Research Article

Comparison of Electrochemical Chloride Extraction Models for Reinforced Concrete Structures Based on Multiple Potential Theories

Wu Xiao-hui,1 Wang Yan-feng,1 Chen Jiejing,2 Cheng Xin,2 and Xia Jin2

1Power Grid Planning Research Center of Guangdong Power Grid Co. Ltd., Guangzhou 510080, China
2College of Civil Engineering and Architecture, Zhejiang University, Hangzhou 310012, China

Correspondence should be addressed to Chen Jiejing; 12112107@zju.edu.cn

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For chloride-contaminated RC structures, steel corrosion is one of the most common reasons causing the deterioration of reinforced concrete (RC) structures. Electrochemical chloride extraction (ECE), which migrates the chloride ions out of the RC structure, is preferred as it is a nondestructive repairing method. In this context, electrokinetic models are often used to investigate ECE processes. Currently, electrokinetic models based on different potential theories, such as the constant potential, electroneutrality, and Gauss’ law, may be used to solve the potential distribution. Although many ECE numerical simulations have been conducted, there has been no systematic comparison of models based on different potential theories. Therefore, in this study, a comprehensive comparative study has been conducted on these models in terms of the potential distribution, current density, quantity of electric charge, and ion concentration. Two commonly used ECE methods, namely, steady voltage and steady current, were numerically simulated and analyzed. The numerical results with actual ECE data were also compared. Although the electrokinetic model based on electroneutrality might overestimate the residual chloride concentration and underestimate current density and hydroxyl concentration, critical analysis suggests that electroneutrality is more appropriate than the constant potential and Gauss’ law for electrokinetic modeling.

1. Introduction

Corrosion of steel bars in reinforced concrete (RC) structures results in performance degradation and major economic losses [1, 2]. RC penetrated by chloride from seawater and deicing salt is regarded as one of the main factors that cause steel corrosion; the corresponding methods for inhibiting or delaying corrosion can be classified into mechanical and chemical techniques [3]. Mechanical techniques improve the durability of a structure by replacing chloride-contaminated sections [4] or improving the performance of concrete [5] and steel rebar [6]. Meanwhile, chemical methods use inhibitors [7], electrode reactions [8], and electrochemical deposition [9, 10] to repair concrete cracks and decrease the risk of corrosion [11–13].

Over the last several decades, much attention has been paid to electrochemical chloride extraction (ECE) [14] as a nondestructive chemical decontamination method. ECE rehabilitates chloride-contaminated concrete by removing chloride ions from the structure and decreases the risk of chloride reinvasion: under the action of an externally applied electric field, chloride ions migrate out of concrete [15] while beneficial particles are introduced into it [16]; alkalinity near the surface of the steel rebar increases due to the hydroxyl groups produced by the cathodic reaction [17], which is beneficial for the regeneration of a passive layer [18]. In summary, an electric field not only promotes ion transport and interaction in the concrete but also induces complex electrode reactions on the surface of a steel bar. Additionally, in terms of DC power supply, there are two methods to...
control the electric field, namely, steady current [19, 20] and steady voltage [21, 22]. The steady current method maintains a constant output current while the steady voltage method applies a constant output potential.

To give guidance on ECE application, standards have been set up such as NACE SP0107-2017 in the United States [23], BS EN 14038-1-2016 in Great Britain [24], and JGJ/T 259–2012 in China [25]. However, the ECE phenomenon is influenced by the internal properties of RC structures [21, 26–28] and ECE protocols [22, 29, 30]. These factors complicate the selection of ECE parameters, such as electric potential, anodic electrolyte concentration, and repairing time, which are very important for improving the efficacy and efficiency of the ECE process. Currently, ECE processes have been studied by numerical simulations [31–33] to select the parameters, and appropriate electrokinetic models are required. As mentioned earlier, the applied electric field affects an ECE process and hence it is necessary to select the appropriate potential theory for modeling. Three potential theories based on constant potential [34], electroneutrality [35–37], and Gauss’ law [38–40] are well known. During ECE, the externally applied electric field and charged particles together control potential distribution in the interior of the concrete. The constant potential theory takes the former into consideration [31, 41], and the potential distribution is constant and independent of ECE duration. Meanwhile, the electroneutrality condition adds the concept of charge balance limitation [42–45] and couples potential distribution with ion concentration distribution. Compared with the electroneutrality condition, Gauss’ law [46, 47] describes the essence of the electric field and imposes stricter limitations.

