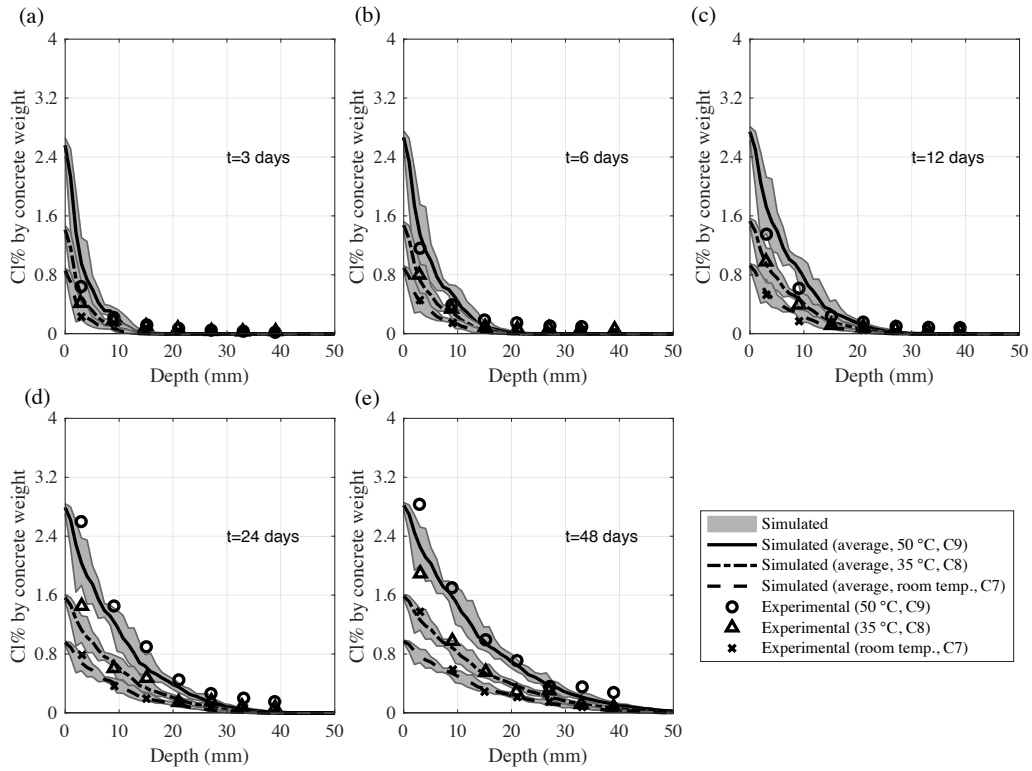


Figure 11: C7 ~ C9 experimental [23] and numerically simulated chloride penetration for different ponding durations,  $w/c = 0.65$ , NaCl concentration = 3%: (a) 3 days; (b) 6 days; (c) 12 days; (d) 24 days; (e) 48 days.

710 It should be noted that although series 3 has different  $w/c$  from series 1 and 2, it is assumed  
 711 that the pore structure was shaped with similar tortuosity since the  $w/c$  are close (0.55 and 0.65).  
 712 Thus, the effect of  $w/c$  was totally lumped in the porosity (acquired from the HTC model) and the  
 713 same apparent tortuosity factor is employed for series 3. Additionally, the values of the material  
 714 parameters  $A_0$  and  $B_0$  are kept unchanged according to the findings in [45], which shows  
 715 that the bound chloride in relation to the free chloride could be considered independent from the  
 716 water-cement ratio if the amount of bound chloride is re-scaled per cement content. By using the  
 717 same parameter values in all the series, it is shown that the proposed model is capable of capturing  
 718 automatically the influence of different  $w/c$ . Nevertheless, if the  $w/c$  varies significantly, it is  
 719 expected that the pore structure characteristics may be more noticeably different and thus, the  
 720 apparent tortuosity factor may need to be recalibrated. All calibrated values are listed in Table 2

721 (column 3). As a strong validation of the model, all simulations of the remaining experimental  
722 results serve as validations.

723 The validation of the model is presented in Fig. 9~ 11 by comparing experimental and  
724 numerical results. The agreement is overall excellent, which proves that the proposed model  
725 is able to predict the chloride ingress in concrete. Fig. 9 ~11 show, for various temperature  
726 gradients, the chloride penetration after ponding for 3, 6, 12, 24, and 48 days. As it can be  
727 observed in the plots, the higher the temperature gradient is, the faster the chloride ions ingress  
728 and the more chloride ions get bound into the gel. This proves that the temperature effect has to  
729 be considered using two different activation energies as proposed by the model for the diffusion  
730 and binding through the exponential coefficient presented in Eq. 5 and Eq. 25.

731 Fig.10 shows the chloride profile in series 2 test, which had higher concentration of NaCl on  
732 the boundary (5%) than series 1 and the same other boundary conditions. So, as expected, the  
733 three samples of series 2 present an higher chloride concentration profile than the corresponding  
734 samples in series 1 for each ponding duration. This feature is well captured by the numerical  
735 simulation using the same parameters as in series 1.

