

Article

Multi-Species Modeling of Chloride Ingress in Heterogenous Recycled Aggregate Concrete: Bidirectional Effects of Old Mortar

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Abstract

The structural application of Recycled Aggregate Concrete (RAC) in marine and coastal structures remains restricted by its highly variable quality and uncertain durability. Although the adhered old mortar is recognized as the most distinctive feature of RAC, its bidirectional influence on chloride transport, acting as a preferential transport pathway and a chloride-binding reservoir, has not yet been systematically elucidated. This study develops a five-phase mesoscopic numerical framework (natural aggregate, new and old mortars, new and old ITZs) to investigate the bidirectional effects on chloride ingress. The proposed model involves multi-species (K^+ , Na^+ , Cl^- , OH^- , Ca^{2+} , SO_4^{2-}) coupling and thermodynamic chloride binding on AFm and C-S-H phases, with different binding capacities in old and new mortar. This model was validated against published experimental data, demonstrating high accuracy in predicting effective diffusivity across varying replacement rates. Parametric sensitivity analyses reveal that RAC's chloride resistance is governed by the competition between the “facilitation effect”, caused by the inherent porosity in attached old mortar, and the “retardation effect”, caused by enhanced binding capacity. This work provides new mechanistic insight into the dual effects of old mortar and establishes a robust theoretical tool for the durability design of RAC structures exposed to chloride environments.

Keywords: multi-species coupling; recycled aggregate concrete; chloride transport; adhered mortar; thermodynamic equilibrium; bidirectional effects; old mortar

1. Introduction

The global construction industry is currently facing a dual challenge: the rapid depletion of natural mineral resources, and the overwhelming accumulation of construction and demolition (C&D) waste [1]. The traditional practice of landfilling not only occupies precious land resources but also causes severe environmental degradation [2]. Therefore, the development of Recycled Aggregate Concrete (RAC) has emerged as a critical strategy for promoting a circular economy and sustainable development within civil engineering.

In recent years, significant progress has been achieved in RAC through an improved mixture design, the increasing availability of high-quality Recycled Concrete Aggregate (RCA) sources, and the incorporation of mineral admixtures [3–7]. These developments have promoted the practical application of Recycled Aggregate Concrete (RAC) in sustainable building construction [8]. Nonetheless, unlike Natural Aggregate (NA), RCA is a more



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complex, multi-phase composite consisting of the original natural stone and a layer of adhered old cement mortar, and old interfacial transition zone (ITZ) between them [9–11]. The adhered old mortar and ITZ in RCA usually contain high porosity and recycling-induced micro-cracks, which provide preferential pathways for ionic transport [9,12,13]. Therefore, accurately predicting and understanding the chloride transport mechanisms in RAC is not only a scientific necessity but also a technical prerequisite for the widespread engineering adoption of recycled materials.

To evaluate the chloride resistance of various types of RACs, a substantial body of experimental research has been conducted. These studies have established that the chloride diffusivity of RAC is a multi-variant function of the parent concrete's strength, the volumetric content of adhered old mortar, the water-to-cement (w/c) ratio, the incorporation of mineral admixtures, and the RCA replacement rate [14–20]. Meanwhile, analytical and numerical frameworks have been increasingly developed to quantify chloride transport properties in RAC. Xiao et al., Ying et al., and Hu et al. developed and implemented fully replaced multi-phase RAC models, involving new mortar, adherent old mortar, new ITZ between the new mortar and the old mortar, and old ITZ between the original natural coarse aggregates and adherent old mortar, to predict the effective chloride diffusion coefficients [9,10,21]. Building upon the framework proposed by these five-phase models, subsequent studies by Wu and Xiao and Peng et al. introduced additional micro-crack phases with varying depths and widths to more accurately capture the detrimental effects of mechanical damage on ion transport [22,23]. Yu and Lin and Yuan et al. presented refined multi-phase numerical and analytical models, respectively, to specifically examine the sensitivity of global diffusivity to the intrinsic quality of the adhered old mortar and the distinctive properties of the old ITZ within the RCA [11,24]. These advancements have laid the foundation for a more granular understanding of the heterogeneous transport environment in RAC.

