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Citation: Chen, X., Fu, F., Wang, H., liang, Q., Yu, A., Qian, K. & Chen, P. (2021). A Multi-phase Mesoscopic Simulation Model for the Long-term Chloride ingress and Electrochemical Chloride Extraction. *Construction and Building Materials*, 270, 121826. doi: 10.1016/j.conbuildmat.2020.121826

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1 Article

2 A Multi-phase Mesoscopic Simulation Model for the 3 Long-term Chloride ingress and Electrochemical 4 Chloride Extraction

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14
15 **Abstract:** Electrochemical chloride extraction (ECE) is one of the effective methods to remove
16 chloride and prolong the service life of reinforced concrete (RC) structures. To fully understand the
17 mechanisms of the long-term chloride ingress and subsequent ECE treatment of RC structure, a
18 multi-phase mesoscopic numerical model is proposed. Unlike most of existing models, the long-
19 term chloride ingress and the effect of chloride binding are considered in the proposed model, and
20 the transport of chloride is simulated through a novel diffusion-migration-reaction process. The
21 numerical simulation results show that the adsorption capacity of concrete to chloride decreases
22 with the increase of chloride ingress time. Interestingly, the free chloride concentration on the
23 surface of concrete decreases dramatically, and the maximum value appears in the concrete
24 protective cover after ECE treatment. Furthermore, ECE treatment time, current density and
25 concrete protective cover have significant influences on ECE treatment efficiency. Besides, the
26 quantitative relationship models between these factors and ECE treatment efficiency have been
27 developed. Moreover, the use of stirrup can improve the efficiency of ECE treatment. The research
28 outcomes reveal previously ignored fundamental aspects of the ECE treatment and provide insights
29 for the durability prediction of RC structures.

30
31 **Key words:** Electrochemical chloride extraction; Chloride ingress; Ions migration; Reinforced
32 concrete

1 Introduction

Reinforced concrete (RC) is the most widely used building material in the construction industry [1,2]. The combination of reinforcement and concrete makes full use of their advantages in mechanical properties. However, reinforcement corrosion in RC structures caused by chloride ingress is one of the most serious problems in marine engineering [3,4]. In the process of RC casting, passive film is formed around the surface of reinforcement in alkaline environment, which can effectively prevent the reinforcement from corroding [5–7]. Nevertheless, chloride in the marine environment diffuses into concrete through the pores of concrete [8,9] during the service life of RC structures. Once the chloride concentration around the surface of reinforcement reaches the critical chloride concentration, the passivation film of reinforcement will be destroyed, resulting in the corrosion of reinforcement, the crack of concrete protective cover, and finally the failure of the structure [10–12]. Therefore, it is essential to remove chloride from RC structures and prolong the service life of RC structures.

For decades, electrochemical repair methods play an important role in protecting the reinforcement embedded in concrete from corrosion [13-17]. Electrochemical repair methods include cathodic protection and electrochemical chloride extraction (ECE) [13–22]. The principle of cathodic protection is to prevent the reinforcement from corrosion by providing an appropriate cathodic polarization current for the reinforcement. [23–25]. Although cathodic protection can effectively inhibit the corrosion of reinforcement, it needs to use current in the whole service life of the RC structure, which requires a high cost [19,26].

Compared with cathodic protection, ECE has many advantages, such as convenient operation, low price and short duration. The ECE system applies an external electric field between the embedded reinforcement bar (as cathode) and the external electrode (as anode, immersed in an electrolyte solution). The external electric field drives the chloride ions to the external anode of concrete, thus removing the chloride from concrete [21,22,27]. ECE treatment has been favored by many researchers since it was first adopted in experimental researches in 1970s. For instance, Fajardo *et al.* [28,29] carried out the ECE treatment experiments on cylindrical concrete samples containing chlorides. The experimental results demonstrated that chloride in RC could be effectively removed by ECE treatment. In addition, after ECE treatment, about 50% ~ 60% of chloride in concrete were removed, while various cations such as Na^+ , K^+ and Ca^{2+} in the concrete pore solution gathered around the reinforcement [28,29]. The study of Garcés *et al.* [30] showed that the efficiency of ECE treatment was influenced by the distributions of reinforcement. Besides, the ECE treatment efficiency can be improved by using graphene as an auxiliary electrode, and the chloride concentration in concrete can be reduced by 70% after 8 weeks of ECE treatment [31]. Furthermore, the environmental temperature also affects the ECE treatment efficiency. When the temperature increased from 0°C to 20°C, the ECE treatment efficiency was improved by two times [4]. Moreover, Yeih *et al.* [31] found that stirrups could increase the efficiency of ECE treatment. However, after ECE treatment, the new cementitious phases containing rich concentrations of sodium, aluminum and potassium were formed. Moreover, the ECE accumulates locally high amounts of alkali ions that stimulate the alkali–silica reaction.

The above experimental studies demonstrate that ECE treatment can effectively remove chloride from concrete. However, concrete is a multiphase composite material composed of

75 aggregate, mortar and interface transition zone (ITZ) [9,32]. The process of the chloride transport
76 in concrete, especially in ITZ, is difficult to be explored by experiments. In contrast, numerical
77 simulations have great advantages in providing detailed information, such as ions transport
78 trajectories and interactions between ions, potential distributions, and so on [33]. The process of
79 ECE can be simulated by using Nernst-Planck equation or Nernst-Planck-Poisson equation[14–16,
80 31, 34, 35]. Through numerical simulations, Wang *et al.* [16] reported that the position of the anode
81 played an important role in the ECE treatment. In addition, by considering the effects of ionic
82 concentrations on the diffusion and migration of charged ions, Li *et al.* [14,15] presented a
83 mathematical model for simulating ECE treatment. Moreover, the ECE treatment numerical model
84 established by Castellote *et al.* [34] took into account the effect of hydrogen ions produced by
85 electrolytic water on the diffusion properties of chloride. Furthermore, Liu *et al.* [33,35] established
86 a mesoscopic numerical model of ECE treatment and regarded concrete as a multiphase material.
87 And the effects of aggregate shape, boundary condition and double electric layer on ECE treatment
88 efficiency were discussed in their work.

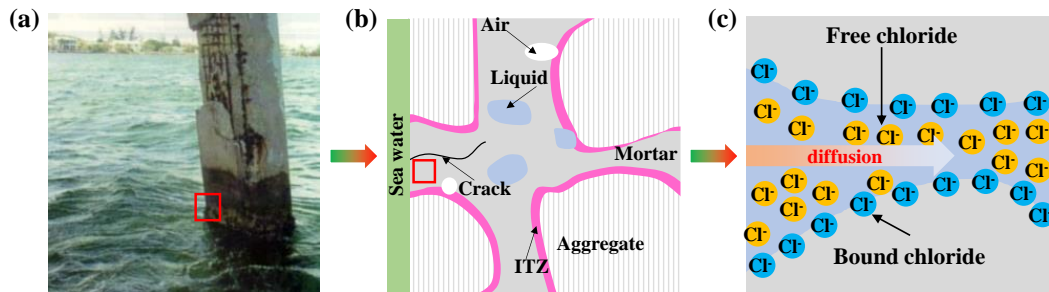
89 The chlorides in concrete can be divided into the free chlorides and the bound chlorides [36,37].
90 In the stage of chloride ingress, the pore structure of concrete adsorbs some of free chlorides and
91 become bound chlorides, reducing the permeability of concrete to chloride ions [38–41]. While, in
92 the stage of ECE treatment, some of bound chlorides are released and become free chlorides.
93 Unfortunately, most of the existing models only consider the free chlorides, and ignore the bound
94 chlorides during the process of ECE treatment [8,31,42]. More importantly, the actual RC structure
95 is attacked by chloride in the marine environment, and chloride concentration is non-uniformly
96 distributed in concrete[43]. The concentration of chloride decreases with the increase of the ingress
97 depth of chloride [39,41,44]. However, most of the existing numerical models for ECE treatment
98 simulation assume that the chloride concentration in concrete is uniformly distributed before ECE
99 treatment[14,21,45,46]. Obviously, this is not consistent to the real situation, and cannot fully reveal
100 the mechanism of ECE treatment.

101 To tackle aforementioned problems, in this paper, a multi-phase mesoscopic numerical model
102 is proposed to simulate the whole process of long-term chloride ingress and subsequent ECE
103 treatment. In the proposed model, concrete is considered as a multiphase composite material
104 composed of aggregate, mortar and ITZ. More importantly, by introducing a reaction phase, the
105 binding effect of chloride ions is considered in the proposed model. In addition, the reliability of the
106 proposed chloride model is verified by the third-part experiments. Furthermore, the distributions of
107 chloride concentration in concrete are displayed in two-dimensional (2D) and three-dimensional
108 (3D) graphics to reveal the evolution of chloride concentration distributions before and after ECE
109 treatment. Moreover, the influences of ECE treatment time, current density, diameter of
110 reinforcement and thickness of concrete protective cover on the efficiency of ECE treatment are
111 discussed. And the quantitative relationship model between ECE treatment efficiency and these
112 factors is presented. Finally, an engineering case is analyzed. The research outcomes reveal the
113 previously overlooked aspects by other researchers in chloride transport mechanism in concrete
114 meso-structure under the ECE treatment and provide insight for the durability prediction of RC
115 structure subjected to chloride attack.

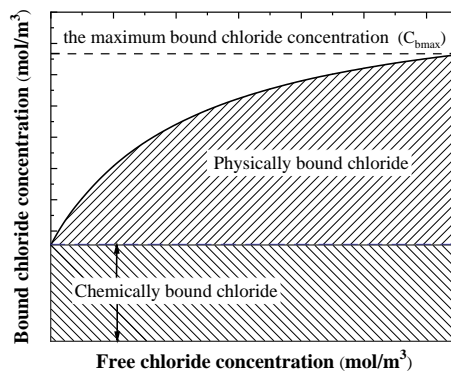
117 **2 Theoretical background**

118 **2.1 Chloride ingress**

119 In the marine environment, chloride mainly diffuses into the RC structure through the pore
120 solution of the concrete, leading to the deterioration of the performance of RC structure. However,
121 the diffusion of chloride in concrete pore solution is quite different from that in ordinary solution
122 (e.g., water). When the external chlorides diffuse into the concrete, part of the free chlorides will
123 become bound chlorides through the physical and chemical reactions, as shown in Fig. 1. On the
124 one hand, the pore structures of concrete have adsorption effect on chlorides [36,37]. Once the
125 chloride in the pore solution gets close to the C-S-H gel wall, some of the free chlorides will be
126 adsorbed, which is called physically bound chloride(adsorption), as shown in Fig. 1. Physical
127 binding is a long process and reversible [44]. On the other hand, some chloride ion reacts with
128 mineral composition of concrete (i.e., residual aluminates, sulfoaluminate phases) to form Friedel's
129 salt ($C_3A \cdot CaCl_2 \cdot 10H_2O$) [36,37,44]. This chemical reaction process is called chemically binding
130 and is generally considered to be instantaneous. The chlorides in chemical reaction are called
131 chemically bound chlorides. Generally, the chloride ion is continuously diffused into the concrete.
132 However, the amount of the mineral composition of concrete (i.e., residual aluminates,
133 sulfoaluminate phases) is constant [36,44]. Therefore, the concentration of the chemically bound
134 chloride is independent of the free chloride concentration and only dependent of the amount of the
135 mineral composition of concrete. And the chemically bound chloride is constant as the concentration
136 of free chloride increases (as shown in Fig. 2). In addition, various chloride adsorption models
137 [38–41] have been proposed to describe the complex chloride binding phenomenon. And the
138 relationship between free chloride and bound chloride can be demonstrated in Fig. 2.