736 Finally, Fig. 11 shows the chloride penetration profile of series 3 for the samples C7~C9  
737 with a lower water-cement ratio of 0.55 and the same boundary conditions as in series 1. Also  
738 in this case the numerical analyses are performed using the same parameters as discussed be-  
739 fore without any changes. Comparing the experimentally measured chloride profiles in series 1  
740 (Fig. 9) and series 3 (Fig. 11), the chloride concentration near the top surface of samples are  
741 relatively higher in series 3 than that in series 1. This can be caused by the increase of hydrated  
742 cement content in series 3, which increases the amount of chloride ions bound to the matrix,  
743 although the lower  $w/c$  produces a relatively smaller porosity that reduces the chloride diffu-  
744 sivity. This difference reaches its maximum at the top surface that is immersed in the external  
745 chloride solution with the free chloride content almost constant. This behavior is fully captured  
746 by the proposed the model as shown by Fig. 12 in which the free (Fig. 12a) and bound (Fig. 12b)  
747 chloride contents in the two series are compared. As shown in the Fig. 12, close to the exposed  
748 surface, both free and bound chloride concentrations in sample C8 are higher than that in sample



749 C2. Considering the fact that the concentration of bound chloride is higher than free chloride by  
 750 about an order of magnitude, the increased total chloride concentration in sample C8 is mainly  
 751 attributed to the binding process. Farther away from the exposed external surface, bound chloride  
 752 and free chloride concentration in sample C2 and C8 become nearly the same, implying that the  
 753 chloride penetration front is not substantially affected by the change of pore structure due to  $w/c$   
 754 difference. This observation also supports the use of a constant tortuosity factor for all series  
 755 samples.

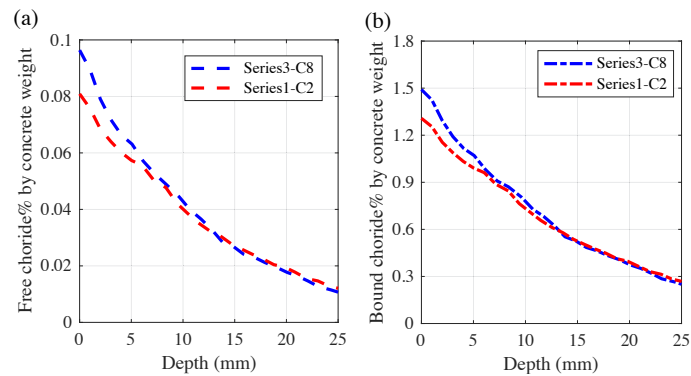


Figure 12: Comparison of free and bound chloride: (a) Free chloride in sample C2 and C8. (b) Bound chloride in sample C2 and C8

756 To summarize the observations from the simulation of this large set of experiments, the en-  
 757 velops between 6 and 48 days of ponding of both experimental and numerically simulated chlo-  
 758 ride concentration profiles for the three series at all three temperatures are shown in Fig. 13.  
 759 Note that only the data from C1 (Fig. 13d), C4 (Fig. 13g) and C2 (Fig. 13e) are used for model  
 760 calibration. As it can be seen, the maximum range of concentrations in these data doesn't exceed  
 761 1.5% Cl concentration by concrete weight, however, the model is able to predict values as high  
 762 as 3.6% Cl concentration by concrete weight for C6 (Fig. 13i). It is clear that the model can  
 763 capture the effects of increasing temperature (going from left to right in Fig. 13) and increase in  
 764  $w/c$  as well as chloride boundary concentrations (going from top to bottom in Fig. 13). It is also  
 765 interesting to notice that the experimental value closest to the top surface of the sample at 48 days  
 766 seems to be higher than the predicted numerical one. As discussed before, that can be due to the  
 767 increased errors in evaluating the concentration at the surface since it is in direct contact with

768 the solution, but also, another reason can be due to the small cracks that may have developed on  
769 the sample surface during early age before demolding and full saturation. Nevertheless, the rest  
770 of the envelop points are in very good agreement with the numerical simulations which shows  
771 that the model is not a mere extrapolation but actually captures mechanisms beyond the ranges  
772 of data it was calibrated with.