Moreover, the influence of RCA on chloride transport is a competitive process involving two opposing mechanisms: the facilitation of ion penetration due to high porosity, and the retardation of ingress through enhanced chloride binding capacity [25]. On the chemical level, the old mortar within RCA contains substantial AFm phases (often in the form of SO_4 -AFm and CO_3 -AFm due to carbonation), which can react with migrating chlorides to form Friedel's salt (Cl-AFm) [26–28]. Experimental evidence provided by Zaccardi et al. demonstrated that for new mortar with $w/c > 0.40$, the penetration depth of water-soluble chlorides in RAC is comparable to that of NAC. This suggests that the superior binding potential of recycled components effectively compensates for the permeability increase caused by their inherent structural defects [29]. Xiao et al. provided critical experimental evidence through 235-day long-term immersion tests, demonstrating that the binding chloride concentration increases linearly with the free chloride concentration across various replacement ratios [30].

Recently, numerical simulations have focused on incorporating chloride binding in RAC through the Langmuir and Freundlich isotherms [30–32]. Nevertheless, the binding parameters in these empirical isotherms strongly depend on material composition and environmental conditions. Moreover, the constant binding coefficients cannot fully reflect the dynamic physicochemical reactions during chloride ingress. Recently, a series of reactive thermodynamic multi-species models are proposed to simulate chloride binding in different types of concrete [28,33–35]. In these models, the surface complexation reactions between free ions and $\equiv SiOH$ sites on the C-S-H surface, and ionic precipitation and dissolution of ions from other phases (CH, AFt, AFm, Friedel's and Kuzel's salts) are considered. These thermodynamic models provided deeper insights into exploring the mechanisms of chloride binding in cementitious composites.

Additionally, the multi-species reactive simulation implemented via the Poisson–Nernst–Planck (PNP) equations highlight that multi-species transport in homogeneous cement matrices is governed by not only the concentration gradient, but also the electrochemical effect aroused by multi-species coupling [36]. The ionic transport environment becomes more complex when concrete structures are subjected to combined chemical attack (e.g., combined magnesium, sulfate, and chloride exposure), where the microstructural transformation of the hydration phases directly influences the macro-scale chloride ingress [37,38]. The combined chloride–sulfate multi-species modeling reveals the co-existence of these ions induces a distinctive spatial and temporal transient competitive antagonism [39–41]. Moreover, to quantify this multi-species coupled effect under severe drying–wetting actions, existing advanced numerical simulations have successfully integrated porosity-dependent and water saturation-dependent convection–diffusion–reaction models [42,43], establishing a rigorous foundation for capturing multi-species multi-phase transport features in RAC.

Despite this progress, the bidirectional impact of adhered old mortar, simultaneously facilitating chloride transport while retarding it through physicochemical adsorption on C-S-H and AFm phases, has not been fully elucidated. This work establishes a multi-species thermodynamic framework to characterize the different chloride-binding behaviors of old and new mortars in RAC, instead of relying solely on empirical binding isotherms. The proposed approach enables the quantitative evaluation of the competing effects between the high permeability of old mortar, which facilitates chloride transport, and the physicochemical chloride binding on AFm and C-S-H phases, which retards chloride ingress. Through a systematic investigation, the influences of thermodynamic capacity, chloride permeability of old mortar, RCA replacement rates, and ITZ qualities are quantitatively clarified. These findings fundamentally improve the understanding of competitive mechanisms underlying the “facilitation effect” and “retardation effect” of old mortar, providing practical guidelines for enhancing the long-term durability, and predicting the service life, of recycled aggregate concrete.

2. Multi-Species and Multi-Phase Models of RAC

2.1. Theoretical Equations

In the saturated multi-species pore solution environment, ion transportation is derived by the concentration gradient and internal electrical field aroused by the different mobilities of ionic species. Therefore, ionic flux in a chloride migration test can be described by the Poisson–Nernst–Planck equation as follows:

$$J_i = -D_i \nabla C_i - D_i C_i \frac{z_i F}{RT} \nabla \phi, \quad i = 1, 2, \dots, n \quad (1)$$

$$\nabla^2 \phi = -\frac{F}{\epsilon_0 \epsilon_r} \sum_{i=1}^n z_i C_i \quad (2)$$

where C_i , J_i , D_i and z_i are the concentration, flux, diffusion coefficient and charge number of i -th ionic species in pore solution, respectively. n is the number of ionic species considered in the simulation. $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ is the gas constant, $F = 96,500 \text{ C/mol}$ is the Faraday constant, T represents the absolute temperature (K), ϕ represents the electrostatic potential (V), and $\epsilon_0 \epsilon_r = 6.93 \times 10^{-10} \text{ C}/(\text{V} \cdot \text{m})$ is the permittivity of water at room temperature 298 K.