In this study, electrokinetic models based on different potential theories were established. Electric field control methods (steady voltage and steady current) were separately considered in these models using different electric boundaries. Through comparative analyses, this study preliminarily explores the applicability of the constructed models. In addition, the accuracy of models was investigated by evaluating the difference between model and experimental results. Through comparison of the applicability and accuracy of different models, the potential theory that is appropriate to simulate ECE procedures was ultimately selected.

2. Theory

2.1. Mass Transport Equation. ECE (Figure 1(a)) can be regarded as a process of ion (i.e., chloride and hydroxyl) transport and electrode reaction under the action of an applied electric field (Figure 1(b)). The transport of ionic species in concrete can be expressed by mass conservation as follows [48]:

$$\frac{\partial C_i}{\partial t} = -\nabla J_i \quad i = 1, \ldots, N,$$

where $C_i$ (mol/m$^3$) is the concentration of the $i$th ionic species in the concrete structure, $t$ (s) represents time, $J_i$ (mol/(m$^2$·s)) is the flux of the $i$th ionic species in concrete, and $N$ is the total number of ionic species in the pore solution.

The Nernst–Planck equation, which accounts for diffusion, convection, and electric migration, has been applied to study ion transport [49–51]. In concrete, convection is negligible unless a moisture gradient exists [34]; therefore, electric migration is the main parameter in this ECE process [52]. If the pore solution is an ideal dilute solution, the flux of ionic species in concrete can be described as follows [53]:

$$J_i = -D_i \nabla C_i - z_i D_i C_i \left(\frac{F}{RT} \nabla \phi \right) \quad i = 1, \ldots, N,$$

where $z_i$ is the valence of $i$th ionic species (i.e., $z_{cl} = -1$), $D_i$ (m$^2$/s) is the diffusion coefficient of the $i$th ionic species in concrete, $R$ is the universal gas constant (8.314 J/(mol·K)), $T$ is the absolute temperature, $F$ is Faraday’s constant (96485 C/mol), and $\phi$ (V) is electrostatic potential.

Substituting equation (2) in equation (1), a multimaterial transmission equation, as shown in equation (3), can be derived to describe ion transport in concrete.

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + z_i D_i C_i \left(\frac{F}{RT} \nabla (C_i \nabla \phi) \right) \quad i = 1, \ldots, N.$$

Chloride ions in mature concrete are generally classified as free and bound chloride ions. Free chloride ions are dissolved in the pore liquid, while bound chloride ions are incorporated in cement hydrate through chemical and physical pathways. Therefore, the chloride ion type has a significant influence on ionic transport and it can be expressed as shown in equation (4) [53]:

$$\frac{\partial C_{fd}}{\partial t} + \frac{\partial C_{bd}}{\partial t} = D_{Cl} \nabla^2 C_{fd} + z_{Cl} D_{Cl} F \left(\frac{F}{RT} \nabla (C_{fd} \nabla \phi) \right),$$

where $C_{fd}$ and $C_{bd}$ (mol/m$^3$) represent free and binding chloride ion concentrations in concrete, respectively, and $D_{Cl}$ (m$^2$/s) is the diffusion coefficient of chloride ion in concrete. To improve model accuracy, the effect of chloride binding was studied. To accomplish this task, in this investigation, the Langmuir-binding isotherm was adopted [54]:

$$c_{bd} = \frac{ac_{fd}}{1 + \beta c_{fd}},$$

where $c_{fd}$ (mol/L) is the free chloride concentration in the pore solution, $c_{bd}$ (mol/kg) is the ratio of chloride ions bound to the cement paste, and $a$ and $\beta$ [54] are relative parameters. Assuming that the concrete is saturated and ion transport takes place only in the pore solution, equation (5) can be expressed as follows:

$$\frac{C_{fd}}{m_{cem}} = \frac{a(C_{fd}/1000\phi)}{1 + \beta(C_{fd}/1000\phi)^2},$$