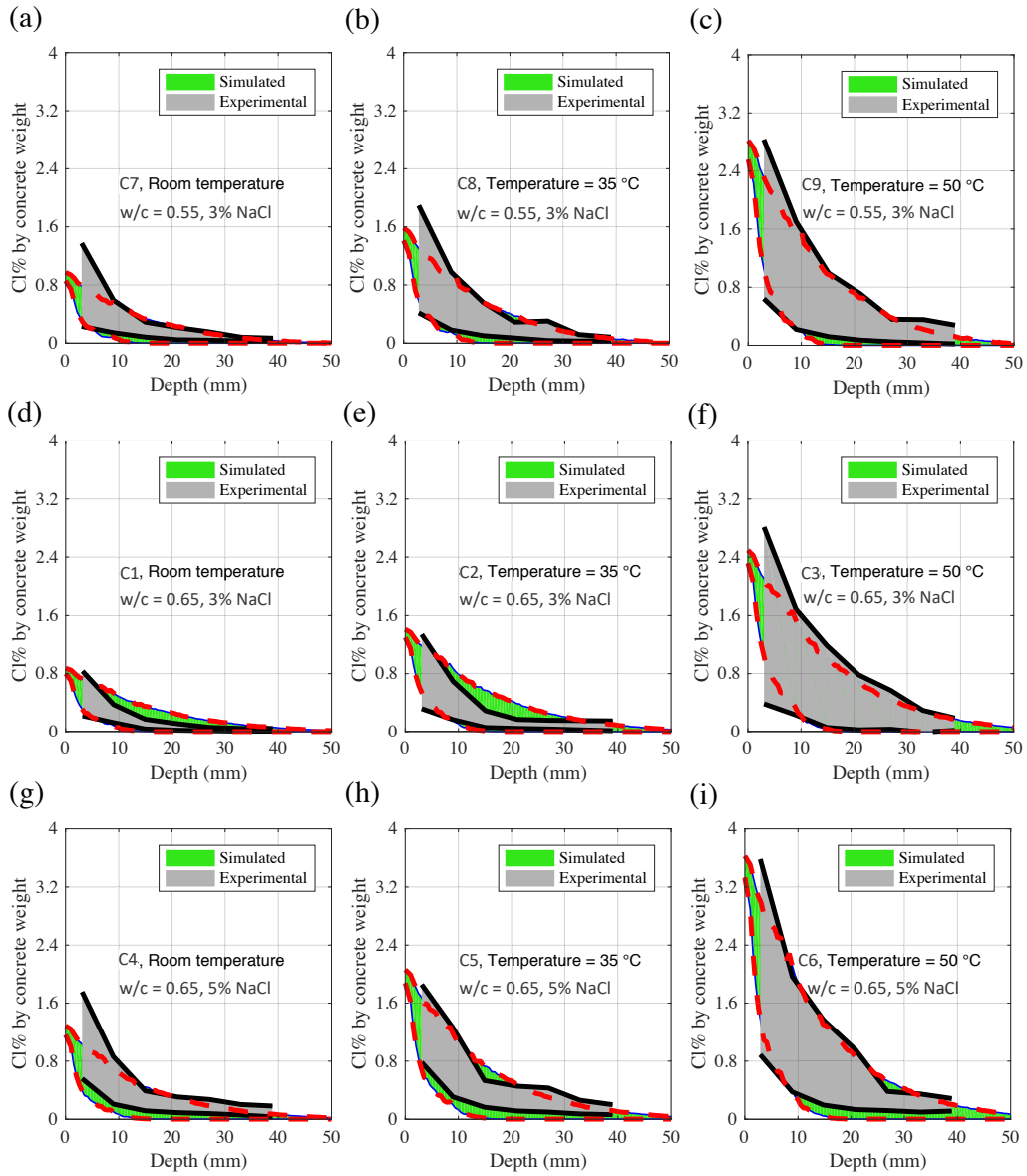


Figure 13: Envelop of experimental [23] and numerically simulated chloride concentration profiles for Series 3 a) to c), Series 1 d) to f), and Series 2 g) to i)

773 7.4. Diffusion in unsaturated concrete

774 For unsaturated concrete, the advection effect contributes to the transport of chloride ions,  
 775 leading to different chloride concentration profiles comparing with the saturated condition, as

776 clearly shown in [24]. To verify that the proposed formulation is also capable of characterizing  
 777 the transport of chloride ions in unsaturated conditions, the numerical simulations of the exper-  
 778 iments in [24] are carried out and the results are compared with the experimental output. As  
 779 summarized in Table 3, two groups of specimens made of the same mixture were adopted in the  
 780 study. The mix contained  $380 \text{ kg/m}^3$  of cement (ASTM C150 Type I) with 0.55  $w/c$  and 4.24  
 781 aggregate to cement ratio. Maximum and minimum aggregate size are assumed to be 19 mm and  
 782 5 mm, respectively and a fuller curve coefficient of 0.5 is used, similarly to the previous section.

783 After 28 days of curing, the first group of samples was immersed in water for 30 days to reach  
 784 full saturation, while the second group of samples was exposed to air in laboratory environment,  
 785 with a temperature of  $22.8 \text{ }^\circ\text{C}$  and relative humidity of 32%. Then both groups were exposed to  
 786 3% and 5% NaCl solution at the top surface and distilled water at the bottom surface. Relative  
 787 humidity of samples in group 2 was monitored at depth of 1 in (25.4 mm) and 2 in (50.8 mm).

788 To calibrate the model, first, the HTC model parameters relevant to moisture diffusion have  
 789 to be calibrated since in this experimental campaign, moisture will move under the humidity  
 790 gradients. These parameters are  $D_{h0}$ ,  $D_{h1}$  and  $n$ . For all other campaigns these parameters  
 791 are not effective since no moisture diffusion is occurring at full saturation. These parameters  
 792 were calibrated by using the humidity profiles from group 2. Note that for full calibration of the  
 793 other HTC parameters, more experimental data would have been needed and thus, the calibration  
 794 started by assuming all other HTC model parameters to be the same as those listed in Table 1.  
 795 Calibration results give  $D_{h0} = 8.05 \times 10^{-8} \text{ m}^2/\text{h}$ ,  $D_{h1} = 2.37 \times 10^{-6} \text{ m}^2/\text{h}$  and  $n = 5.0$ . As it can  
 796 be seen from Fig. 14, the HTC model can capture very well the changes in the moisture content  
 797 of the unsaturated concrete and its evolution over time.