The chloride ingress will break the equilibrium between free ions in the pore solution and cementitious hydrations in the hardened phase, and lead to new precipitation/dissolution of hydration products and physical adsorption/desorption. Chemical binding primarily occurs through an anion exchange process within the AFm phases, where chloride ions displace interlayer sulfates to form Friedel’s salt. The liberated sulfate ions

subsequently react with the remaining AFm phases to facilitate the formation of ettringite (AFt) [44]. Physical adsorption is driven by the surface effects of the calcium-silicate-hydrate (C-S-H) gel, specifically through the interaction between chloride ions and the deprotonated silanol groups ($\equiv\text{SiOH}$) on the gel surfaces via electrostatic attractions or cation bridging. The phase equilibrium of hydration phases and the physical absorption between ions and the C-S-H surface can be expressed by the mass action law as follows:

$$K_{peq} = \prod_X (\gamma_X C_X)^{n_{Xp}} \quad p = 1, \dots, L \quad (3)$$

$$K_{ceq} = \frac{[\equiv\text{SiOHX}]}{[\equiv\text{SiOH}]\gamma_X C_X} \exp\left(\frac{-F\psi_d}{RT}\right) \quad X = \text{K}^+, \text{Ca}^{2+}, \text{Na}^+, \text{Cl}^- \dots \quad (4)$$

where K_{peq} and K_{ceq} represent the equilibrium constant of the formation and dissolution of p -th hydration product, and that of the physical reaction between C-S-H and free ions, respectively. γ_X , C_X , and n_{Xp} are the activity coefficient, concentration coefficient, and stoichiometric coefficient of X -th ionic species in the formation and dissolution of p -th hydration phase, respectively. The terms in brackets are the concentrations of surface species (mol/m^3). ψ_d is the surface potential of C-S-H caused by physical absorption. In this study, only the main absorption is considered. Given the relatively inert nature of portlandite and the limited substitution capacity of ettringite, the chloride-binding capacity of the cementitious matrix is predominantly determined by the synergetic interaction between these AFm and C-S-H phases. The physicochemical reactions involved in this study are given in Table 1.

Table 1. Thermodynamic reactions involved in this study and their forward reaction rate coefficients k_f^f ($\text{mol}/\text{m}^2/\text{s}$) and equilibrium constants.

Physicochemical Binding Reactions	k_f^f	Log (Keq)	References
$\text{C}_3\text{ACaSO}_4 \cdot 12\text{H}_2\text{O} + 2\text{Cl}^- \leftrightarrow \text{C}_3\text{ACaCl}_2 \cdot 10\text{H}_2\text{O} + \text{SO}_4^{2-}$	6.76×10^{-12}	−1.1	[45]
$\text{C}_3\text{ACaSO}_4 \cdot 12\text{H}_2\text{O} + 2\text{SO}_4^{2-} + 2\text{Ca}^{2+} \leftrightarrow \text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 12\text{H}_2\text{O}$	7.08×10^{-13}	15.67	[46]
$\equiv\text{SiOH} + \text{Cl}^- \leftrightarrow \equiv\text{SiOHCl}^-$	instantaneous	−0.35	[46]

In cementitious systems, multiple ions (such as K^+ , Na^+ , Cl^- , OH^- , Ca^{2+} , SO_4^{2-}) can compete for these adsorption sites. Our previous research indicated that the adsorption capacity of these competing ions on the C-S-H surface is significantly smaller than that of chloride ions [28]. Therefore, to avoid excessive computational complexity and parameter uncertainty, we adopt a simplified single-surface complexation reaction between chloride ions and $\equiv\text{SiOH}$ in this study, as shown in Table 1.

In this study, physical and chemical binding reactions operate on different time scales. Physical adsorption is assumed to be instantaneous, which is solved using the local thermodynamic equilibrium assumption. In contrast, chemical reactions involving hydrate phase transitions (such as AFm, AFt, and Friedel's salt) are treated as time-dependent processes. With the assumption that all chemical reactions in chloride ingress are reversible and single-step reactions, the reaction rate can be described as:

$$r_{ij} = k_j^f \prod_{i \in \text{react}} (\gamma_{ij} C_{ij})^{n_{ij}} - \frac{k_j^f}{K_{eqj}} \prod_{i \in \text{prod}} (\gamma_{ij} C_{ij})^{n_{ij}} \quad j = 1, \dots, n \quad (5)$$

where k_j^f and K_{eqj} represent the forward reaction coefficient and equilibrium constant for j -th thermodynamic reactions in concrete, respectively. r_{ij} , γ_{ij} , C_{ij} , and n_{ij} are the reaction rate, activity coefficient, concentration, and stoichiometric coefficient of i -th species in j -th reaction, respectively.