where $m_{cem}$ (kg/m$^3$) is the mass of cement paste in concrete, and $\phi$ (%) is the porosity of concrete. Substituting equation (6) in equation (4), it is convenient to use a parameter $y = am_{cem}/1000\phi/((1 + \beta C_{fd}/1000\phi)^2$ to express the...
proportionality between the concentration rates of free and bound chloride ions:

\[
(1 + \gamma) \frac{\partial C_{fcl}}{\partial t} = D_{Cl} \nabla C_{fcl} + z_{Cl} D_{Cl} \nabla C_{fcl} \left( \frac{F}{RT} \nabla \phi \right). \tag{7}
\]

Equation (7) is a modified form of equation (3), which takes into account the chloride-binding isotherm. Equation (7) couples the mass conservation and Nernst–Planck equations; it involves \(N+1\) variables corresponding to potential and \(N\) kinds of ionic concentrations, but only \(N\) concentration equations. To solve the numerical model, electric potential equations are required.

2.2. Electric Potential Equation. In this section, three potential theories corresponding to constant potential, electroneutrality, and Gauss’ law were considered. In addition, as the electric boundary of a model can be divided into steady voltage and steady current, different electric potential equations were employed to solve the model.

2.3. Constant Potential Condition

2.3.1. Steady Voltage. In the constant potential condition, an electric potential is linearly distributed and remains constant, which can be expressed as follows:

\[
\frac{\partial \phi}{\partial t} = 0. \tag{8}
\]

\[
\nabla^2 \phi = 0. \tag{9}
\]

The electric potential has a unidirectional coupling relationship with ion transport, resulting in independent transport for different types of ions. Combining equations (8) and (9) with equation (3), the constant potential model with a steady voltage boundary can be solved.

2.3.2. Steady Current. In the constant potential condition, the electrolyte is regarded as a conductor. Therefore, the bulk conductivity of the conductor can be used to define the electrolyte potential drop. In this context, Ohm’s law can be used to describe the current flow in the concrete structure as follows:

\[
I = \sigma \nabla \phi, \tag{10}
\]

where \(I\) (A/m²) and \(\sigma\) (S/m) represent the current density and electrical conductivity of concrete, respectively. Taking the derivative of equation (10) and combining it with equation (9), the current density was found to be independent of location:

\[
\nabla I = 0. \tag{11}
\]

Finally, by combining equation (10) with equation (3), it becomes possible to solve the constant potential model with a steady current boundary.

2.4. Electroneutrality Condition

2.4.1. Steady Voltage. Assuming that there is no electric charge due to the external environment, the electroneutrality condition can be expressed as shown below:

\[
\sum_{i=1}^{N} z_i C_i = 0. \tag{12}
\]

The electric current in the electrolyte is related to ion flux and can be expressed as follows:

\[
I = F \sum_{i=1}^{N} z_i J_i. \tag{13}
\]

Together, equations (1), (12), and (13) yield equation (14), which shows that electric current is only a function of time and is not related to the position.

\[
\nabla I = 0. \tag{14}
\]

Finally, combining equation (2) with equations (12) and (13), a bidirectional coupling relationship can be built between electric potential and ion concentration under the electroneutrality condition.
2.4.2. Steady Current. Under the steady current condition, combining equations (2) and (13) yields equation (16).

\[
\frac{F}{RT} \sum_{i=1}^{N} z_i D_i C_i \nabla \phi = -\sum_{i=1}^{N} z_i D_i \nabla^2 C_i. \tag{15}
\]

By combining equations (15) and (3), the electroneutrality potential model with a steady voltage boundary can be solved.

2.5. Gauss’ Law

2.5.1. Steady Voltage. The Poisson equation related to Gauss’ law is the constitutive law of electric potential and includes strict limitations; this equation formulates the relationship between potential and net charge as shown below:

\[
\nabla^2 \phi = -\frac{F}{\varepsilon_0 \varepsilon} \sum_{i=1}^{N} z_i C_i, \tag{17}
\]

where \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \) is the permittivity of vacuum, and \( \varepsilon = 10 \) [55] is the relative permittivity of concrete. In addition, it can be found from equation (17) that the order magnitude of \( F/\varepsilon_0 \varepsilon \) is \( 10^{15} \), which suggests that an insignificant electric change can generate a strong Laplacian potential. By combining equation (17) with equation (3), the electrokinetic model based on Gauss’ law with a steady voltage boundary can be solved.