Table 3: Testing series and experimental data of [23]

Group	1		2	
Sample number	SC1	SC2	UC1	UC2
Saturation condition	saturated		unsaturated	
Cl concentration at the boundary	3%	5%	3%	5%

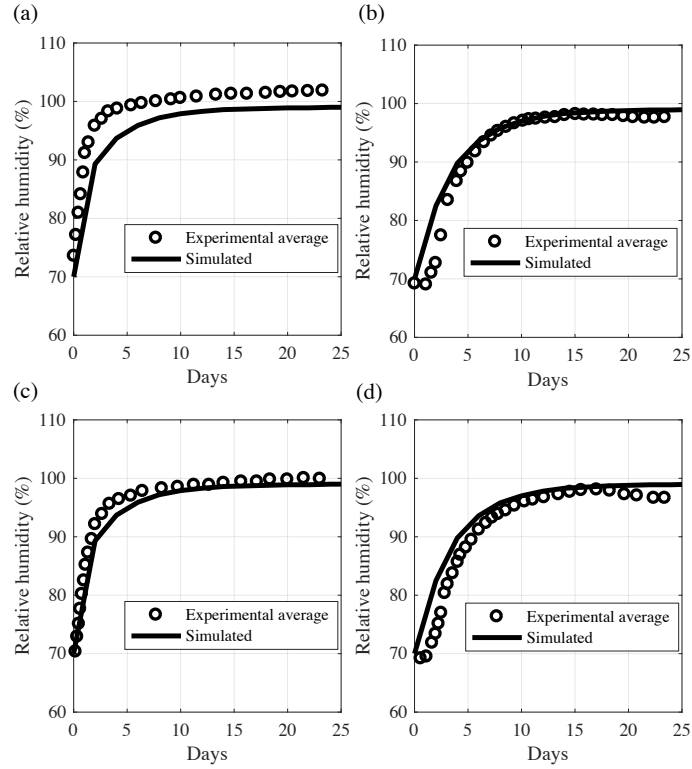


Figure 14: Experimental [24] and numerically simulated relative humidity evolution. (a) Depth = 1 in., NaCl concentration = 3%, (b) Depth = 2 in., NaCl concentration = 3%, (c) Depth = 1 in., NaCl concentration = 5%, (d) Depth = 2 in., NaCl concentration = 5%

798 As shown in Fig. 14a, the experimental relative humidity being obviously higher than the  
 799 simulated one might be caused by measurements errors because after 15 days the recorded ex-  
 800 perimental relative humidity is above 100%. In addition, typically, relative humidity sensors have  
 801 large errors close to saturation that can reach up to 5% errors. Another reason for this difference  
 802 is the fact that the concrete was put in a very dry condition (only 32% relative humidity) to speed  
 803 up the moisture removal, as a result, some surface drying cracks must have formed and that  
 804 would have increased the relative humidity close to the surface which explains why the model  
 805 predictions at 1 in depth are slightly below the experimental values (see Fig. 14a,c).

806 Once the HTC model parameters are calibrated, the chloride penetration profile of the satu-  
 807 rated specimen exposed to 3% and 5% NaCl solution for 30 days (see Fig. 15a,c) is then adopted  
 808 to calibrate the chloride diffusion parameters following the ideal calibration procedure. Since

809 no temperature gradients exist in this set, the activation energies can not be calibrated and their  
810 effects are not considered (since  $T = T_0$ ). Calibrated parameters are displayed in Table 2 (col-  
811 umn 4). Similarly here, all the remaining experimental data serve as validation including the two  
812 other penetration curves at full saturation and the four penetration curves at partial saturation.

813 The effects of the humidity gradients are clearly captured by the model. When the concrete is  
814 unsaturated, the gradient of relative humidity causes advection and contributes to the flux speed,  
815 leading to a faster transport of chloride than that in saturated concrete, which is a fact that can  
816 be easily observed by comparing Fig. 15 and Fig. 16. Note also here that the model captures  
817 the scatter again within the concrete sample which is an important feature that is lacking in  
818 macroscopic continuum models.

819 As in the previously considered cases, the proposed model captures very well the chloride  
820 transport under different chloride concentrations and for different ponding durations (Fig. 15).  
821 More importantly, for unsaturated concrete, with the same parameter values, the proposed model  
822 is capable of predicting quantitatively the chloride transport under different chloride concentra-  
823 tions and for different ponding durations too (see Fig. 16). This emphasizes the fact that the  
824 model is correctly representing the physical transport processes within the pore solution and  
825 therefore, it predicts the concentration correctly by just adding the convective part without the  
826 need to adjust the chloride diffusion coefficient  $D_c$ . In other words,  $D_c$  as predicted by the model  
827 accounts correctly for all physical phenomena that occur within the concentrated concrete pore  
828 solution as it moves through the porous structure and links them correctly to a single constant  
829 chloride diffusion coefficient in dilute solution  $D_0$ .