142 **Fig. 1.** Multi scale diffusion schematics of chloride ions. (a) Reinforced concrete column in marine environment
143 [67]. (b) Multiphase composite structure of concrete. (c) Micro diffusion process of chloride.



156 **Fig. 2.** Illustration of physically bound chloride and chemically bound chloride [44].

In addition, both the chemical binding and the physical binding can be regarded as a specific "reaction" of free chloride[48]. Consequently, the transport of chloride into concrete in the marine environment is essentially a diffusion-adsorption process. Without considering the electric field and the flow field, the governing equation of diffusion-adsorption of chloride can be expressed by the mass conservation equation as follows [48]:

$$\frac{\partial c_{cl}}{\partial t} = D_{cl} \frac{\partial^2 c_{cl}}{\partial x^2} + D_{cl} \frac{\partial^2 c_{cl}}{\partial y^2} - k_b \frac{c_{cl}}{c_{bmax}} (c_{bmax} - c_{cl}) \quad (1)$$

$$\frac{\partial c_b}{\partial t} = k_b \frac{c_{cl}}{c_{bmax}} (c_{bmax} - c_{cl}) \quad (2)$$

where C_{cl} is the free chloride concentration (mol/m^3), D_{cl} is the effective chloride diffusion coefficient (m^2/s), k_b is adsorption rate of bound chloride, C_b is the bound chloride concentration (mol/m^3), and C_{bmax} is the maximum concentration of bound chloride (mol/m^3).

2.2 Electrochemical chloride extraction

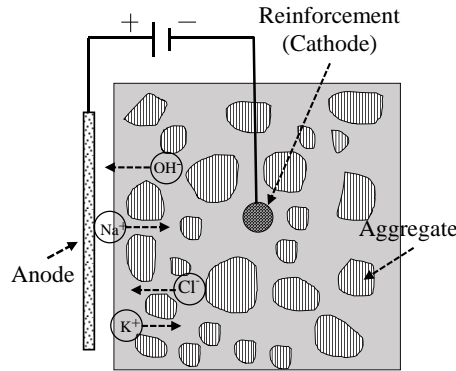


Fig. 3. Schematic representation of ECE treatment for concrete.

ECE is a process of directional movement of ions in concrete by applying an external electric field[21,22]. In the process of ECE, the cation ions move towards the positive electrode, while the anion ions move towards the surface of reinforcement embedded in concrete [4], as schematically illustrated in Fig. 3. Generally, the steel mesh immersed in the anode electrolyte is used as the positive electrode[28], and the reinforcement embedded in the concrete is used as the negative electrode[49,50]. In order to improve the conductivity of anodic system, in this paper, electrolyte solution with $50 \text{ mol}/\text{m}^3$ NaOH, $10 \text{ mol}/\text{m}^3$ LiOH and $5 \text{ mol}/\text{m}^3$ KOH is used. Under the external electric field, the transport of various ions in concrete is not only the diffusion of ions caused by the concentration gradient, but also the migration of ions caused by the potential difference. Based on the conservation of mass, hence, the transport of various ions in concrete can be expressed as follow[15,34,51]:

$$\frac{\partial c_i}{\partial t} = -\nabla J_i + k_{iR} \frac{c_b}{c_{bmax}} (C_{iECE} - C_i) \quad (3)$$

where J_i is the molar flux of the i^{th} ionic species in the concrete ($\text{mol}/(\text{m}^2 \cdot \text{s})$), C_{iECE} is ionic concentration at the beginning of ECE treatment, and k_{iR} is the release rate of the bound ions of the i^{th} ionic species.

The molar flux of ions per unit area per unit time can be expressed by Nernst-Planck equation[5]:

$$J_i = -D_i \nabla C_i - z_i D_i C_i \left(\frac{F}{RT} \nabla \phi \right) \quad (4)$$

where z_i is the charge number of the i^{th} ionic species, $F = 96480$ is the Faraday constant (C/mol), $T = 298$ is the absolute temperature (K), and $R = 8.134$ is the ideal gas constant (J/(mol·K)).

Substituting Eq. (4) into (3), it can yield the following equation:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i + \frac{z_i D_i F}{RT} \nabla (c_i \nabla \phi) + k_{iR} \frac{c_b}{c_{b\max}(c_{iECE} - c_i)} \quad (5)$$

According to the electric neutrality and current conservation, it yields [15,16,20,22]:

$$\sum_{i=1}^N z_i C_i = 0 \quad (6)$$

$$I = F \sum_{i=1}^N z_i J_i \quad (7)$$

where I is the current density (A/m²).

Substituting Eq. (4) into (7), we have

$$\frac{F}{RT} \nabla \phi = - \frac{I/F + \sum_{i=1}^N z_i D_i \nabla C_i}{\sum_{i=1}^N z_i^2 D_i C_i} \quad (8)$$

It is worth to mention that the boundary conditions and initial conditions should be given in the simulations when calculating the concentration distribution of various ions in concrete. Under the external electric field, electrochemical reactions occur at the cathode and anode electrodes[21]. For the cathode, the oxygen absorption and the hydrogen evolution reactions occur on the surface of reinforcement embedded in the concrete [17]. And the chemical reactions at the cathode can be express as follows:



From Eq. (9) and (10), it is known that only OH⁻ ions are generated on the surface of reinforcement embedded in the concrete, and the flux of all the other ions is zero. Hence, the flux of OH⁻ on the surface of reinforcement embedded in the concrete is equal to the externally applied current density[28,49,51]:

$$J_{OH^-} = \frac{I_c}{z_{OH^-} \cdot F} \quad (11)$$

where I_c is the current density externally applied to the cathode.

Note that the volume of the anode electrolyte is quite large compared with that of the concrete pore solution, and the anode electrolyte is regularly replaced in the actual ECR treatment. Consequently, although the chlorides in the concrete transport to the anode electrolyte, the variation of ions concentration in anode electrolyte can still be ignored [52]. Therefore, in the simulation of ECE treatment process, the ions concentration in the anode electrolyte could be conservatively assumed to be constant[15]. And the initial values and boundary conditions used in the simulation of ECE treatment process are shown in [Table 1](#).

213

Table1

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Initial and boundary conditions in the simulation of ECE treatment [15,45,53–55].

Ions	Boundary concentration (mol/m ³)	Initial concentration (mol/m ³)	Charge number
Chloride	10	$C_{cl}(x, y, t_c)^*$	-1
Hydroxide	50	398.1	-1
Potassium	5	227.1	+1
Sodium	55	136.6	+1

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* $C_{cl}(x, y, t_c)$ refers to the concentration of chloride in concrete in the t_c th year of chloride ingress.

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2.3 Effective diffusion coefficient of various ions

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As can be seen from Eq. (1) and (5) that the diffusion speed of ions in concrete is determined by the diffusion coefficient of ions. According to the diffusion theory for porous media, the effective specified ion diffusion coefficient in concrete can be calculated by the porosity, tortuosity and constrictivity of concrete[56], which can be expressed by

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$$D_i = D_{s,i} \frac{\varphi \cdot \delta}{\lambda} \left(\frac{t_{ref}}{t} \right)^m \quad (12)$$

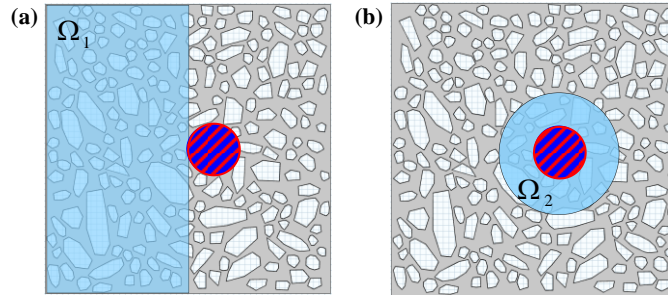
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where $D_{s,i}$ is diffusion coefficient of the specified i^{th} ion in aqueous solution (m²/s), ε is the porosity of concrete, δ is constrictivity of concrete, λ is tortuosity of concrete, t_{ref} is reference time (28d), t is chloride ingress, and m is the time attenuation index of chloride diffusion coefficient.

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2.4 ECE treatment efficiency indexes

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Fig. 4. Schematic representation of integral domains. (a) The integral domain of the concrete protective cover Ω_1 .

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(b) The integral domain close to the reinforcement Ω_2 .

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The purpose of ECE treatment is to remove chloride ions from concrete as much as possible, especially region close to the surface of reinforcement [13]. In order to evaluate the effect of ECE treatment, the efficiency indexes of ECE treatment (i.e., P_1 and P_2) are defined. One of the ECE treatment efficiency indexes (P_1) is used to describe to the reduction of chloride concentration in the concrete protective cover domain, and the other efficiency index (P_2) is used to describe the reduction of chloride concentration in the region around the reinforcement, as shown schematically in Fig. 4a and b, respectively.

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$$P_1 = \frac{\int_{\Omega_1} C(x,y,t_c) dA - \int_{\Omega_1} C(x,y,t_R) dA}{\int_{\Omega_1} C(x,y,t_c) dA} \quad (13)$$

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$$P_2 = \frac{\int_{\Omega_2} C(x,y,t_c) dA - \int_{\Omega_2} C(x,y,t_R) dA}{\int_{\Omega_2} C(x,y,t_c) dA} \quad (14)$$

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where P_1 and P_2 are efficiency indexes of ECE treatment, respectively; t_c is the moment when chloride concentration on the surface of reinforcement reaches critical chloride concentration; t_R

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241 is the ECE treatment time; x and y are chloride position coordinates; A is the area; $C(x, y, t_R)$ is
 242 the free chloride concentration after ECE treatment; Ω_1 and Ω_2 are the integral domains, as
 243 shown in Fig. 4a and b, respectively.