There is a possibility that any ionic species will participate in more than one physico-chemical reaction. Therefore, the mass transfer rate of a specific species in the pore solution can be calculated as follows:

$$R_i = \sum_j n_{ij} r_{ij} \quad (6)$$

With the consideration of the reactions between ions in the pore solution and hydration products of both new and old mortar, the mass conservation of each ionic species in concrete can be expressed as follows,

$$\frac{\partial C_i}{\partial t} + \nabla \cdot J_i = R_i \quad (7)$$

where R_i represents the mass transfer rate of i -th ionic species aroused by the reactive reactions between liquid and solid phases. Submitting Equations (1) and (6) into Equation (7), it yields

$$\frac{\partial C_i}{\partial t} = \frac{D_i}{\tau^2} \nabla^2 C_i + \frac{D_i}{(a_0 \tau)^2} \frac{z_i F}{RT} \nabla (C_i \nabla \phi) + \sum_j n_{ij} r_{ij} \quad (8)$$

In this study, six ionic species, potassium, sodium, chloride, hydroxyl, calcium and sulfate ions, are considered in this section. The diffusion coefficient, initial and boundary conditions of each ionic species, and reaction rate are given in Table 2.

Table 2. The input parameters in the present chloride ingress model.

Parameter	Notation	Value	References
Diffusion coefficient in new mortar ($\times 10^{-11}$ m ² /s)	K ⁺	1.96	[45]
	Na ⁺	1.33	
	Cl [−]	2.03	
	OH [−]	5.26	
	Ca ²⁺	0.79	
	SO ₄ ^{2−}	1.07	
Left boundary (mol/m ³)	NaCl	500	[10]
Right boundary (mol/m ³)	NaOH	300	
Initial concentration (mol/m ³)	K ⁺	400	[33]
	Na ⁺	100	
	Cl [−]	0	
	OH [−]	500	
	Ca ²⁺	3	
	SO ₄ ^{2−}	2	
	AFm	150	
	AFt	160	
	C-S-H reaction sites ($\equiv$ SiOH)	2132	
	Friedel's salt	0	

2.2. Geometric Model and Meshing

Figure 1 shows a series of 50 × 50 mm multi-phase concrete models with the same total volume fraction of aggregates in concrete, same replacement rate of RC, and same volume fraction of old mortar in RC. In these RAC models, NA and/or RCA are generated and located randomly in the cement matrix using a MATLAB R2023a program. The size

distributions of both NAs and RCAs follow the Fuller gradation, with their radii ranging from 2 mm to 15 mm. New and old natural aggregates (blue region in NA and orange region in RCA) in all models are assumed to be impermeable.

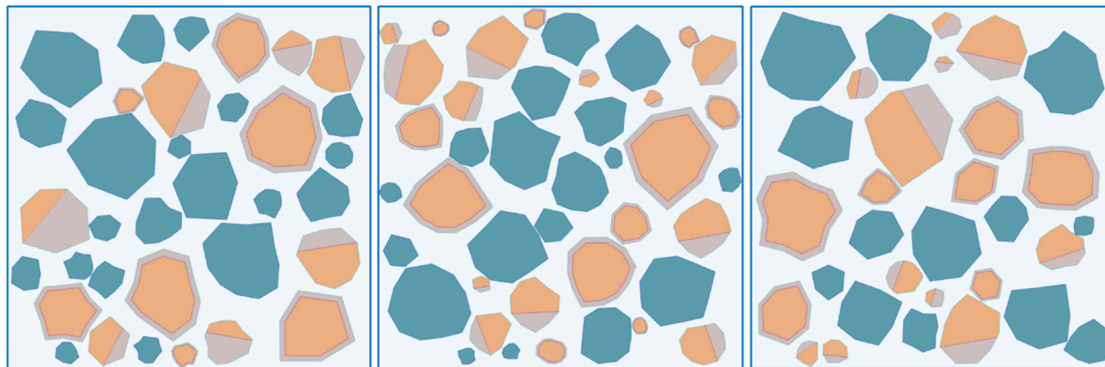


Figure 1. Multi-phase concrete models with irregular aggregates ($V_{TA} = 0.5$, $V_{RCA} = 0.5$, $V_{om} = 0.3$).