2.5.2. Steady Current. The boundary condition for solving Poisson’s equation is shown below as follows:

\[
\begin{bmatrix}
  a \phi + b \frac{\partial \phi}{\partial n} \\
\end{bmatrix}_e = \phi(e, t), \tag{18}
\]

where \( a \) and \( b \) are constants, and they cannot be 0 at the same time, \( \partial \phi/\partial n \) is the directional derivative of potential, and \( e \) is a point on the boundary. Using equation (16) to link current density with the potential gradient, the steady current electric boundary is transformed into the Neumann boundary condition. It makes solving Poisson’s equation possible. However, Poisson’s equation coupled with the Nernst–Planck equation increases the nonlinearity of the model, and using equation (16) to set the electric boundary further aggravates this nonlinearity. This increased nonlinearity makes it more difficult to solve the model; furthermore, this means that the model does not have an analytical solution. Therefore, when the electric boundary follows the steady current rule, Gauss’ law might not be appropriate.

2.6. Boundary Condition. During an ECE process, electrode reactions (Figure 1(b)) occur on the surfaces of the cathodic steel bar and auxiliary anode. The oxygen consumption and hydrogen evolution reactions on the surface of cathodic steel rebar can be expressed as follows [56]:

\[
2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- = 4\text{OH}^- . \tag{19}
\]

\[
2\text{H}_2\text{O} + 2\text{e}^- = 2\text{OH}^- + \text{H}_2. \tag{20}
\]

According to equations (19) and (20), on the surface of the cathodic steel bar, the flux of the generated hydroxyl ions is equivalent to the externally applied current density, while the flux of all other ions is zero.

\[
J_k = 0 \quad k \neq \text{OH}^-. \tag{21}
\]

\[
J_{\text{OH}^-} = \frac{I_c}{z_{\text{OH}^-} F}. \tag{22}
\]

where \( I_c (\text{A/m}^2) \) is the current density on the cathodic steel bar.

In the experimental scheme, the volume of the anodic electrolyte was large enough such that over time, although chloride ions were transported through the electrolyte, their concentration remained negligible when compared to chloride content in the corrosion layers [57]. In addition, the anodic electrolyte is regularly replaced in actual ECE conditions [58]. Therefore, the ionic concentration at the anodic boundary of the model could be assumed to be constant [48]. In case there is no anode or cathode, the boundary conditions are assumed to be insulating, and hence, there occurs no flux as the current density is zero and ion transport is absent.

2.7. Calculation of Ion Concentration. According to equations (1) and (2), the variation in chloride concentration is related to ion flux in terms of diffusion \( \Delta C_{cl,d}(t) \) and electric migration \( \Delta C_{cl,m}(t) \).

\[
C_{cl}(t) = C_{cl}(0) + \Delta C_{cl,d}(t) + \Delta C_{cl,m}(t). \tag{23}
\]

\[
\Delta C_{cl,d}(t) = \int_{x_0}^{x_1} \int_0^t D_{cl} \nabla^2 C_{cl} \, dt \, dx \quad x_1 - x_0 \tag{24}
\]

\[
\Delta C_{cl,m}(t) = \int_{x_0}^{x_1} \int_0^t z_{cl} D_{cl} F/RT \nabla \phi \, dt \, dx \quad x_1 - x_0 \tag{25}
\]

Here, \( C_{cl}(0), C_{cl}(t), \) and \( \Delta C_{cl,d}(t) \) and \( \Delta C_{cl,m}(t) \) represent the initial chloride concentration, average chloride concentration at time \( t \), and evolution of chloride concentration from 0 to \( t \) due to diffusion and electric migration. The ratio of \( \Delta C_{cl,d}(t) \) to \( \Delta C_{cl,m}(t) \) on different days was plotted as shown in Figure 2(d).