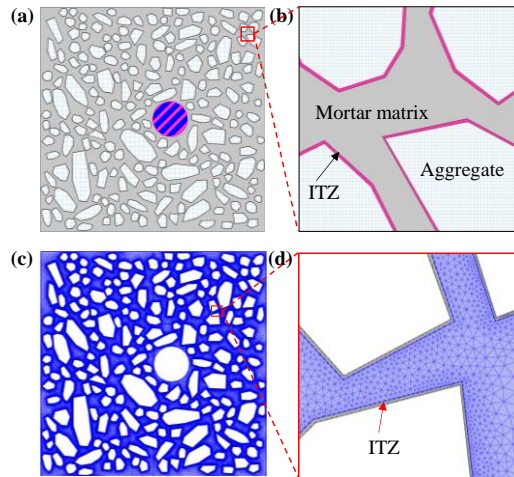
244 3. Numerical simulations

245 In the numerical simulations, concrete is regarded as a multiphase composite material
 246 composed of aggregate, mortar matrix and ITZ, as schematically illustrated in Fig. 5a-b. In order to
 247 transform 3D concrete aggregate gradation into 2D concrete aggregate gradation, one of the widely
 248 applied aggregate distribution methods is Walraven's equation, which can be expressed as [9,57,58]:

$$249 \quad P(d) = 1.065(d/d_m)^{1/2} - 0.053(d/d_m)^4 - (d/d_m)^6 - 0.0045(d/d_m)^8 - 0.0025(d/d_m)^{10} \quad (15)$$

250 where d is the diameter of aggregate; d_m is the maximum diameter of aggregates; $P(d)$ is the
 251 cumulative percentage passing a sieve with aperture diameter d .

252 In the proposed model, the shape of aggregate is random polygon, and the position of aggregate
 253 is also random. The diffusion coefficient of ions in aggregate is two orders of magnitude smaller
 254 than that in mortar matrix and ITZ [43]. Hence, the aggregate is regarded as impermeable body and
 255 the diffusion coefficient of ions in aggregate is set to be zero in the simulations. The thickness of
 256 ITZ is related to the construction technology, water/binder ratio and concrete curing conditions.
 257 Generally, the thickness of ITZ is between 20 μm and 100 μm [9,32,59]. In the proposed simulation
 258 model, the thickness of ITZ is random and obeys normal distribution, and the average thickness of
 259 ITZ is 60 μm . Fig. 5c shows the finite element mesh of the proposed numerical model, and there are
 260 more than 8 million degrees of freedom. Besides, all the other parameters used in the numerical
 261 simulation are listed in Table 2.



262
 263 **Fig. 5.** Schematic of 2D multi-phase meso-structure of concrete. (a) Meso-structure of concrete. (b) Local
 264 magnification of the meso-structure. (c) Finite element mesh. (d) Local magnification of the finite element mesh

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Table 2

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Basic parameters in the numerical simulations.

No.	Parameters	Value	Unit	Meaning	References
1	D_{scl}	1.07×10^{-10}	m ² /s	Diffusion coefficient of chloride in solution	[15,21,22,45,46]
2	D_{sNa}	2.7×10^{-11}	m ² /s	Diffusion coefficient of sodium in solution	[15,21,22,45,46]
3	D_{sK}	3.9×10^{-11}	m ² /s	Diffusion coefficient of potassium in solution	[15,21,22,45,46]
4	D_{sOH}	5.28×10^{-10}	m ² /s	Diffusion coefficient of hydroxyl in solution	[15,21,22,45,46]
5	δc	0.75	--	Constrictivity of concrete mortar	[56]
6	τc	2	--	Tortuosity of concrete mortar	[56]
7	φc	12%	--	Porosity of concrete mortar	--
8	δ_{ITZ}	0.85	--	Constrictivity of ITZ	--
9	τ_{ITZ}	1	--	Tortuosity of ITZ	--
10	φ_{ITZ}	29%	--	Porosity of ITZ	--
11	m	0.2	--	Time attenuation index	[55]

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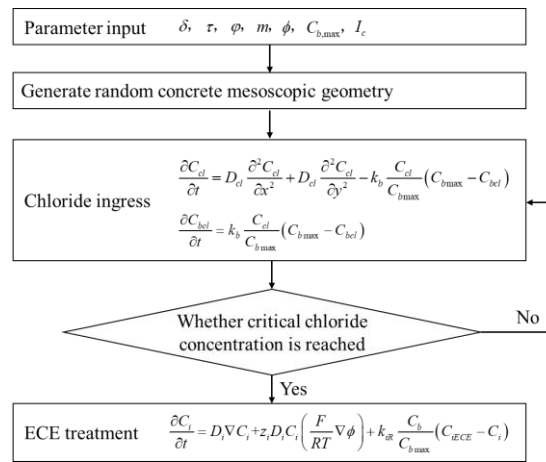
A sodium chloride (NaCl) solution with a concentration of 471.8 mol/m³ is set to the left side of the concrete to simulate marine environment. It's worth noting that only when the chloride concentration around the reinforcement surface reaches the critical chloride ion concentration, the ECE treatment is carried out by applying an external electric field. The flow chart of the derivation of the proposed multiphase numeric model is presented in Fig. 6

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Fig. 6. The Flow chart of the chloride ingress and ECE treatment of the proposed multiphase numeric model.

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In order to investigate the influence of current density, diameter of reinforcement, and thickness of concrete protective cover on the efficiency indexes (*i.e.*, P_1 and P_2) of ECE treatment, we calculate 24 different cases in the simulations, and the detailed parameters are listed in Table 3.

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Table 3

Detailed parameters of each case.

Cases	Repair time (weeks)	Current density (A/m)	Thickness of concrete over (mm)	Diameter of reinforcement (mm)	Explications
Case 1	8	2	50	16	Benchmark Model
Case 2	1	3	50	16	Different treatment time
Case 3	2	3	50	16	
Case 4	3	3	50	16	
Case 5	4	3	50	16	
Case 6	5	3	50	16	
Case 7	6	3	50	16	
Case 8	7	3	50	16	
Case 9	8	3	50	16	
Case 10	8	0.5	50	16	Different current densities
Case 11	8	1	50	16	
Case 12	8	1.5	50	16	
Case 13	8	2.5	50	16	
Case 14	8	3	50	16	
Case 15	8	2	50	10	Different reinforcement diameters
Case 16	8	2	50	14	
Case 17	8	2	50	18	
Case 18	8	2	50	22	
Case 19	8	2	50	26	
Case 20	8	3	30	16	Different thicknesses of concrete protective cover
Case 21	8	3	35	16	
Case 22	8	3	40	16	
Case 23	8	3	45	16	
Case 24	8	3	50	16	

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4. Model validation

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The reliability of the model proposed in this paper can be verified by the measured data of chloride concentration in concrete by Wu *et al.* [55]. The test objects of the experiments were taken from Fangcheng port, Qinzhou port (as shown in Fig. 7), and Tieshan port in China [55]. A detailed description about the test objects, including construction time, building structure type and chloride ingress time, is presented in Table 4. The water/binder ratio of concrete for all the three ports is 0.4 and the concrete strength grade is C40. Additionally, the concrete powders were taken from the external wall of the structures in the in-situ test. When taking the sample from the ports, the drilling

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301 depth was 56 mm and was divided into eight equal sections. The chloride concentration was
 302 measured by Rapid Chloride Concentration Tester (RCT). Here, we compare our simulation results
 303 of free chloride concentration in concrete with the experimental data, as demonstrated in Fig. 8a-c.
 304 Due to the randomness of aggregate distribution in concrete, the chloride concentration at the same
 305 ingress depth is slightly different. It is evident from Fig. 8a-c that the numerical simulation results
 306 are very close to the experimental data, implying that the proposed numerical model is reliable.



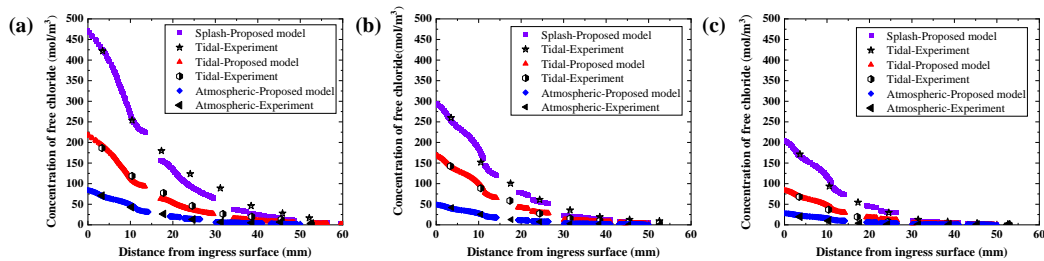
308
309 **Fig. 7.** Qinzhou port [55]

310 **Table 4**

311 Detailed description of the test objects.

No.	Dock	Built year	Structure types	Ingress time (months)
1	13# Dock of Fangcheng port	2005	Gravity type thin-walled cylindrical caisson structure	80
2	10# Dock of Qinzhou port	2008	The category of large cylinder gravity structure	62
3	1# Dock of Tieshan port	2009	The category of gravity caisson structure	35

312 Through the comparison of chloride concentration in concrete of splash region, tidal region
 313 and atmospheric region, it is obvious that the corrosion degree of RC structure of splash region is
 314 the most serious, as shown in Fig. 8a-c. This demonstrates that RC structure of Splash region is the
 315 first to fail in the marine environment. Therefore, it is of great significance to repair the RC structure
 316 of Splash region. In our work, the RC structure of Splash region is taken as the research object.



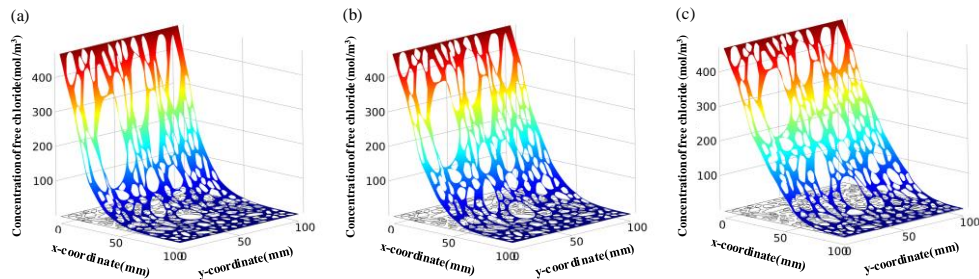
318

319 **Fig. 8.** Comparison of free chloride concentration between numerical results and experimental data. (a) Fangcheng
 320 port, (b) Qing zhou port, and (c) Tieshan port.

321
 322
 323 **5. Results and discussions**

324 **5.1 Long-term chloride ingress simulations**

325 The distribution of chloride concentration in concrete plays a vital role in evaluating the service
 326 performance of RC structure and judging whether the reinforcement is corroded or not [60,61].
 327 Despite the continuous progress of experiments, it is time-consuming and costly to implement the
 328 long-term chloride ingress experiments[62]. And the long-term experiments with chloride ingress
 329 over 20 years have not been reported. However, for RC structures, the minimum service life required
 330 by the Code for Concrete Design is 50 years [68]. Therefore, it is significant to study the long-term
 331 chloride ingress process in RC structure, such as 25 years and 50 years of chloride ingress. To
 332 address these critical issues, herein, numerical simulation has been used to study the long-term
 333 chloride ingress process in RC structure and reveal the evolution process of chloride concentration.