In real recycled concrete, the actual geometry of the old mortar in RCA is highly variable and complex. Therefore, to provide a bounded and representative numerical evaluation, this study adopts two extremely simplified patterns of old mortar (gray region) in RCA commonly used in the existing literature [10,24]: the fully enclosed pattern and the single-sided attachment pattern, as shown in Figure 1. In the present mesoscopic model, the fraction of each pattern is controlled to be exactly 50%. This 50–50% allocation of extreme boundary states ensures that the geometric model can capture both the maximum and minimum ITZ transport effects. Consequently, the simulated global chloride diffusivity represents a statistically balanced average of the heterogeneous concrete domain, making the simplified geometric framework both computationally efficient and physically realistic. More recently, vision-based approaches, DeepLab and EfficientNet, are proposed to improve the realism of the mesoscopic concrete model [47–50]. This may provide a more direct way to characterize old mortar distribution, ITZ thickness, and crack morphology in RAC for more realistic numerical simulations in future.

The diffusivity of old mortar is influenced by two main factors: the microcracks caused by the crushed process and the water/cement ratio of parent concrete. On the one hand, these microcracks would provide extra transport paths for chloride ions. On the other hand, the chloride diffusion coefficient decreases with decreasing water/cement ratio of parent concrete, which means that old mortar may have a higher chloride resistance than new mortar. Existing research reported that the chloride diffusivity ratio between new and old mortar ($k_{om} = D_{nm}/D_{om}$) commonly ranges from 0.24 to 5 times [9,10,51]. Based on this, a realistic range of 0.5–2.5 for our parametric analysis was set. Within this range, $k_{om} = 0.5$ represents high-quality RCA derived from superior parent concrete, while $k_{om} = 2.5$ represents degraded RCA with mechanical damage during crushing and service life. The extremely high ratios (e.g., $k_{om} > 2.5$) are not included in the present parametric study, as very low-quality RCAs are generally excluded in practical engineering to ensure structural durability and safety.

Moreover, it should be noted that the old mortar also introduces additional chloride binding sites that hinder chloride diffusion in concrete. Physical binding is considered through surface complexation reactions between chloride ions and silanol groups ($\equiv\text{SiOH}$) on C-S-H. Chemical binding occurs through an anion exchange process within the SO_4 -AFm and/or CO_3 -AFm due to carbonation on old mortar. In this study, the influence of the enhanced binding capacity of old mortar is investigated by varying the ratio of both

physical (on C-S-H) and chemical (on AFm phases) reaction sites between old and new mortar ($R = R_{om} / R_{nw}$), as given in Table 3.

The ITZ between aggregate and mortar is more porous than the adjacent mortar, which leads to a lower chloride penetration resistance of this zone [52,53]. As shown in Figure 2, blue and red shells or strips represent new and old ITZs, respectively. Existing research has concluded that the thickness of new and old ITZs usually varies from 20 to 80 μm [54,55]. Existing experimental and numerical studies have reported that the chloride diffusivity ratio between ITZ and mortar ($k_{itz} = D_{nm} / D_{nitz} = D_{om} / D_{oitz}$) commonly varies from 1.3 to 18.5 depending on the porosity and microstructural properties of ITZs [9,10]. To avoid excessive computational cost and mesh instability caused by explicitly modeling variable ITZ thicknesses, a constant geometric thickness (40 μm) was adopted for all simulations. The variability of old and new ITZ properties was represented by varying the diffusivity ratio (k_{itz}) from 1 to 20. Since chloride transport through ITZ is controlled by both its thickness and diffusivity, this simplified approach can effectively capture the influence of different ITZ conditions.

To better understand the effect of each phase on chloride penetration, parametric analysis is conducted with various property settings. Table 3 shows the parameter setting of the replacement rate of RCA (V_{RCA}), old ITZ thickness (h_{oitz}), new ITZ thickness (h_{nitz}), total volume fraction of aggregates e (V_{TA}), and volume fraction of old mortar in RCA (V_{om}) in standard and parametric analysis cases. Figure 3 shows the finite element mesh of a five-phase RAC model. Due to the extremely thin interfacial transition zone and the significant difference in chloride diffusivity between individual phases, the finite element size near interfaces between two phases must be extremely small to get a convergent numerical solution. Triangular meshing is adopted with a minimum mesh element size of 3.75×10^{-6} m, requiring approximately 500,000~600,000 free triangle elements in the domain.