Combining equation (2) with equations (10) and (22), and neglecting the diffusion term, the threshold value of hydroxyl concentration in Model I can be calculated as follows:
COH 3

Modeling and Validation

The process of ECE based on different potential theories and electric boundaries was analyzed and compared through COMSOL, a multiphysical field finite element analysis software that can solve the ECE model through potential equations in Section 2.2. For the steady voltage electric boundary, the ECE models based on constant potential (Model I), electroneutrality (Model II), and Gauss’ law (Model III) were compared. Nevertheless, Gauss’ law, considered the most rigorous potential distribution condition, was constantly used under steady voltage electric boundary but rarely applied under steady current electric boundary. For the steady current electric boundary, it was

\[ \Delta C_{cl,m}(t) = \frac{\sigma RT}{z_{OH}^2 F D_{OH}} \]  

Figure 2: Chloride distribution: (a) in Model I, (b) in Model II, (c) in Model III, and (d) ratio of ion flux in terms of diffusion \( \Delta C_{cl,d}(t) \) to electric migration \( \Delta C_{cl,m}(t) \).
found that Model III (Gauss' law) has the disadvantage of poor convergence and difficulty in yielding analytical solutions through the simulation; therefore, only Model I and Model II were compared.

3.1. Electrokinetic Model Setup. The geometry of the model represents the concrete cover with a thickness of 40 mm (as is shown in Figure 3); in the figure, the cathode and anode are positioned at $x = 0$ and 40 mm, respectively. The porosity of concrete $\phi$ was 15% [59], and the water-to-cement ratio was 0.5. The transport of and interaction between five ionic species in the pore solution, namely, Cl$^-$, OH$^-$, K$^+$, Na$^+$, and Ca$^{2+}$ [48, 60], were considered. Their initial ion concentrations, diffusion coefficients, and valence and boundary conditions are listed in Table 1. The purpose of this study is to transversely compare the ECC processes under different electrokinetic models, and the change in porosity and the corresponding change in ion diffusion coefficient are not considered for the numerical model simplification.

3.2. Model Validation. To explore the validity of the proposed models, there were three previous experiments. These experiments were divided into two groups based on the type of the electric boundary. One experiment [22] was controlled using a steady current, while the other two [16,63] were controlled using a steady current. To simulate the experimental conditions, all the models were considered to be two-dimensional with the same size as the cross section of the specimens.

3.3. Steady Voltage

3.3.1. Experimental Data. The speciment dimensions were set at 150 mm $\times$ 150 mm $\times$ 300 mm (Figure 3(a)) in Xia et al. [22]'s experiment, and the sampling point was set as shown in Figure 3(b). The ECE duration was set at 15 d, while the potential difference between the anode and cathode was set at 24 V with saturated Ca(OH)$_2$ as the anodic electrolyte.

3.3.2. Chloride Concentration Distribution. Figure 4 shows the chloride concentration distribution in the concrete cover. Under the influence of the electric field, the chloride ion in concrete shows a nonlinear transmission behavior. The overall tendency obtained by the experiment is close to those obtained by simulation. From the perspective of numerical simulation, the deviation between the experiment results and simulation results is difficult to eliminate, especially in heterogeneous material. The closer to the transmission boundary, the apparent the deviation from the experiment results. As observed in the experimental data, as the distance from the concrete cover ($x = 40$ mm) increased, chloride concentration initially increased and then experienced a slight decline. Similar to the experimental results, model data on chloride concentration also exhibited a signal peak. Compared to Model I, the chloride concentration distributions predicted by Model II and Model III were consistent and conform to the experimental data better. This agrees with the findings in the above section, where Gauss' law might be replaced by electroneutrality in the model that was described.

3.4. Steady Current

3.4.1. Experimental Data. Jin et al. [63] employed specimens with dimensions of 100 mm $\times$ 100 mm $\times$ 200 mm (Figure 5(a)) and an ECE duration of 35 d with saturated Ca(OH)$_2$ as the anodic electrolyte at a current density of 2 A/m$^2$. Powder samples were obtained from a depth of 2 mm (from the concrete surface toward the steel rebar), as illustrated in Figure 5(b). Meanwhile, Xu et al. [16] employed 150 mm $\times$ 150 mm $\times$ 300 mm specimens (Figure 5(c)) with an ECE duration of 30 d. In this case, as well, the current density and anodic electrolyte were 2 A/m$^2$ and saturated Ca(OH)$_2$, respectively. The sampling point is illustrated in Figure 5(d).