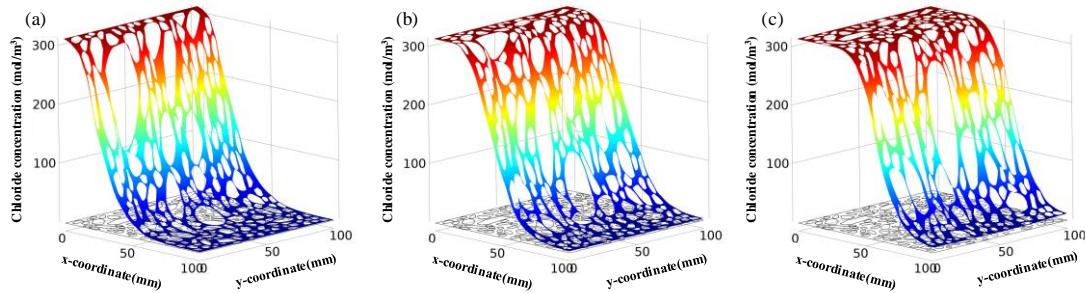
334
 335 **Fig. 9.** Spatial distributions of free chloride at three different ingress times. (a) 10th year, (b) 25th year, and (c) 50th
 336 year, respectively.

337 In the experiments conducted by Wu *et al.* [55], the free chloride concentration in concrete of
 338 splash region of Fangcheng port was measured only after 80 months of chloride ingress. To better
 339 demonstrate the evolution process of chloride concentration in concrete, distributions of free
 340 chloride concentration at three different ingress times (*i.e.*, 10th year, 25th year, and 50th year) is
 341 investigated, as shown in Fig. 9a-c. It should be mentioned that the diameter of reinforcement is 16
 342 mm and the thickness of concrete protective cover is 50 mm in the simulation. The horizontal
 343 coordinates (*i.e.*, x and y coordinates) in Fig. 9a-c represent the coordinates of the concrete meso-
 344 structures, and the vertical coordinate (*i.e.*, z coordinate) represents the free chloride concentration.
 345 And the chloride erodes along the direction of x -axis. It is obvious from Fig. 9a-c that the free
 346 chloride concentration increases with the increases of chloride ingress time at the same ingress depth.
 347 This indicates that with the increase of ingress time, if no repair measures are taken, it will inevitably
 348 lead to the corrosion of reinforcement in RC structure. The spatial distributions of free chloride
 349 concentration in Fig. 9a-c could not only clearly reflect the evolution of chloride concentration, but
 350 also manifest the tortuosity effect of the chloride diffusion.

351 Additionally, the spatial distributions of bound chloride concentration at three different ingress
 352 times (*i.e.*, 10th year, 25th year, and 50th year) are demonstrated in Fig. 10a-c. It is apparent from Fig.
 353 10a-c that the bound chloride concentration will not increase after reaching a stationary value, and
 354 the bound chloride reaches the saturation state. This indicates that the region where the bound

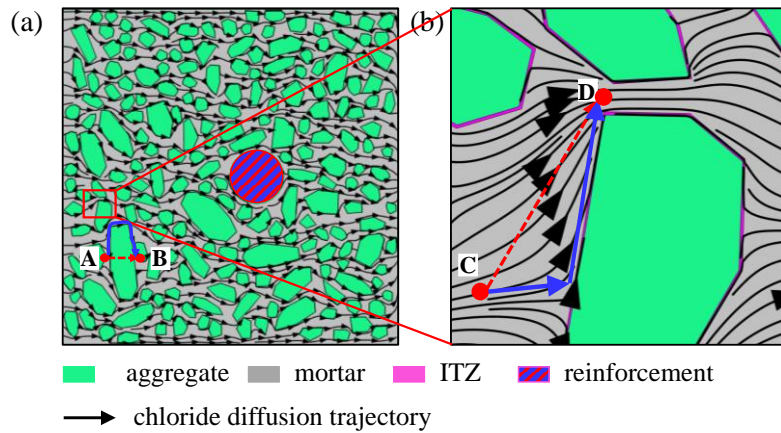
355 chloride reaches saturation state will no longer have the adsorption capacity of chloride and the
 356 adsorption capacity of concrete to chloride decreases with the increase of chloride ingress time.

357



358

359 **Fig. 10.** Spatial distributions of bound chloride at three different times. (a) 10th year. (b) 25th year, and (c) 50th year,
 360 respectively.



361

362 **Fig. 11.** Free chloride diffusion trajectories in meso-structures of concrete. (a) Overall concrete section (b) Local
 363 amplification.

364 The diffusion trajectories of chloride in the concrete meso-structures have been clearly presented
 365 in Fig. 11a-b. It is obvious from Fig. 11a-b that the aggregate increases the diffusion paths of
 366 chloride and hinders the diffusion of chloride. For example, in Fig. R11a, the chloride ions at point
 367 A cannot diffuse through the aggregate to point B along a straight line, but must diffuse around
 368 aggregate to point B, which significantly increases the diffusion path of the chloride ions. In order
 369 to study the influence of ITZ on chloride diffusion, Fig11 is partially enlarged. It is found that the
 370 chlorine ions at point C do not diffuse to point D along a straight line. Instead, the chlorine ions at
 371 point C diffuse first to the ITZ and then along the ITZ region to point D (as shown in Fig. 11B),
 372 indicating that ITZ is a fast channel for chlorine ion diffusion. This phenomenon has not been found
 373 in previous studies. Consequently, the mechanism of ITZ promoting the chloride diffusion in
 374 concrete can be well understood by this phenomenon. Moreover, the existence of random aggregates
 375 in concrete leads to the non-uniformity distribution of chloride concentration at the same ingress
 376 depth. This is quite different from the existing model [21] treating concrete as a single homogeneous
 377 material. In their models, the distribution of chloride concentration is uniform at the same ingress
 378 depth [21]. The proposed model with random distribution of aggregates is more consistent with the
 379 reality.

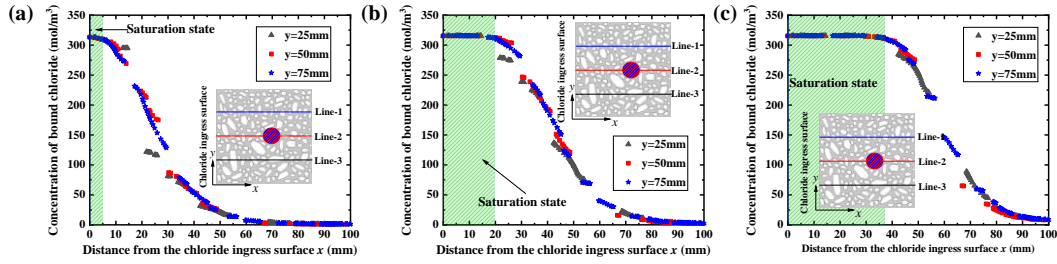


Fig. 12. The bond chloride profiles at three different ingress times. (a) 10th year. (b) 25th year, and (c) 50th year, respectively.

In order to further quantitatively study the distributions of chloride concentration in concrete, Fig. 12a-c shows how the bound chloride concentrations change with penetration depth at three different ingress times (*i.e.*, 10th year, 25th year, and 50th year). The simulation data of bound chloride concentration is extracted from the left to the right of the concrete at three random places inside the concrete (as shown in Fig. 12a-c by Line-1, Line-2, and Line-3). Obviously, due to the random distribution of aggerates in concrete, the data of three chloride concentration curves (Line-1, Line-2, and Line-3) are not completely coincident. It can also be seen from Fig. 12a-c that the saturated bound chloride region is gradually increasing with the increase of chloride ingress time. The depths of saturated bound chloride region are only 5 mm and 19.5 mm at 10th and 25th year of chloride ingress, respectively. However, it reaches to 37.2 mm at 50th year of chloride ingress.

Moreover, once the free chloride concentration on the surface of the reinforcement reaches the critical chloride concentration of 33.8mol/m³[63–65], the reinforcement will begin to rust [65]. As can be seen from Fig. 13a, at 10th year of chloride ingress, the free chloride concentration on the surface of the reinforcement (*i.e.*, 13.2mol/m³) is lower than the critical chloride concentration, and the reinforcement does not corrode at this stage. However, the free chloride concentration on the surface of the reinforcement (*i.e.*, 33.8mol/m³) has reached the critical chloride concentration at 25th year of chloride ingress (as showed in Fig. 13b), indicating that the reinforcement embedded in concrete begins to rust and the service life of RC structures is only 25 years. This is far lower than the service life required by Code for Concrete Design (*e.g.*, 50 years) [68]. To extend the service life of RC structures, it is necessary to take measures to remove chloride from concrete during the service life of the concrete. In the next section, the removal of chloride from concrete by ECE treatment will be described in detail.

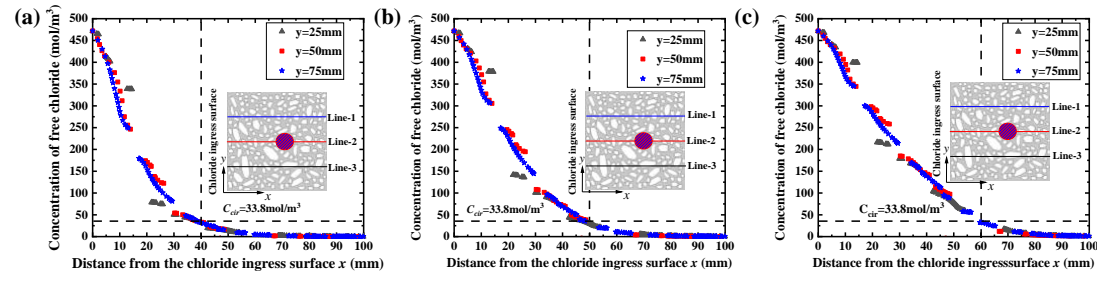
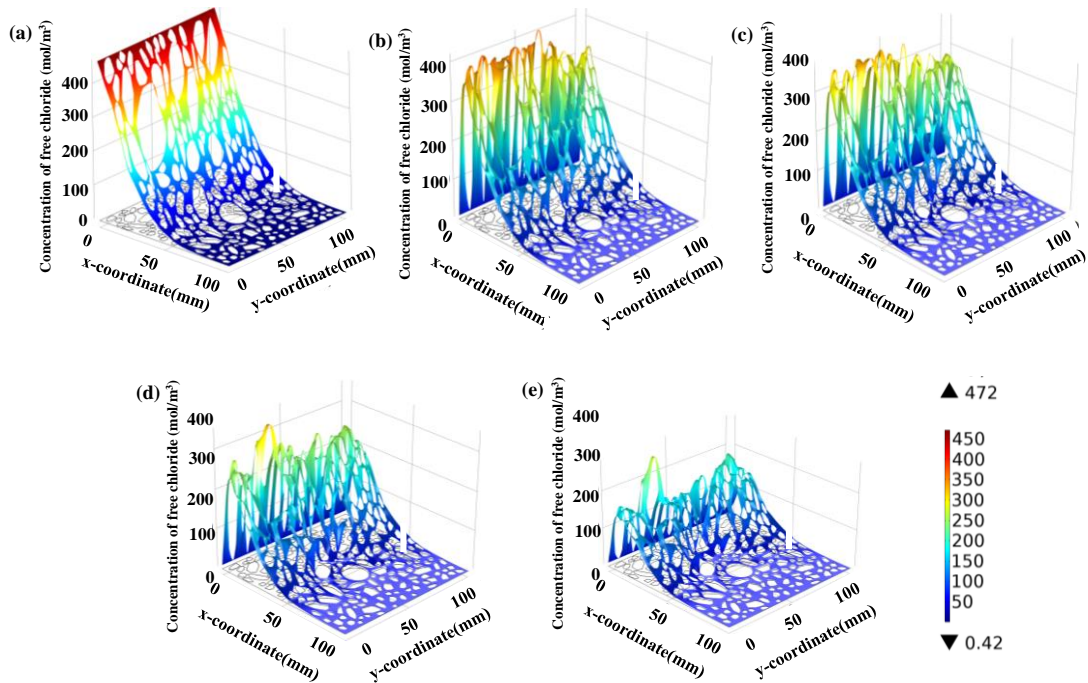


Fig. 13. The free chloride profiles at three different ingress times. (a) 10th year. (b) 25th year, and (c) 50th year, respectively.