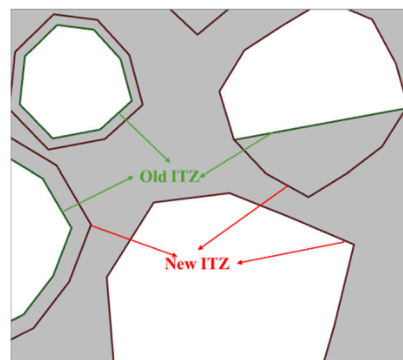


Figure 2. Zoomed-in schematic of RAC ($V_{RCA} = 0.5$, $V_{om} = 0.3$, $h_{nitz} = h_{oitz} = 40 \mu\text{m}$).

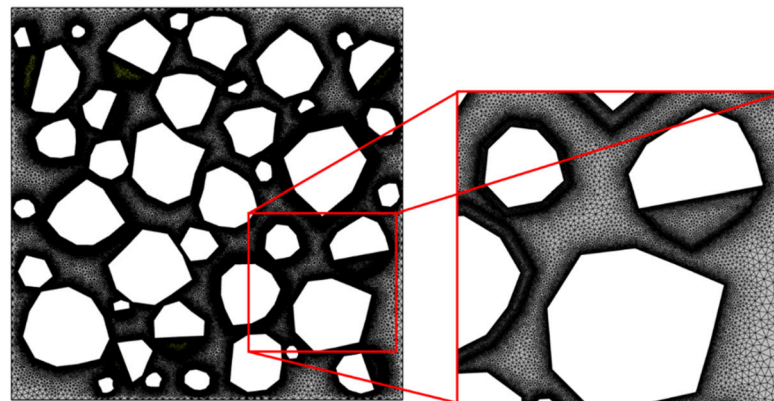


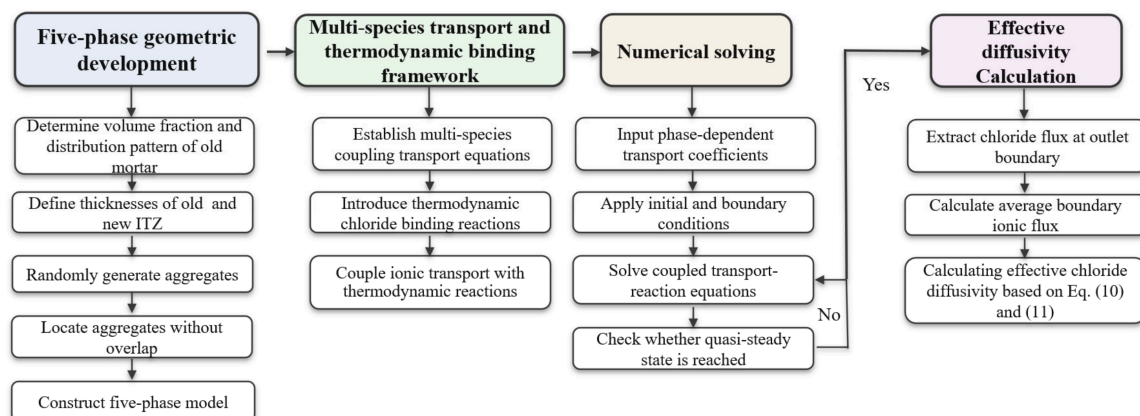
Figure 3. Meshing of RAC model ($V_{RCA} = 0.5$, $V_{om} = 0.3$, $h_{nitz} = h_{oitz} = 40 \mu\text{m}$).

Table 3. Volume parameters and ionic diffusivities of multiple species in each phase in standard and parametric analysis cases.

Input Parameters	Standard Case	Parametric Cases	References
Volume fraction of total aggregate V_{TA}	0.5	0.5	
RCA replacement rate V_{RCA}	0.5	0, 0.2, 0.4, 0.6, 0.8, 1	
Volume fraction of old mortar in RCA V_{om}	0.3	0.1, 0.2, 0.3, 0.4, 0.5	[10]
Old or new ITZ thickness h_{oitz} , h_{nitz} (μm)	40	40	[54,55]
Diffusivity ratio between ITZ and mortar k_{itz}	3	2~20	[9,10]
Diffusivity ratio between old and new mortars k_{om}	1.5	0.5, 1.0, 1.5, 2, 2.5	[9,10,51]
Physicochemical reaction sites (on C-S-H and AFm phases) ratio between new and old mortars R	2	1, 2, 3	[28]

2.3. Simulation Procedure

The research program adopted in this study is summarized in Figure 4. The methodology consists of four main sub-steps: five-phase geometric development, multi-species ionic transport and thermodynamic binding modeling, and calculation of the effective chloride diffusivity.