3.4.2. Chloride Concentration Distribution. Figure 6 shows the chloride concentration distributions obtained from modeling and experimental results. When comparing the modeling results against those obtained by Jin et al. (Figure 6(a)), Model II predicted a chloride concentration almost equal in different regions of the concrete cover with no apparent peak value, which is similar to the experimental data. Meanwhile, in Model I, as the distance from the anode ($x = 0$ mm) increased, chloride concentration gradually decreased. Comparing the modeling results with the results obtained by Xu et al. (Figure 6(b)), it can be noted that the chloride concentration was overestimated in the region near the anode ($x = 0$ mm) in Model I. Instead, there was a better agreement between Model II and the experimental results.

3.4.3. Hydroxyl Concentration Distribution. In their study, Xu et al. also measured the hydroxyl concentration distribution after ECE. Here, these results are compared with those predicted by Model I and Model II. As shown in Figure 7, there were distinct differences between the predicted and experimental results. In both Model I and Model II, the hydroxyl concentration was underestimated. However, in Model II, the hydroxyl distribution trend conforms with the experimental data. Hydroxyl concentration gradually increased as the distance from the anode ($x = 40$ mm) increased, while in Model I, the hydroxyl concentration was almost constant and equal in different regions.

When a steady current condition is employed for the electric boundary, irrespective of the value or distribution trend corresponding to chloride and hydroxyl concentration, the results in Model I differed from the experimental data. In contrast, the results of Model II exhibited better conformity with the experimental data. Furthermore, the ion distribution trend in Model II was similar to that experimentally observed.

In summary, for ECE simulation, the constant potential model is not applicable as it neglects the influence of ion transport on potential distribution. It leads to an
unreasonable distribution in the current density and hydroxyl concentration. The model based on Gauss’ law yields results similar to those of the model based on electroneutrality. Compared with the constant potential model, the results of the electroneutrality and Gauss’ law models exhibit better conformity with the experimental values. As the convergence of the model based on Gauss’ law is poor and not appropriate for models with a steady current electric boundary, it is rational to use the electroneutrality condition for ECE modeling.

4. Different Electric Boundary Discussion

To compare the process of electrochemical chloride extraction of reinforced concrete structures under different potential theories and different electric boundaries, a parameter analysis was conducted. For the steady voltage electric boundary, the potentials at the anode and cathode were set as 10 and 0 V, respectively (Figure 8). For the steady current electric boundary, the current density was 1 A/m² at the cathode (Figure 8). Corresponding parameters of the model are shown in Table 1.

### 4.1. Steady Voltage

Chloride concentration is one of the main factors responsible for the corrosion of steel rebar and the deterioration of its durability. Therefore, it is thought that the extraction of chloride ions from concrete can effectively decrease the risk of steel rebar corrosion. In this study, it has been observed that with an increase in the ECE duration, chloride concentration gradually decreased and this phenomenon was especially obvious in the region near the cathode (Figure 2). Under the action of the applied electric field, chloride ions move toward the anode, which led to their accumulation. In contrast, near the cathode, they experience outflow. Thus, chloride removal efficiency is higher at the cathode than in other regions.

The average chloride concentrations in Model II and Model III were 14.36 mol/m³ and 14.50 mol/m³,
respectively, while that in Model I was 18.12 mol/m$^3$. In Model I, the peak value of chloride concentration existed at the anode (Figure 2(a)), while in Model II and Model III, it was found at a distance of about 2 mm from the anode (Figure 2(b) and 2(c)). As ion concentration distribution is affected by potential distribution, the consistent chloride concentration distribution in Model II and Model III suggests that their potential distributions might be similar. The position of the maximum chloride ion concentration shifts to the cathode, and the concentration peak value decreases over time, which is mainly due to the large change in potential gradient in the repaired surface area. The chloride ion emigration flux in the surface concrete area is greater than the chloride ion migration flux, resulting in the

Figure 5: (a, c) Specimen dimensions and (b, d) sampling points used in the experimental studies: (a, b) Jin et al. [63] and (c, d) Xu et al. [16].