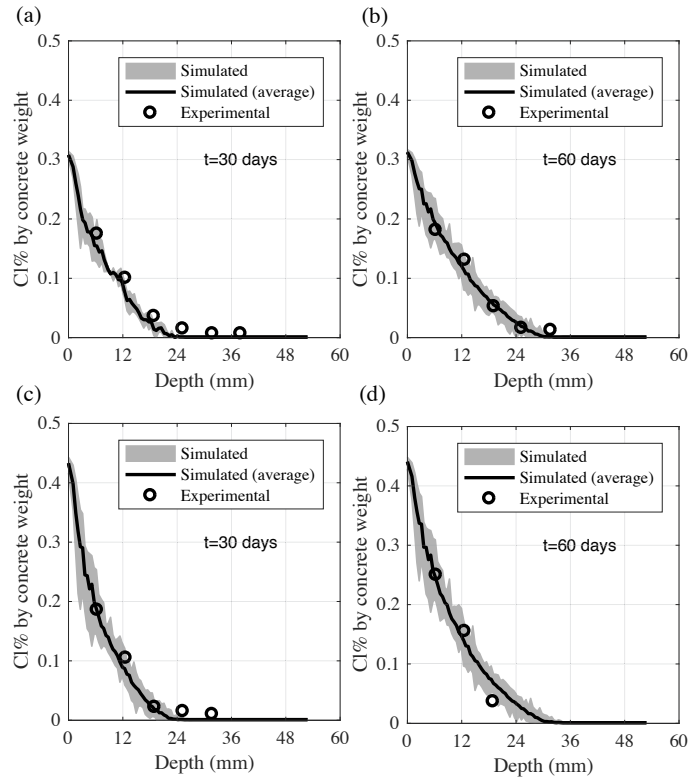


Figure 15: Experimental [24] and numerically simulated chloride penetration for fully saturated specimens at different ponding days. (a) and (b): Specimens exposed to 3% NaCl solution (SC1), (c) and (d): Specimens exposed 5% to NaCl solution (SC2)

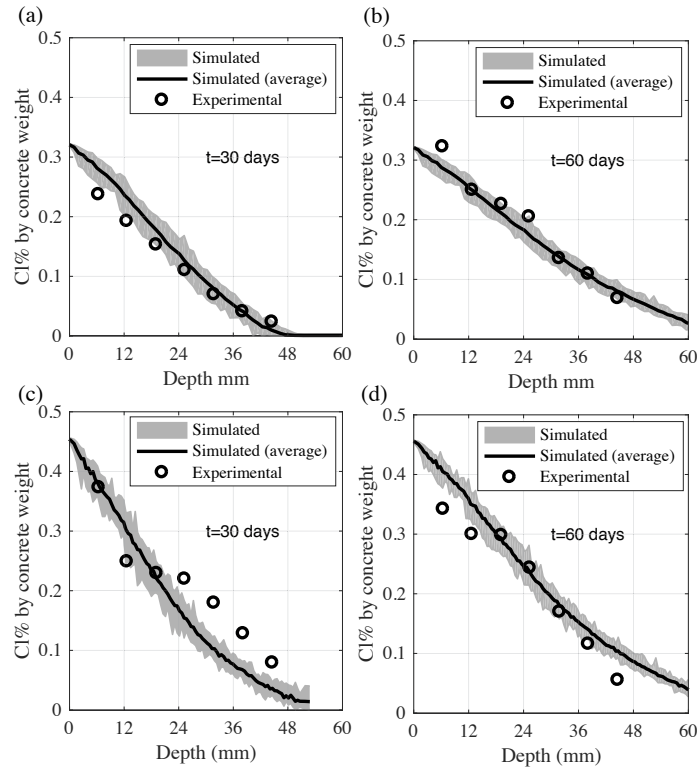


Figure 16: Experimental [24] and numerically simulated chloride penetration for unsaturated specimens at different ponding days. (a) and (b): Specimens exposed to 3% NaCl solution (UC1), (c) and (d): Specimens exposed to 5% NaCl solution (UC2)

### 830 7.5. Discussion of calibration and simulation results

831 Here, the postulated benefits (see Sec.2) of the modeling approach are discussed based on  
 832 the numerical analyses of the considered experimental results and their corresponding calibrated  
 833 parameters.

#### 834 7.5.1. Representation of inherent physics with limited model parameters

835 As shown in the simulation results, the presented model can simulate accurately a wide vari-  
 836 ety of experimental data relevant to two cement pastes and two concrete mixes with a maximum  
 837 aggregate size of 19 mm. The  $w/c$  varied from 0.4 to 0.6. Chloride concentrations varied be-  
 838 tween 3% and 5% at the boundaries. Variable ponding durations, thermal gradients, and hygral  
 839 gradients were also considered. This means that a wide variety of microstructure characteristics



840 and exposure conditions are covered (not mentioning the variation in curing conditions too). For  
841 all these varieties, only four basic parameters are calibrated for isothermal conditions and only  
842 two additional parameters are calibrated to capture thermal effects. In addition, no extra param-  
843 eters are used to capture the unsaturated conditions and just the correct inclusion of coupling  
844 between the thermal and hygral processes with the chloride diffusion process accounts for the  
845 unsaturated conditions differences. All other physics are considered in the modeling framework  
846 by using comprehensive formulations from literature with predefined fixed material parameters.  
847 This shows that the model successfully strikes a good balance between physics and simplicity.