**Figure 4.** Flowchart of proposed research program.

First, a five-phase geometric model of recycled aggregate concrete is established following the introduction in Section 2.2. Second, the multi-species ionic transport and thermodynamic binding framework is established based on the Nernst–Plank–Poisson equations (Equations (2) and (8)) and thermodynamic reactions (Equations (3)–(6)). Thirdly, ionic transport derived by Equation (8), electric field derived by Equation (2) and physicochemical reactions derived by Equations (3)–(6) can be synchronously solved by the Nernst–Plank–Poisson module and Chemical module in COMSOL Multiphysics 6.2. With the initial and boundary conditions listed in Table 2, the distributions of all ionic species and relative phases can be obtained.

Finally, the effective chloride diffusivity of the five-phase model is calculated based on a quasi-steady-state approach. The transport of multiple ionic species and aroused internal electric fields induced by different ionic diffusivities are inherently interdependent, creating a non-linearly coupled system. Consequently, a true steady-state solution is analytically elusive when considering multi-species coupling. In this study, a quasi-steady-state approach is implemented to determine convergence. Specifically, the system is considered to have reached a pseudo-equilibrium state when the relative variation in the chloride flux at the right boundary between consecutive time steps is less than 1%. The

pseudo-equilibrium state flux of chloride at the boundary exposed to NaOH solution, as shown in Figure 3, can be expressed as

$$J_{x=l} = \frac{\int_0^h J(t = t_1, l, y) dy}{h} \quad (9)$$

where l and h are the length and height of 2-D concrete models. t_1 represents the time to reach a pseudo-equilibrium state. In the macro-scale view, the 50 mm × 50 mm concrete specimen can be treated as a representative homogeneous element. Therefore, the average steady-state flux of chloride at the right boundary of meso-concrete can also be described as

$$J_{x=l} = -D_{eff} \frac{\partial C}{\partial x} = D_{eff} \frac{C_s}{l} \quad (10)$$

where D_{eff} is the effective chloride diffusion coefficient of NAC or RAC. C_s is the chloride concentration at the boundary exposed to NaCl solution. Substituting Equation (9) into (10), the effective chloride diffusion coefficient can be solved as follows:

$$D_{eff} = -\frac{l}{C_s h} \int_0^h J(t = t_1, l, y) dy \quad (11)$$

In practical applications, the computed effective chloride diffusivity (D_{eff}) can be directly incorporated into conventional service-life prediction models, such as Fick's laws-based approaches, to estimate chloride penetration depth and the initiation time of reinforcement corrosion in macro-scale RAC structures exposed to chloride environments.

3. Validation of Numerical Model

To validate the accuracy of the present multi-phase numerical model, a series of calibrated models were developed in accordance with experimental research conducted by Kou and Poon [51]. The mix design used in the experiment was 410 kg/m³ of binder (75%OPC + 25%FA), 611 kg/m³ of sand, and 1017–1048 kg/m³ of natural and recycled coarse aggregates. Accordingly, the total volume fraction of coarse aggregates is about 0.4. Four replacement rates of RA (combined stone, RCA, and masonry aggregate), 0, 0.2, 0.5, and 1, were employed in experiments and adopted in benchmark models. The volume fraction of old mortar in RAs is 0.13, which is estimated based on the density of NAs and Ras given in [51]. The thicknesses of old and new ITZs adopted in the benchmark model are the same as those used in a standard case. The experimental data reported in [51] were used to validate the proposed model because they provide representative chloride diffusion results for RAC under controlled conditions. It should be noted that the present validation is limited to a typical RAC system and is mainly intended to verify the applicability of the developed five-phase model.