Figure 6: Comparison between the observed experimentally chloride concentration distributions and predicted by Model I and II: (a) Jin et al.’s study and (b) Xu et al.’s study.
decrease in ion concentration in this area and the shift of chloride ion concentration peak value to the reinforcement. The chloride ion concentration near the repair anode surface is lower than the internal peak value, and the chloride ion concentration first increases and then decreases with the increase in the distance from the repair surface.

The value of $\Delta C_{cl,i}(t)/\Delta C_{cl,m}(t)$ varied from $-3\%$ to $-0.1\%$, with negative values indicating that the transport directions of chloride diffusion and electric migration are opposite to each other (as expected). Electric migration results in chloride ions moving toward the anode and generating a concentration gradient. Owing to the concentration gradient, chloride ions start diffusing toward the cathode. Compared to electric migration, the evolution of chloride concentration due to diffusion is negligible [64]. Therefore, in establishing an electrokinetic model, it is necessary to select the appropriate potential theory, which can highlight the importance of electric migration. Figure 9 shows the potential distribution in the three models considered in this study.

In Model I, ion transport and potential distribution follow one-way coupling as the potential distribution affects ion transport; potential distribution does not vary with time (Figure 9(a)). In Model II and Model III, the potential and ionic concentration distributions follow bidirectional coupling. The applied electric field induces ion transport, and in turn, the evolution of ion concentration changes the potential distribution. As is shown in Figures 9(b) and 9(c), the potential distribution is time dependent and spatial dependent.

According to equation (2), ion flux is determined by electric migration and diffusion. As the absolute ratio between diffusion and electric migration is lower than 3$, the potential gradient (Figure 10), which significantly affects electric migration, is important. A high potential gradient corresponds to a high ion transport velocity. In the case of
chloride ions, a high potential gradient results in better chloride removal.

As the size of a one-dimensional model is 40 mm, and the potential difference between cathode and anode is 10 V, the average potential gradient in models is 250 V/m. The potential gradient in Model I stabilized at 250 V/m (Figure 10(a)). In Model II and Model III, the electric field influences ion transportation, and in turn, ion distribution affects the potential distribution. Therefore, the potential gradient in Model II and Model III becomes spatial dependent and time dependent. When the potential gradient was lower than 250 V/m, the corresponding area was defined as the inhibition zone; in all other cases, these areas were considered as promoting zones. Figure 10(d) shows the boundary of inhibition and promoting zones. The peak value of the boundary was lower than 20 mm (half of the distance between the anode and cathode), and the inhibition area was smaller than the promoting area. Hence, chloride removal efficiency in Model I was lower than that in Model II and Model III. In Model II and Model III, the potential gradient

Figure 9: Potential distribution: (a) in Model I, (b) in Model II, and (c) in Model III.
near the anode was higher than that in other regions (Figure 10(b) and 10(c)) and chloride ions rapidly moved out of the model.

Due to the cathodic reaction, hydroxyl ions accumulate in the region near the cathode. Under the action of an electric field, these ions move toward the anode. Hydroxyl concentration also increases in regions far from the cathode. With an increase in the ECE duration, in Model II and Model III, hydroxyl concentration near the cathode continuously increased. However, in Model I, the peak value of hydroxyl concentration was constant at 298.4 mol/m³.

Figure 11 shows the current density in different models. In Model I, the constant current density (Figure 11(d)) leads to a constant hydroxyl yield at the cathode and increased the hydroxyl concentration. Under the action of an electric field, hydroxyl ions were transported to the anode. When the production and consumption of hydroxyl ions reached a dynamic equilibrium, the increase in hydroxyl concentration ceased (Figure 12).
In Model II and Model III, according to equations (15) and (17), the quantity of electric charge $\sum_{i=1}^{n} z_i C_i$ can influence the potential distribution of different models, as is shown in Figure 13(b). In Model II and Model III, the absolute value of the quantity of electric charge varied from $10^{-15}$ to $10^{-10}$, which was as expected in the electroneutrality condition. In Model I, where there was no limitation on the charge number, its absolute value varied in the range of $10^2$–$10^4$. Therefore, the modeling results of Model I differ from that of Model II and Model III.