848 7.5.2. *Robustness of the calibrated model parameters*

Table 4: Sensitivity analysis based on the simulation in Sec. 7.2

Parameter	Concentration at 15 mm	Variation ( $\Delta C/C$ )	Depth of Pene- tration (mm)	Variation ( $\Delta d_p/d_p$ )
Temperature = 23 °C				
$\tau_a(+10\%)$	0.75%	5.63%	36.34	3.80 %
$\tau_a(-10\%)$	0.66%	-7.04%	32.83	-6.22%
$A_0(+10\%)$	0.67%	-5.63%	37.80	7.97%
$A_0(-10\%)$	0.76%	7.04 %	32.11	-8.28%
$B_0(+10\%)$	0.78%	9.86%	30.37	-13.25%
$B_0(-10\%)$	0.63%	-11.27%	40.32	15.17%
$f_v(+10\%)$	0.67%	-5.63%	34.56	-1.29%
$f_v(-10\%)$	0.66%	-7.04 %	35.36	1.00%
Temperature = 38 °C				
$U(+10\%)$	0.99%	0.02 %	45.89	3.10%
$U(-10\%)$	0.95%	-0.02%	43.86	-1.46%
$U_b(+10\%)$	0.97%	0.00%	44.57	0.13%
$U_b(-10\%)$	0.96%	-0.01%	45.02	1.15%

849 As shown in Table 2, three of the four basic parameters of the chloride diffusion model  
850 have values that vary within the same order of magnitude:  $A_0$  is between 0.45 and 0.7,  $B_0$  is  
851 between 1.0 and 1.9, and  $f_v$  varies from 400 to 600. Only the apparent tortuosity  $\tau_a$  shows a  
852 larger range (one order of magnitude difference). By studying  $\tau_a$  in light of the experimental  
853 data, one could infer some explanations. First, comparing the two cement pastes, the differences  
854 are not that large and are very acceptable since they were made using two different cements,  
855 a US ASTM C150 Type I cement (Sec. 7.1) compared to a Canadian CSA T10 cement (Sec.  
856 7.2). So, the slight difference between the two general purpose cements may be the reason for  
857 such range. Additionally, controlling bleeding is very challenging when making cement paste  
858 especially when  $w/c$  is high. Therefore, the increased diffusivity identified by a higher  $\tau_a$  in  
859 the second set (Sec. 7.2) could be a result of some bleeding that was inevitable in making the  
860 paste. Note that this does not affect the concrete and this is why, the same  $\tau_a$  represented well  
861 all samples in the third experimental campaign (Sec. 7.3). As for the two concrete experiments,  
862 the difference in  $\tau_a$  is relatively large although they have similar  $w/c$  (0.55 and 0.65). Here one  
863 must consider the contribution of multiple factors. By comparing the two sets and especially  
864 Series 3 in Sec. 7.3 with SC1 in Sec. 7.4, both have identical mix designs and are exposed  
865 to the same chloride concentrations yet, the surface chloride% content is significantly different:  
866 C7 (from Series 3 at room temperature) has about 1% content (see Fig. 11), while SC1 has a  
867 Cl% of 0.32 (see Fig. 15a and b) which is almost one third that of C7. Therefore it is expected  
868 that the preparation and/or curing of the two experimental campaigns is the reason for such an  
869 observed difference in their experimental results. This observed difference explains why  $A_0$  and  
870  $B_0$  are higher for Sec. 7.3 (to account for the higher surface concentration) and also provides  
871 some explanation to why  $\tau_a$  is also higher. In addition, by comparing the extent of the chloride  
872 concentration-depth profiles for C7 at 48 days (see Fig. 11e in Sec. 7.3) and SC1 at 60 days (see  
873 Fig. 15b in Sec. 7.4), it can be seen that the penetration went beyond 40 mm after only 48 days  
874 for C7 and was less than 36 mm for SC1 after 60 days. Thus the depth of penetration is clearly  
875 larger in C7 and this requires a larger  $\tau_a$  as previously explained. So, this proves that the model  
876 parameters are robust since within one experimental campaign Sec. 7.3) a single set of model

877 parameters is used but it does cover a wide range of penetration profiles under varying  $w/c$ ,  
878 chloride concentrations at the boundaries and temperature conditions even with a nonuniform  
879 diffusion profile.

880 In regards to the thermal effect parameters  $U$  and  $U_b$ , the fact that only one additional curve  
881 is used to calibrate them in the third experimental set (Sec. 7.3) and the results are valid for 40  
882 other curves prove the robustness of these two parameters too. Note that 9 test cases C1 to C9  
883 with 5 different ponding durations are simulated (45 curves) after calibration by using only 5  
884 curves with 4 curves to calibrate the 4 basic parameters and fine tune them, then only 1 curve to  
885 calibrate  $U$  and  $U_b$ , and then  $(45 - 5 =) 40$  curves for validation.

886 To further study the robustness and sensitivity of the calibrated parameters, a sensitivity anal-  
887 ysis of the parameter values is performed based on the numerical simulation of the second exper-  
888 imental investigation (Sec. 7.2). The chloride penetration model parameters in Table 2 (column  
889 2) are separately varied by  $\pm 10\%$ . Simulations of the effects of varying the 4 basic parameters  
890 are performed using the case at room temperature. The activation energy parameters have to be  
891 investigated at a temperature other than  $T_0$ , which is assumed to be the room temperature and  
892 thus, they are tested using the simulation at 38 °C. The results of these numerical simulations  
893 are then compared with the corresponding previous ones, i.e. based on the calibrated parame-  
894 ters. The comparison has been done based on two quantities: (1) the total chloride concentration  
895 (weight percentage)  $C$  at a clear cover of 15 mm (typical cover for stirrups in RC beams); (2) the  
896 depth of penetration  $d_p$  measured from the exposure surface at which, the chloride concentration  
897 drops below a threshold of 0.01% (typical for fresh water). The numerical analysis results are  
898 shown in Table 4 together with their variations with respect to the results of the original simu-  
899 lations: at room temperature,  $C = 0.71\%$  and  $d_p = 35.01$  mm, while at 38 °C,  $C = 0.97\%$  and  
900  $d_p = 44.51$  mm. In general, all parameters show reasonable robustness, presenting mild changes  
901 as the parameters vary without any chaotic behavior. It is expected though that the response  
902 would be most sensitive to  $B_0$  since it is the exponent of 10 in the Freundlich isotherm (Eq. 4).  
903 Nevertheless, the change in the concentration from the variation of  $B_0$  is still within an accept-  
904 able range. This is a very important feature of this model making it very dependable despite the