410 **5.2 ECE treatment simulations**

411 The ECE method is adopted to remove chloride from concrete when the free chloride
 412 concentration on the surface of the reinforcement reaches the critical chloride concentration. Note
 413 that ECE treatment can significantly reduce chloride in RC structures in a very short period of time
 414 (usually 4~8 weeks) [29,66]. Therefore, the longest ECE treatment time in our simulation is 8 weeks.
 415 In the existing ECE treatment literatures, the distributions of chloride concentration in concrete were
 416 assumed to be uniform before ECE treatment, and the chloride concentration in concrete was set to
 417 be a constant, such as 380 mol/m³ [14–16,33] or 200 mol/m³ [22,66] and so on. However, this was
 418 not consistent with the actual situation.

419 In this section, the removal of chloride from concrete by ECE treatment is implemented at the
 420 25th year of chloride ingress (as shown section 5.1). The current density applied to the reinforcement
 421 is 2 A/m², and the ECE treatment time is from 1 to 8 weeks with a step of one week. More detail
 422 information is presented in Table 3 (case 1 to case 8).

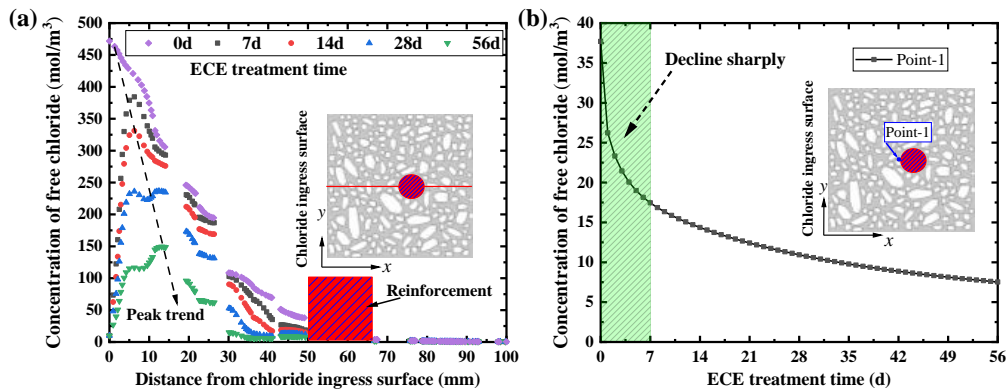


423
 424 **Fig. 14.** Spatial distributions of free chloride concentration after different ECE treatment time. (a) Before ECE
 425 treatment. (b) After 1 weeks of ECE treatment. (c) After 2 weeks of ECE treatment. (d) After 4 weeks of ECE
 426 treatment. (e) After 8 weeks of ECE treatment, respectively.

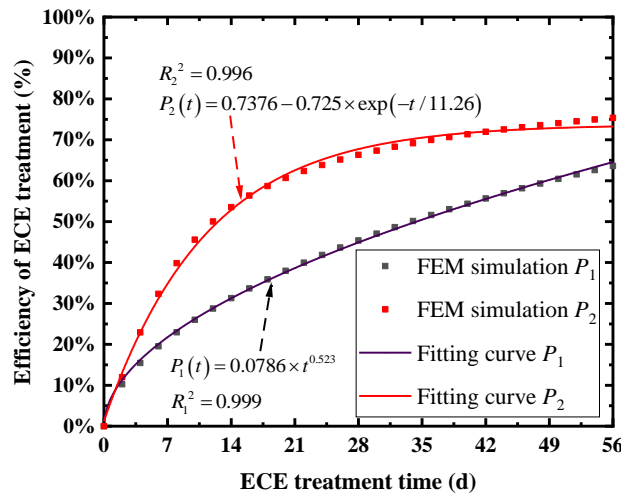
427
 428 The spatial distributions of free chloride concentration in RC structures after 1~8 weeks of
 429 ECE treatment have been calculated, as shown in Fig. 14b-e. For comparison, the spatial
 430 distributions of free chloride concentration in RC structures before ECE treatment is also presented
 431 in Fig. 14a. By comparing Fig. 14a and Fig. 14b, it is apparent that spatial distributions of free
 432 chloride concentration in RC structures changes dramatically after ECE treatment. Before the ECE
 433 treatment, the distribution of free chloride in the concrete decreases gradually as the ingress depth
 434 increases (as depicted in Fig.14a). However, after ECE treatment, the distribution of free chloride
 435 in the concrete first increases and then decreases with the increase of the ingress depth. This
 436 indicates that the maximum value of free chloride concentration appears inside the concrete after

437 ECE treatment (as depicted in Fig.14b-e), and not appears on the chloride ingress surface anymore
 438 (as shown in Fig.14a). This phenomenon has not been shown in the existing ECE treatment
 439 literatures[15,17,21,22,34]. More importantly, with the increase of ECE treatment time, the
 440 maximum value of free chloride concentration in concrete is significantly reduced, as shown in
 441 Fig14b-d, indicating that ECE method can effectively remove chloride in concrete.

442 Furthermore, Fig. 15a shows how the chloride concentrations change with increase of the ECE
 443 treatment times. It can be clearly seen from the Fig. 15a that with the increase of ECE treatment
 444 time, the maximum value of chloride concentration in concrete decreases, and the position of the
 445 peak is moving towards the interior of concrete. In addition, the chloride concentrations on the
 446 surface of reinforcement for different ECE treatment times have also been calculated, as shown in
 447 Fig. 15b. It is obvious from Fig. 15b that the chloride concentration on the surface of the
 448 reinforcement decreases sharply at the initial stage of ECR treatment, and then decreases gradually
 449 with the increase of desalting time. Similar results has also been found in the existing research
 450 work [17,21].



451
 452 **Fig. 15.** Free chloride concentration profiles (a) at $y = 50$ mm with different ECE treatment time, (b) on the surface
 453 of reinforcement.



454
 455 **Fig. 16.** Relationship curves between efficiency indexes (*i.e.*, P_1 and P_2) of ECE treatment and ECE treatment
 456 time.

457 In order to further quantitatively characterize the efficiency of ECE treatment, the efficiency
 458 indexes (*i.e.*, P_1 and P_2) of ECE treatment are calculated based on Eq. (13) and (14) and plotted in

459 Fig. 16. It can be apparent from the Fig. 16 that P_2 increase rapidly at first and then tends to be
 460 stable, and P_1 increase gradually with the increasing of ECE treatment time. In addition, the ECE
 461 treatment efficiency in concrete protective cover (P_1) is less than that around the reinforcement (P_2)
 462 for the same ECE treatment time. Moreover, after 8 weeks of ECE treatment, P_1 and P_2 have reached
 463 63.6% and 75.4%, respectively. This also indicates that ECE treatment can effectively remove
 464 chloride from concrete.

465 Furthermore, the following formula fitted from the data of numerical simulation can be obtained
 466 by regression analysis, which can be used to describe the quantitative relationship between the
 467 efficiency indexes of ECE treatment and the ECE treatment time.

$$468 \quad P_1(t) = 0.0786 \times t^{0.523} \quad (16)$$

$$469 \quad P_2(t) = 0.7376 - 0.725 \times \exp(-t/11.26) \quad (17)$$

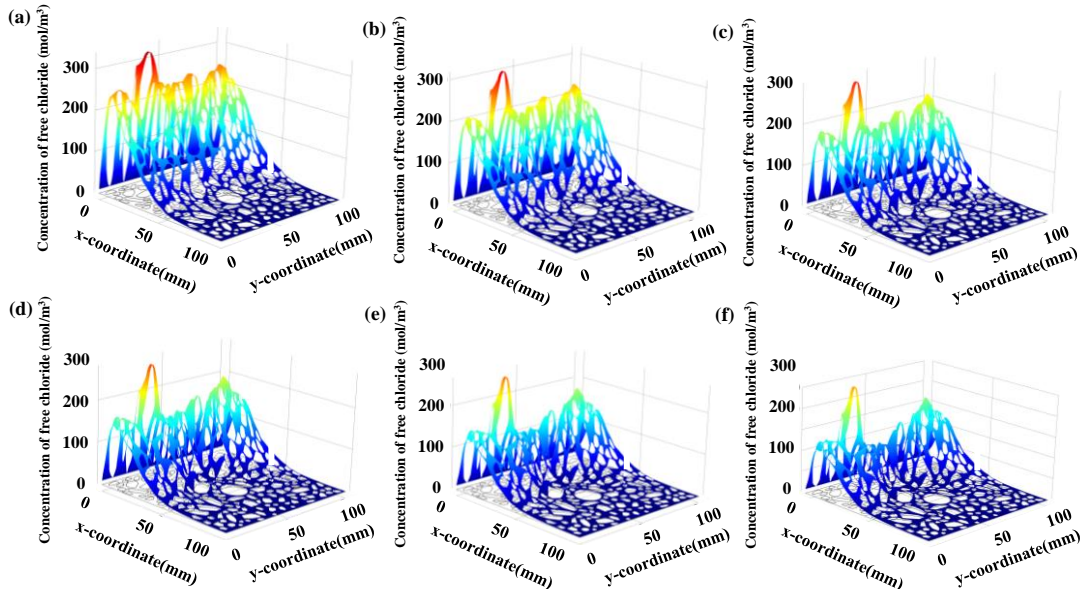
470 where t denotes ECE treatment time (d).

471 5.3 Parametric analysis

472 To gain further insight into the efficiency of ECE treatment, the influence of some key factors
 473 (current density, diameter of reinforcement, and thickness of the concrete protective cover) on the
 474 efficiency of ECE treatment has been investigated.