Actually, Gauss’ law in Model III is a constitutive law representing potential distribution. In fact, the constant potential condition with electroneutrality is the simplified form of Gauss’ law. In this study, the modeling results obtained from Model II (electroneutrality) and Model III (Gauss’ law) were consistent and differed from that of Model I (constant potential).

4.2. Steady Current. The chloride concentration is shown in Figure 14. The position of the maximum chloride ion concentration shifts to the cathode with the decreased peak

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**Figure 11:** Current density: (a) in Model I, (b) in Model II, and (c) in Model III, and (d) current density at different ECE durations.
value, which can be attributed to the large change of potential gradient in the repaired surface area, and the chloride ion electromigration flux in the concrete area is asymmetric and unsteady. Similarly, chloride concentration on the 5th day is even higher than the initial value that may be caused by the fluctuation and instability of electric flux when the model is close to the transmission boundary in the case of a short transmission time. The potential distributions in Model I and Model II are shown in Figures 15(a) and 15(b), respectively. In Model I, based on current density and electric conductivity, the potential distribution could be calculated by equation (14). In Model II, the potential difference between the anode and cathode varied over time. Except for the region near the cathode, in most regions, the potential gradient of Model II was higher than that of Model I (Figure 15(c) and 15(d)); a higher potential gradient corresponds to a higher ion transport velocity. The total chloride removal efficiency in Model I is lower than that in Model II. In the local region near the cathode, as the potential gradient was lower in Model II than in Model I, the residual chloride concentration in Model II was higher.

**Figure 12**: Hydroxyl distribution: (a) in Model I, (b) in Model II, and (c) in Model III.
Figure 13: Limitation of potential theory: (a) Laplace equations and (b) absolute value of the quantity of electric charge.

Figure 14: Chloride concentration: (a) in Model I and (b) in Model II.
In both Model I and Model II, current density did not vary with time (Figure 16). As \( \nabla I = 0 \), current density was independent of position. According to equation (21), hydroxyl production due to the cathodic reaction is determined by current density. As current density at the cathode was equal in Model I and Model II (Figure 16), their corresponding hydroxyl contents were the same. However, in Model II (Figure 17(a)), hydroxyl concentration near the cathode was remarkably higher than that in Model I (Figure 17(b)). This was because, near the cathodic boundary, the potential gradient in Model II was lower. It is more difficult to transport hydroxyl ions in this region, which resulted in their accumulation. In Model I (Figure 17(a)), the peak value of hydroxyl concentration was 298.4 mol/m³ when the electric field is controlled by a steady current. This value was the same as that in Model I when the electric field is controlled by a steady voltage (Figure 13(a)). This can be explained by equation (26), and the peak value of hydroxyl concentration has no relation to potential distribution or current density. The applicability of Model III is poorer.
when compared to that of Model I and Model II due to its lower convergence; therefore, it is not appropriate for use in models with a steady current electric boundary. Model I and Model II are effective for both steady voltage and steady current electric boundaries. Apart from applicability, the accuracy of a model is also very important.

5. Conclusions

1. Using the potential theory in electrokinetic models directly affects modeling results. In the constant potential condition, oversimplification of the potential equation leads to current densities and hydroxyl concentrations different from those...
experimentally observed. Models based on electroneutrality and Gauss’ law conditions consider the influence of ion concentration on potential distribution. The results of these two models are similar and conform better with the experimental data when compared to the results of the model based on the constant potential condition.

(2) Compared to Gauss’ law condition, which is the constitutive law for potential determination, the electroneutrality condition is simplified. This simplification is acceptable according to the simulated results of a similar tendency of potential distribution, current density, and ion concentration under Gauss’ law condition and electroneutrality condition. As the convergence of the electrokinetic model based on electroneutrality is ideal and facilitates an analytical solution, this model is preferred for simulating ECE processes.

(3) In the model based on the electroneutrality condition, the predicted chloride concentration does not always completely conform to the experimental data. The hydroxyl concentration might be underestimated. However, the predicted distribution trend corresponding to ion concentration and current density is similar to those experimentally obtained. Therefore, efforts may be made to improve the accuracy of this model, such as considering the evolution of porosity and ITZ.

Data Availability

Data will be provided upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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