905 fact that it uses a limited number of free parameters.

### 906 7.5.3. Representation of the discrete meso-scale features

907 The importance of implementing this model in a discrete approach with a conduit transport  
908 network has its own clear merits. As it was shown in all simulation results, a small scatter around  
909 the average numerical simulation curve exists, which is due to the random geometry of the model  
910 representing the meso-scale heterogeneity of the material.

911 As shown in the slice in Fig. 8, chloride concentration is not radially varying in uniform  
912 contours yet it is very well representative of the experimental data and their scatter. To further  
913 explain this feature, Fig. 17 shows a vertical slice cut from the top of the modeled cylinder repre-  
914 senting C6 at 50 °C after 48 days which corresponds to the chloride penetration profile shown in  
915 Fig. 10e. The location of the cut is schematically shown on the top right corner of the figure. The  
916 conduits (straight colored lines) are shown in Fig. 17a around the aggregate pieces (gray spheres)  
917 connecting the matrix space centers (colored small spheres). Colors show the Cl% concentration  
918 along the conduits and inside the matrix spaces. Note that the color ranges are spaced on a log  
919 scale (see right color bar). By removing the aggregate (see Fig. 17b) concentration bands can be  
920 clearly seen and one can see the variations in colors along any horizontal line. To better see this  
921 variation, three zoomed locations are presented in Fig. 17c that clearly show the presence of two  
922 different chloride concentrations at the same depth (see orange and red in the middle picture) or  
923 even a lower concentration existing above a higher concentration (yellow above orange in the left  
924 picture and dark blue above light blue in the right picture). Again, such local heterogeneity is an  
925 important feature of this model that can not be replicated with classical macroscopic continuum  
926 models which do not differentiate aggregate and matrix and treat concrete as a homogeneous  
927 material. Here the model is capable of representing the meso-scale tortuosity induced by relative  
928 aggregate sizes and spatial locations. It has to be noted here though that this only represents  
929 part of the heterogeneity since the conduit constitutive laws represent volume-averaged values  
930 of the matrix and aggregate properties, yet, once experimental data are made available in which  
931 chloride concentrations in both matrix and aggregate are differentiated, the model can be easily  
932 modified to account for this additional source of heterogeneity.

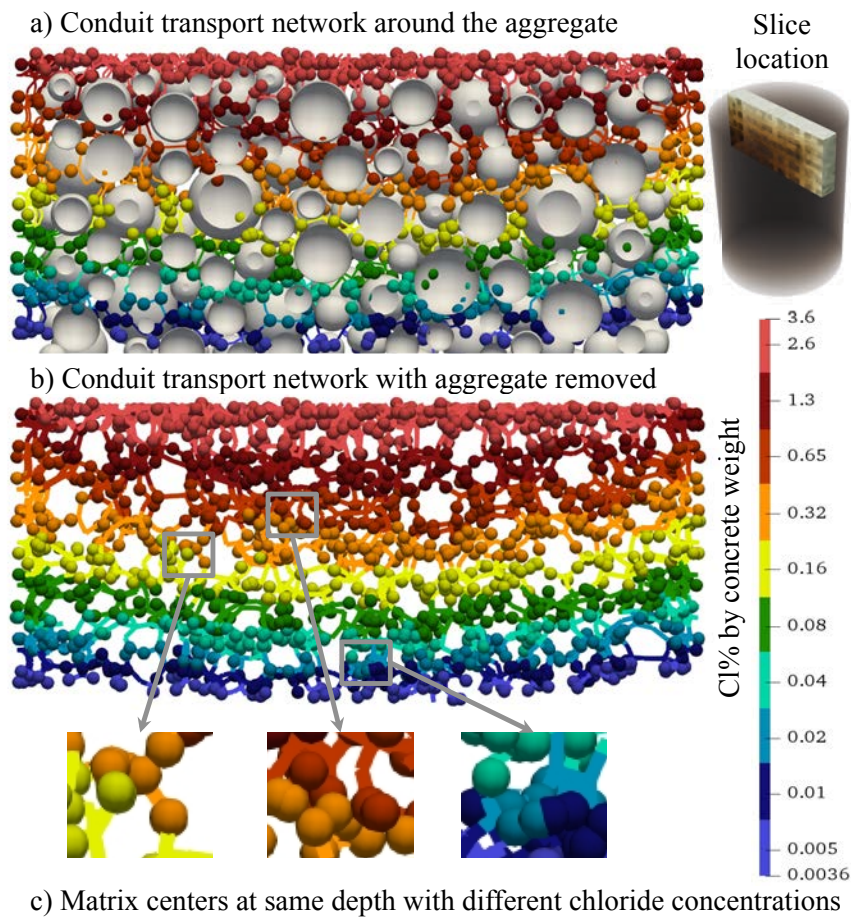


Figure 17: Conduit transport network ability to capture meso-scale heterogeneity in Cl% concentration by concrete weight (a) Network between matrix space around aggregate (b) Aggregate removed, and (c) Zoomed locations within the network showing concentration differences