475 5.3.1 Current density

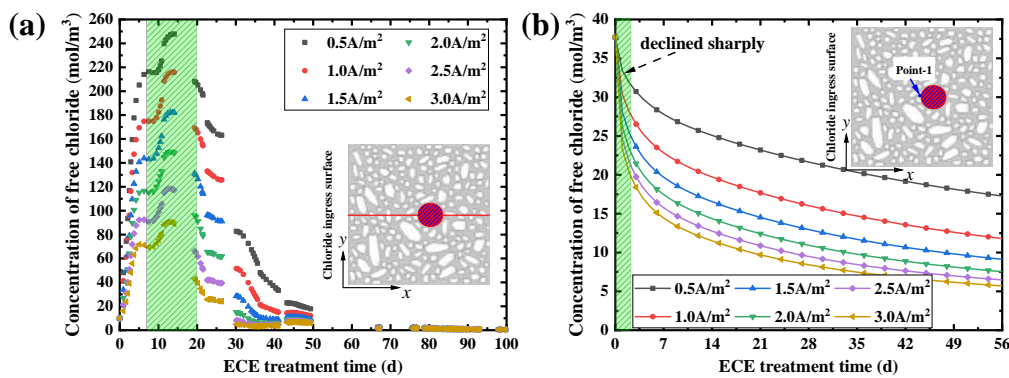
476 The current density on the surface of reinforcement is one of the important factors affecting
 477 the efficiency of ECE treatment[33]. When the current density is too small, the efficiency of ECE
 478 treatment is reduced and the time of ECE treatment is prolonged [14,34]. To reveal the effect of
 479 current density on ECE treatment, ECE treatment of concrete with different current densities from
 480 0.5 A/m² to 3 A/ m² have been investigated. Details are listed in Table 1 (*i.e.*, case 10 to case 14).
 481 Except for the current density, the simulation conditions from case 10 to case 14 are the same, which
 482 can eliminate the interference of other variables on the ECE treatment.



483
 484 Fig. 17. Spatial distributions of free chloride concentration after 8 weeks of ECE treatment. (a) 0.5 A/m², (b) 1 A/m²,
 485 (c) 1.5 A/m², (d) 2 A/m², (e) 2.5 A/m², and (f) 3 A/m², respectively.

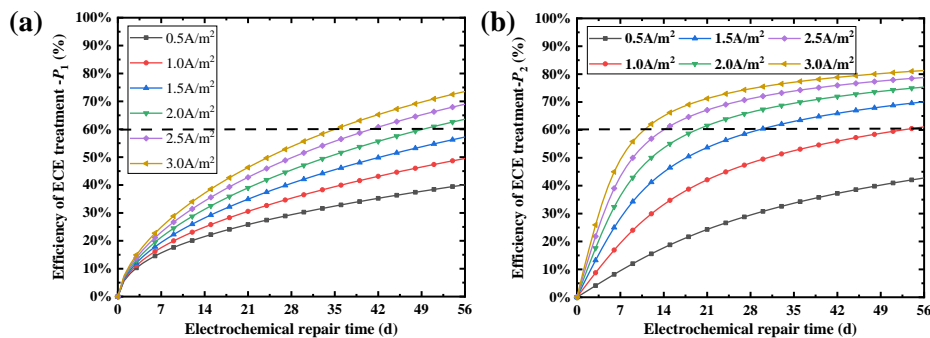
486 After 8 weeks of ECE treatment, the distributions of free chloride concentration with different
 487 current densities are as shown in Fig. 17. Obviously, the overall characteristic spatial distributions

488 of free chloride concentration are consistent regardless of current density. For instance, all the peaks
 489 of free chloride concentration with different current densities are distributed between reinforcement
 490 and chloride ingress surface. This indicates that the current density of cathode does not change the
 491 distribution trend of free chloride concentration. However, with the increase of current density, the
 492 concentration of free chloride in concrete decreases gradually. It is worth noting that the current
 493 density on the surface of the reinforcement is proportional to the potential difference of the applied
 494 external electric field. A large potential difference will lead to a large current density. In addition,
 495 the migration rate of chloride in the electric field can be improved by increasing the potential
 496 difference according the Eq. (5). Therefore, large migration rate of chloride will mean that more
 497 chlorides will be removed from the concrete in the same repairing time, resulting a reduction of
 498 chloride concentration in concrete.



499
 500 **Fig. 18.** Free chloride concentration profiles (a) at $y = 50$ mm, and (b) on the surface of reinforcement with different
 501 current density.

502 In order to quantitatively describe the effect of current density on ECE treatment, the
 503 distributions of free chloride concentration at $y = 50$ mm after 8 weeks of ECE treatment are
 504 calculated and demonstrated in. Fig. 18a. It reveals that with the increase of current density, the
 505 maximum value of chloride concentration is gradually decreasing. Besides, the peak position of
 506 chloride concentration is distributed between 8 mm and 20 mm away from the chloride ingress
 507 surface. Moreover, Fig. 18b shows the change curves of free chloride concentration on the surface
 508 of reinforcement with current densities. What stands out in this figure is the rapid decrease of the
 509 free chloride concentration in the initial stage of ECE treatment (0~3 days). In the later stage of
 510 ECE treatment, the free chloride concentration surrounding the reinforcement declines gradually.
 511 This is mainly due to that the chloride concentration around the reinforcement is very low in the
 512 later stage of ECE treatment.



513

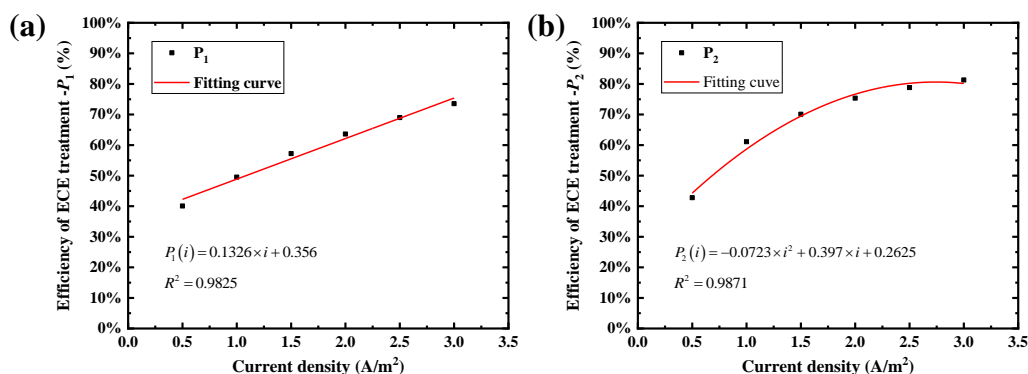
514 **Fig. 19.** Comparison of influences of different current densities on the efficiency indexes of ECE treatment. (a) The
 515 efficiency index P_1 of ECE treatment, (b) The efficiency index P_2 of ECE treatment.

516 **Fig. 19a-b** reveal that ECE treatment efficiency indexes P_1 and P_2 increase with the increase of
 517 current density. It is obvious from Fig. 19a-b that increasing current density can improve the
 518 removal of chloride ions at the same ECE time. Similar results have also been obtained from
 519 experimental researches conducted by Saraswathy *et al.* [67]. After 8 weeks of ECE treatment, the
 520 ECE treatment efficiency indexes P_1 and P_2 with current density of 2 A/m² are 63.6% and 73.2%,
 521 respectively. While the ECE treatment efficiency indexes P_1 and P_2 with current density of 3 A/m²
 522 after 8 weeks of ECE treatment are 75.3%, and 81.3%, respectively. However, with the increase of
 523 current density, the hydrogen generated on the surface of reinforcement is increasing. The hydrogen
 524 generated by ECE treatment will make the reinforcement brittle, which is not conducive to the
 525 overall performance of the RC structure [33]. Considering the damage of hydrogen to reinforcement,
 526 the optimized current density is 2 A/m².

527 In order to further reveal the relationship between current density and ECE treatment efficiency
 528 (*i.e.*, P_1 and P_2), the change trend of ECE treatment efficiency (*i.e.*, P_1 and P_2) with current density
 529 is shown in Fig. 20a-b. It can be clearly seen from Fig. 20a-b that with the increase of current density,
 530 P_1 increases linearly, and P_2 first increases and then stabilizes. Through regression analysis, the
 531 correlation between current density and the ECE treatment efficiency (*i.e.*, P_1 and P_2) can be express
 532 as follows:

$$533 \quad P_1(i) = 0.1326 \times i + 0.356 \quad (18)$$

$$534 \quad P_2(i) = -0.0723 \times i^2 + 0.397 \times i + 0.2625 \quad (19)$$



535 **Fig. 20.** The change trend of ECE treatment efficiency. (a) The efficiency index P_1 of ECE treatment, (b) the
 536 efficiency index P_2 of ECE treatment.

538 5.3.2 Diameter of reinforcement

539 In the process of ECE treatment, the reinforcement embedded in concrete is regard as the
 540 cathode electrode[26,31]. In marine engineering, the diameters of reinforcement used in different
 541 building structures are different[68,69]. However, the diameter of the reinforcement can directly
 542 affect the distribution of the electric field and the formation range of hydroxides [14,33]. Therefore,
 543 it is necessary to discuss the influence of reinforcement diameter on the ECE treatment. In this
 544 section, the ECE treatment of RC structures with different reinforcement diameters (*i.e.*, 10 mm, 14
 545 mm, 18 mm, 22 mm and 26 mm) are simulated. And all the other parameters used in the simulations
 546 are listed in Table 1 (case 15 to case 19). It should be noted that the simulation conditions of case

15 to case 19 are the same, except for the diameter of the reinforcement, which can eliminate the interference of other variables on the ECE treatment.

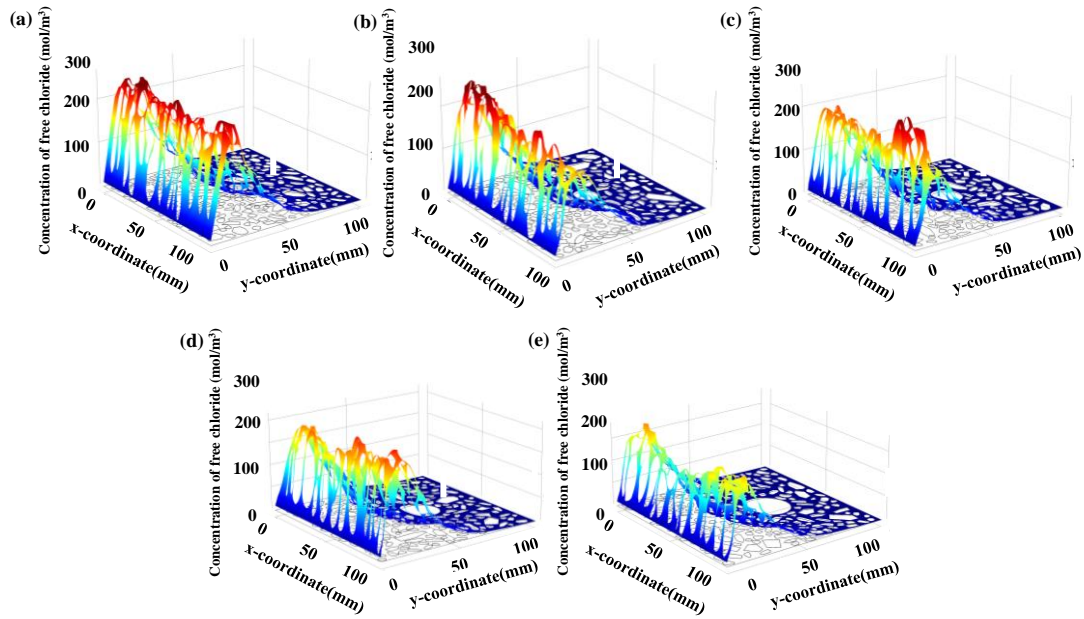


Fig. 21. Spatial distributions of free chloride concentration after 8 weeks of ECE treatment for different diameters of the reinforcement. (a) $\phi = 10$ mm, (b) $\phi = 14$ mm, (c) $\phi = 18$ mm, (d) $\phi = 22$ mm, and (e) $\phi = 26$ mm, respectively.

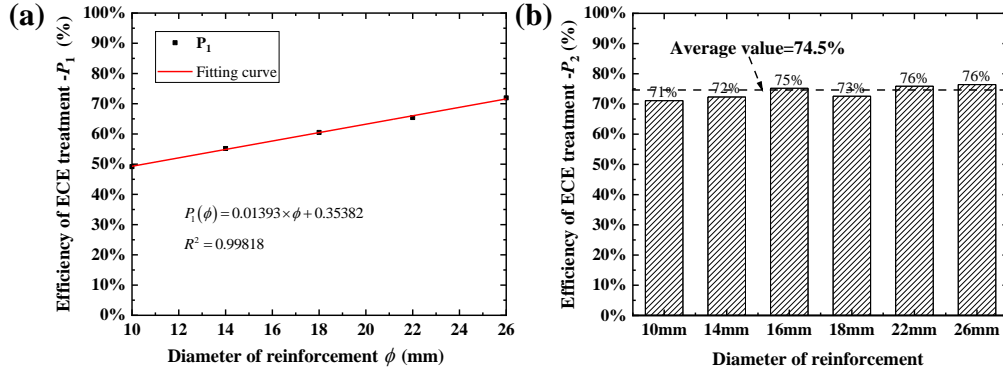
The spatial distributions of free chloride concentration for different diameters of reinforcement after 8 weeks of ECE treatment are calculated, as shown in Fig. 21a-e. It is apparent from Fig. 21a-e that the free chloride concentration in the concrete gradually decreases with the increase of reinforcement diameter. It is worth noting that the reinforcement embedded in concrete is regarded as the cathode electrode, and the cathode has a repulsive effect on chloride. With the increase of reinforcement diameter, the repulsive effect is more obvious. Hence, ECE treatment effect is getting better and better with the increase of reinforcement diameter. However, compared with the current density, the free chloride concentration does not decrease significantly with the increase of reinforcement diameter, and the reinforcement diameters had little effect on ECE treatment. compared with the current density.

In addition, the relationship between efficiency indexes (P_1 and P_2) of ECE treatment and reinforcement diameter are shown Fig. 22a and b. The ECE treatment index P_1 increases linearly with the increase of the reinforcement diameters, as depicted in Fig. 22a. Through linear regression analysis, the quantitative relationship between them can be expressed as:

$$P_1(\phi) = 0.01393 \times \phi + 0.35382 \quad (20)$$

where ϕ is diameter of the reinforcement.

Fig 22b describes the histogram of the ECE treatment index P_2 with different reinforcement diameters. Obviously, with the increase of reinforcement diameter, the change of efficiency index P_2 of ECE treatment is trifling. The maximum value of P_2 is 76%, and the minimum value is 71% with a difference of only 5%. Therefore, the influence of reinforcement diameter on ECE treatment indexes of P_2 could be ignored.



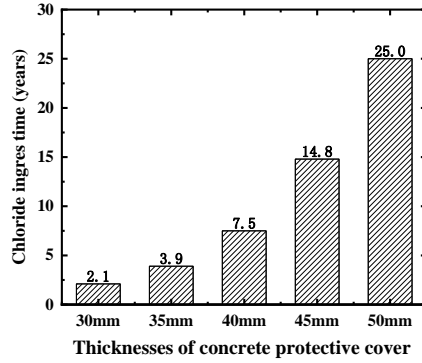
575
576 **Fig. 22.** Comparison of the influence of different reinforcement diameters on the efficiency indexes of ECE treatment.
577 (a) The efficiency index P_1 of ECE treatment, (b) the efficiency index P_2 of ECE treatment.

578 **5.3.3 Thickness of concrete protective cover**

579 The concrete protective cover thickness is stipulated in detail in the Code for durability Design
580 of concrete structures [68], and different structures have different requirements for the minimum
581 thickness of concrete protective cover. For examples, for a harbor wharf with a designed service life
582 of 50 years, it is stipulated that the minimum thickness of the concrete protective cover should be
583 50 mm. While, for construction projects far away from the marine environment, the required
584 minimum thickness of concrete protective cover is only 30 mm. Therefore, it is necessary to
585 investigate the influence of the thickness of concrete protective cover on the ECE treatment.

586 In order to illustrate the influence of the thickness of concrete protective cover on the ECE
587 treatment, it is necessary to simulate the ECE treatment of concrete with different concrete
588 protective cover thicknesses. The thickness of the concrete protective cover is from 30 mm to 50
589 mm with a step of 5 mm, the diameter of reinforcement is 16 mm, and the current density is 2 A/m².
590 When the free chloride concentration on the surface of the reinforcement reaches the critical chloride
591 concentration (33.8mol/m³), the chloride from concrete will be removed by ECE treatment.
592 According the theory of chloride ingress described in section 2.1, the chloride ingress time of
593 concrete with different thickness of the concrete protective cove are calculated when the free
594 chloride concentration on the surface of the reinforcement reaches the critical chloride concentration,
595 as shown in Fig. 23. It can be seen from Fig. 23 that the chloride ingress time corresponding to the
596 critical chloride concentration increases exponentially with the increase of the concrete protective
597 cover thickness. The thicker the concrete protective cover, the longer the service life of the RC
598 structure.

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600
601

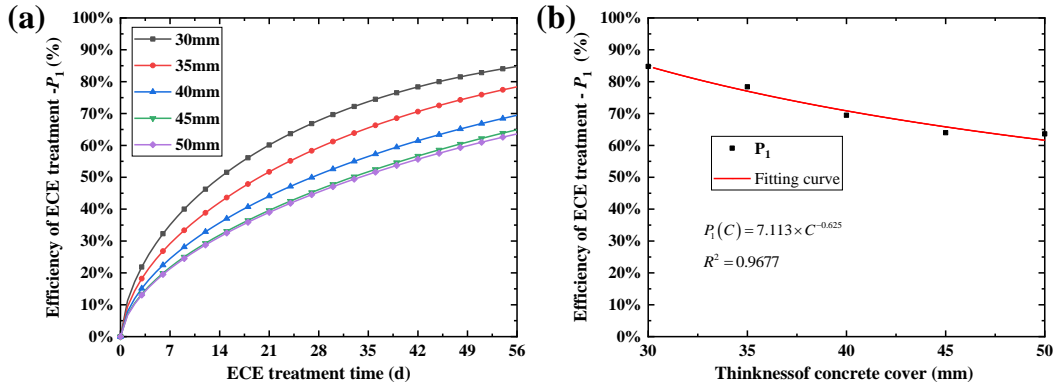


602
603 **Fig. 23.** Chloride ingress time corresponding to the critical chloride concentration for different thicknesses of
604 concrete protective cover.

605 It is clearly from Fig. 24a that with increasing of ECE treatment time, the ECE treatment
606 efficiency index P_1 with different concrete protective cover thicknesses increases gradually.
607 Additionally, the curves of ECE treatment efficiency index P_1 for 45 mm and 50 mm concrete
608 protective cover are very close. This manifest that the influence of concrete protective cover
609 thickness on the efficiency index P_1 of ECE treatment can be ignored when the thickness of concrete
610 protective cover is more than 45 mm. Furthermore, with the increase of the thickness of the concrete
611 protective cover, the efficiency index P_1 of ECE treatment after 8 weeks of ECE treatment gradually
612 decreases and tends to be stable, as plotted in Fig. 24b. Similar phenomenon have also been observed
613 from the experimental results of Garbacz *et al.* [70]. To express the quantitative relationship
614 between thickness of the concrete protective cover and the ECE treatment efficiency index P_1 , we
615 obtain the following fitting formula model through nonlinear analysis:

$$616 \quad P_1(C) = 7.113 \times C^{-0.625} \quad (20)$$

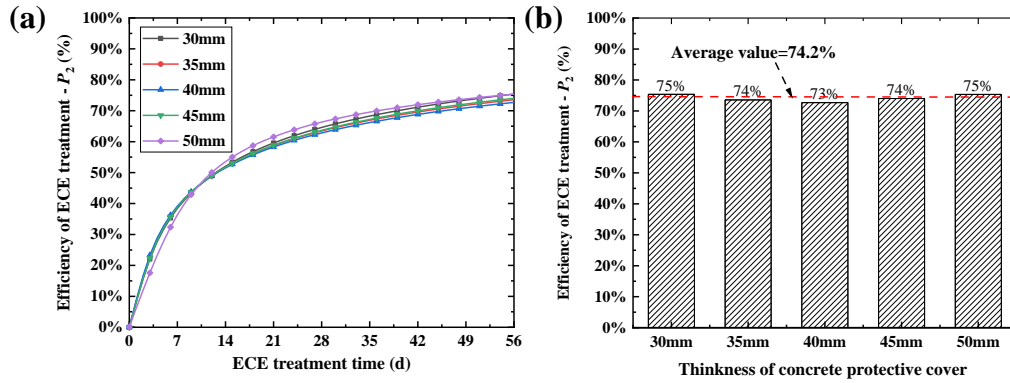
617 where C is the thickness of concrete protective cover (mm).



618
619 **Fig. 24.** The profiles of ECE treatment efficiency index P_1 . (a) Comparison of the influence of different thicknesses
620 of concrete protective cover on the ECE treatment efficiency index P_1 . (b) The relationship between thickness of
621 concrete protective cover and ECE treatment efficiency index P_1 after 8 weeks ECE treatment.

622 What can be clearly seen from Fig. 25a is that with increasing of ECE treatment time, the ECE
623 treatment efficiency index P_2 with different thicknesses of concrete protective cover also gradually
624 increases. However, the curves of ECE treatment efficiency index P_2 with different thicknesses of
625 concrete protective cover are very close, which indicates that the thickness of concrete protective
626 cover has slight effect on P_2 . Fig. 25b demonstrates the histogram of the efficiency index P_2 of ECE
627 treatment for different thicknesses of concrete protective cover after 8 weeks of ECE treatment.