## 933 8. Potential extension of the model

934 Mimicking the internal meso-structure pathways makes it possible for the model to capture  
 935 additional physics of the transport process if relevant comprehensive experimental data are avail-  
 936 able. First, the model can replicate the effects of meso-scale constrictivity if the volume assigned  
 937 to each discrete conduit represents the matrix volume only (assuming impermeable aggregate),  
 938 or if the different diffusivities are used for the aggregate and matrix. This will enable more ac-  
 939 curate prediction of the local chloride concentration which is essential for explicit prediction of

940 the location and size of anodic and cathodic areas on the rebar surface during early stages of  
941 chloride-induced corrosion.

942 A natural second extension of the model is to consider the effects of cracking on the diffu-  
943 sion process, and how that accelerates ingress of corrosive agents into the RC member which  
944 accelerates corrosion and then creates more cracking. In addition to corrosion, other sources of  
945 cracking found in the field include load application as well as drying and wetting or freeze/thaw  
946 cycles. Without accurate prediction of such processes, chloride penetration rates derived from  
947 controlled lab experiments would not predict accurately the actual field conditions. The pro-  
948 posed model has the potential to solve this problem through physical representation of cracking  
949 effects on diffusion rather than empirical representation and extrapolation. Note that the conduit  
950 network is located along the preferential locations for cracking and damage between aggregate  
951 pieces. This enables very realistic coupling between damage and diffusion where diffusivity can  
952 be updated based on the crack opening that is resolved explicitly down at the meso-scale, as done  
953 in modeling concrete thermal spalling during fire exposure [30] and moisture diffusion behavior  
954 of self-healing concrete [31].

## 955 **9. Conclusions**

956 This study presents a comprehensive multi-physics model calibrated and validated through  
957 experimental data to simulate the chloride transport in saturated and unsaturated cementitious  
958 materials. From the previous sections, the following main conclusions can be drawn:

- 959 (1) The proposed model can predict efficiently the chloride penetration in cementitious materi-  
960 als from cement paste to concrete under varying thermal, hygral and chloride concentration  
961 exposure conditions. Only 4 basic parameters are to be calibrated under isothermal condi-  
962 tions and only two additional parameters are needed to account for thermal effects. This  
963 is achieved by considering the main electro-chemical and physical processes in chloride  
964 transport as embedded mechanisms with predetermined parameters taken from previous  
965 experiments in the literature.

- 966 (2) Coupling the chloride penetration with moisture diffusion, heat transfer and evolution of  
967 the cementitious material hydration reactions enables the framework to accurately repre-  
968 sent effects of aging of the pore structure, effects of thermal gradients, and effects of hygral  
969 gradients (in unsaturated concrete).
- 970 (3) Ionic transport within the pore solution is represented by accounting for both pore solution  
971 chemistry (ionic activity and counter ion potentials) and pore solution concentration (ionic  
972 frictional/mechanical interactions).
- 973 (4) Effects of the pore structure on ionic transport are modeled by considering the effects of  
974 pore electric potential as well as the pore volume, tortuosity and constrictivity.
- 975 (5) Representing tortuosity and constrictivity as functions of the pore volume change is an  
976 effective simplification of model parameters that still enables the model to capture aging  
977 effects.
- 978 (6) Changes in pore structure due to aging are significant and important to consider when  
979 trying to correlate lab scale experiments done at young material ages to the behavior over  
980 prolonged time periods.
- 981 (7) By introducing thermal dependence into both chloride binding and diffusivity in pore solu-  
982 tion, the model can capture the effect of temperature on chloride penetration in cementitious  
983 materials. The presented model is shown to be robust given its ability to represent a wide  
984 variety of conditions without significantly unexplained parameter variations, achieving a  
985 good balance between modeled physics and simplicity.
- 986 (8) Using a discrete conduit transport network enables capturing the meso-scale tortuosity  
987 which represents a part of the meso-scale heterogeneity effects on varying the chloride  
988 concentration. This is a very important feature for predicting the initiation and formation  
989 of micro-cell corrosion of reinforcement, which cannot be replicated using any classical  
990 macroscopic continuum model.

## 991 **10. Acknowledgements**

992 The authors would like to acknowledge Prof. Tyler Ley at Oklahoma State University and  
993 Prof. Yunping Xi at University of Colorado at Boulder for providing helpful information regard-  
994 ing their experiments that we simulated in this work. Authors also would like to acknowledge the  
995 support from the Rensselaer Polytechnic Institute Center for Computational Innovations (CCI)  
996 to run the simulations in this paper using the High performance computing cluster. The second  
997 author gratefully acknowledges the support by the project Reshealience - Rethinking coastal de-  
998 fense and green-energy Service infrastructures through enHancEd-durAbiLity high-performance  
999 cement-based materials (EU Horizon H2020).

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