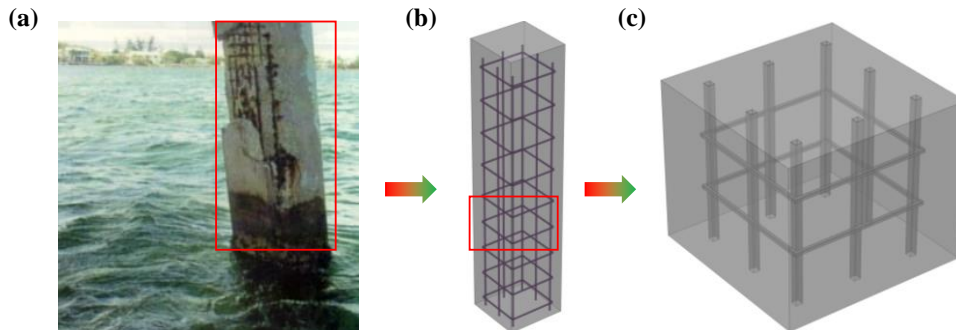
628 Obviously, the difference of P_2 between the maximum value and the minimum value is only 2%,
 629 which is very small and can be ignored.



630
 631 **Fig. 25.** The profiles of ECE treatment efficiency index P_2 . (a) Comparison of different thicknesses of concrete
 632 protective cover on the efficiency index P_2 of ECE treatment. (b) The histogram of the efficiency index P_2 of ECE
 633 treatment after 8 weeks ECE treatment.

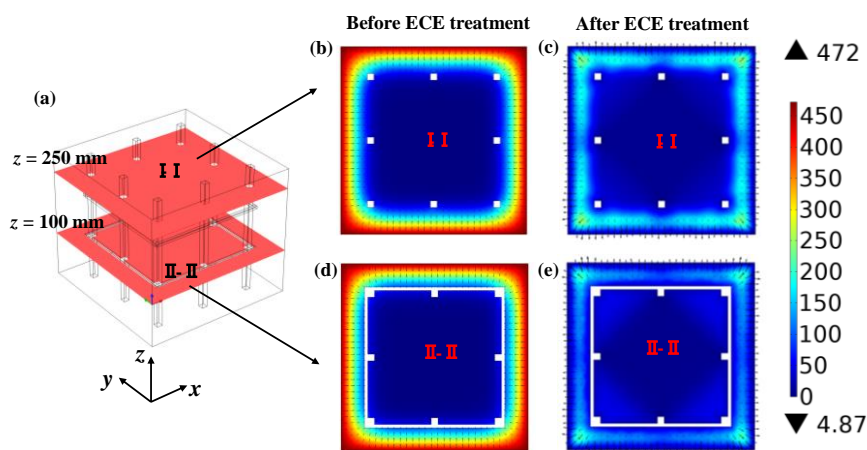
635 6 Engineering application

636 The above two-dimensional multi-phase mesoscopic numerical presents a detailed and clear
 637 picture of the transport of chloride in the process of chloride ingress and subsequent ECE treatment.
 638 In this section, a three-dimensional numerical model is established to simulate the chloride ingress
 639 and subsequent ECE treatment process for actual ocean engineering. Fig. 26a provides a corrosion
 640 picture of concrete column[71], which shows the corrosion damage caused by chloride ingress in
 641 marine engineering. And a geometric model including stress reinforcements and stirrups is
 642 established, as shown in Fig. 26b. In order to reduce the computational time of numerical simulation,
 643 two basic units are selected as the research object. And the cylindrical reinforcements are simplified
 644 to cuboid reinforcements with the same cross-sectional area[22], as shown in Fig. 26c. The
 645 diameters of the reinforcements are 16 mm, the thickness of concrete protective cover is 50 mm,
 646 and the current density on the surface of reinforcement is 2 A/m². Specially, the stirrups are
 647 considered in the simulations, and the diameters of the stirrups are 10 mm. In addition, the ECE
 648 treatment method is adopted to remove chloride from concrete when the chloride concentration
 649 around the surface of reinforcement reaches the critical chloride concentration.



650
 651 **Fig. 26.** 3D geometric model schematics of ECE treatment. (a) Reinforced concrete column in marine environment
 652 [71]. (b) Finite element geometric model. (c) Representative units.

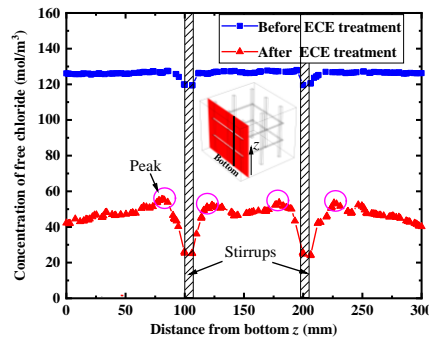
654 The distributions of chloride concentration in the $z = 100$ mm plane and $z = 250$ mm plane
655 before ECE treatment and after 8 weeks of ECE treatment are demonstrated in Fig. 27 a-e.
656 Compared with free chloride concentration before treatment (Fig. 27 b and d), the free chloride
657 concentration after 8 weeks of ECE treatment is significantly lower (Fig. 27 c and e). This indicates
658 that ECE treatment is a good non-destructive repair method for chloride removal. In practical
659 engineering, in order to avoid damage to the concrete structure, the reinforcing steel with the
660 protective layer falling off due to corrosion is generally used to connect with the cathode, without
661 artificial damage to the reinforced concrete structure. Furthermore, the angle reinforcements are
662 more severely corroded by chloride compared with the middle reinforcements, as shown the Fig.
663 27b and d. This is mainly due to that the angle reinforcements are corroded in both x and y directions,
664 while the middle reinforcements are corroded only is one direction (*i.e.*, x -direction or y -direction).
665 Similar results have also been obtained from experimental researches conducted by Chang *et al.*
666 [66]. In addition, the concentration of free chloride in the cross-section plane with stirrups ($z = 100$
667 mm) is significantly lower than that in the cross-section plane without stirrups ($z = 250$ mm) after 8
668 weeks of ECE treatment, as shown in Fig. 27c and e. This indicates that the use of stirrup can
669 improve the efficiency of ECE treatment. This can be attribute to that the use of stirrups could
670 generate a potential gradient along the length direction (*i.e.*, z direction) of reinforcement, thus
671 promoting the removal of chloride from the concrete.



672
673 **Fig.27.** Chloride concentration distribution before and after ECE treatment. (a) Schematic diagram of the cross-
674 sectional position of $z = 100$ mm and $z = 200$ mm. (b) Chloride concentration distribution in the cross-section of $z =$
675 250 mm before ECE treatment. (c) Chloride concentration distribution in the cross-section of $z = 250$ mm after 8
676 weeks ECE treatment. (d) Chloride concentration distribution in the cross-section of $z = 100$ mm before ECE
677 treatment. (e) Chloride concentration distribution in the cross-section of $z = 100$ mm after 8 weeks ECE treatment.

678 In order to quantitatively analyze the effect of ECE treatment, the free chloride concentration
679 profiles along the length direction (*i.e.*, z direction) of reinforcement before treatment and after 8
680 weeks of ECE treatment are calculated, as demonstrated in Fig. 28. It can be clearly seen from the
681 Fig. 28 that the average concentration of free chloride before repair is 127 mol/m^3 , while the average
682 concentration of chloride after 8 weeks of repair is only 49.3 mol/m^3 . This indicate the concentration
683 of free chloride in concrete is significantly reduced after ECE treatment. Moreover, the free chloride
684 concentration at the surface of stirrup is the lowest (23 mol/m^3), and the chloride concentration
685 reaches the maximum (58 mol/m^3) at about 20 mm away from the stirrups. This can be owing to

686 that the stirrup is used as cathodic, and the chloride around stirrup migrates outward under the
687 electric field.



688
689 **Fig. 28.** Concentration profiles of free chloride along the length direction of reinforced concrete column.

690 7 Conclusions

691 A multi-phase mesoscopic numerical model is proposed to fully understand the mechanisms
692 of the long-term chloride ingress and the subsequent ECE treatment of RC structure. The influence
693 of key factors (*i.e.*, current density, diameter of reinforcement, and thickness of the concrete
694 protective cover) on the efficiency of ECE treatment is investigated. In addition, the quantitative
695 relationship models between ECE treatment and these factors are established. Finally, a three-
696 dimensional numerical model is developed to simulate the long-term chloride ingress and ECE
697 treatment for actual ocean engineering. Based on a systematic study, the following conclusions can
698 be drawn:

699 1. The proposed multiphase numerical model presents a detailed and clear picture of the
700 transport of chloride in the process of chloride ingress and the subsequent ECE treatment, providing
701 engineers an effective tool in tackling corrosion problems of RC concrete structures.

702 2. With the increase of chloride ingress time, if no repair measures are taken, it will inevitably
703 lead to the corrosion of reinforcement. More importantly, the bound chloride concentration will not
704 increase after reaching a stationary value, indicating that the adsorption capacity of concrete
705 decreases with the increase of chloride ingress time.

706 3. The spatial distributions of free chloride concentration in RC structures changes dramatically
707 after ECE treatment. Additionally, the chloride concentration on the surface of the reinforcement
708 decreases sharply at the initial stage of ECR treatment, and then decreases gradually with the
709 increase of desalting time.

710 4. The ECE treatment efficiency can be improved by increasing the current density. And the
711 optimized current density is 2 A/m^2 . Moreover, the ECE treatment efficiency index P_1 increases
712 linearly, and P_2 first increases and then stabilizes with the increase of current density.

713 5. The reinforcement diameters has little effect on the ECE treatment efficiency. In addition,
714 the ECE treatment efficiency index P_1 gradually decreases and tends to be stable, while P_2 remains
715 stable with the increase of the thickness of the concrete protective cover.

716 6. The concentration of free chloride in the cross-section plane with stirrups is significantly
717 lower than that in the cross-section plane without stirrups after ECE treatment. And the free chloride
718 concentration on the surface of stirrup is the lowest.

721 **Author Contributions:**

722 **Xuandong Chen:** Data curation, Writing, Conceptualization, Methodology, Software, Investigation.

723 **Feng Fu:** Writing- Reviewing and Editing; **Hai Wang:** Writing- Reviewing and Editing,

724 Supervision; **Qiuqun Liang:** Writing- Original draft preparation, Writing- Reviewing and Editing,

725 Investigation. **Aiping Yu:** Software, Data curation. **Kai Qian:** Methodology, Software. **Ping Chen:**

726 Validation, Software.

727

728 **Acknowledgements:**

729 Authors appreciate the financial supports from the National Natural Science Foundation of China

730 (No. 51968014), Guangxi Key Laboratory of New Energy and Building Energy Saving Foundation

731 (No. 19-J-21-17, 19-J-21-30), and Guangxi Universities Scientific Research Project

732 (2020KY06029), Natural Science Foundation of Guangxi Province (No. 2018GXNSFAA138199),

733 Ph.D. research startup foundation of Guilin University of Technology (No. 002401003523).

734

735 **Conflicts of Interest:** The authors declare no conflict of interest.

736

737 **References**

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