For comparison, the chloride resistance capacity of RAC is normalized as the ratio between the effective diffusivity of RAC and NAC (D_{eff}/D_{eff0}). D_{eff} and D_{eff0} represent the effective chloride diffusion coefficient of RAC and NAC, respectively. The diffusivity ratio between old and new mortars k_{om} are 1.8 and 0.6 for the $w/b = 0.45$ and $w/b = 0.55$ new mortars used in the validation models, respectively. To evaluate the uncertainty of this calibration, a sensitivity analysis of k_{om} was performed for the $w/b = 0.45$ validation case at a replacement rate of 1.0. When we varied k_{om} by $\pm 20\%$, the predicted relative chloride diffusivity changed by only $\pm 4.54\%$. This very small change confirms that our validation results are stable and robust against the variation in k_{om} .

Figure 5 shows that the predicted results agree well with the experimental results. This confirms the accuracy and appropriateness of the present multi-phase numerical model for calculating the effective chloride diffusivity of both NAC and RAC. Meanwhile, a goodness-

of-fit analysis was further conducted by comparing the simulated and experimental chloride concentrations under both water-to-cement ratios. As shown in Figure 5, the coefficients of determination are $R^2 = 0.98145$ for $w/c = 0.55$ and for $R^2 = 0.99581$ for $w/c = 0.55$, demonstrating that the proposed model accurately reproduces the experimental results under the investigated conditions.

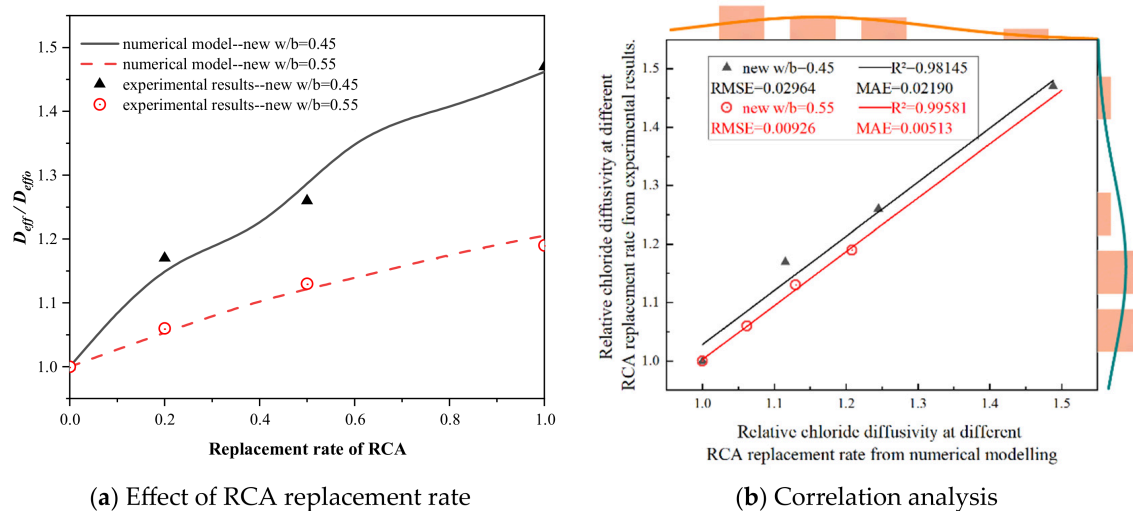


Figure 5. Comparison of relative chloride diffusivity of predicted results from present five-phase model and measured results from experiments conducted by Kou.

Additionally, the normalized chloride diffusivity decreases with increasing w/b in new mortar. It should be noted that the normalized value represents the chloride diffusivity ratio between RAC and NAC, rather than the absolute chloride diffusion coefficient of concrete. Therefore, this decreasing trend does not imply that RAC with lower w/b in new mortar exhibits higher chloride resistance. Instead, it suggests that the use of RCA has a more significant influence on the chloride resistance of concrete with a lower w/b ratio.

4. Results and Discussion

As shown in Figure 1, although aggregate parameters in five-phase concrete are the same ($V_{TA} = 0.5$, $V_{om} = 0.3$, $V_{RCA} = 0.5$, $d_{min} = 2$ mm, $d_{max} = 15$ mm, Fuller gradation), the distribution of aggregates in these models exhibits variability and uncertainty because all aggregates are randomly generated and positioned. Yu and Lin reported that the mechanical and durability properties of NAC or RAC may vary due to the random distribution of aggregates [24]. And they found that the mechanical properties of concrete gradually tend to stabilize as the number of samples increases. If the number of numerical samples is too small, effective chloride diffusivity cannot be accurately assessed. A large number of numerical samples will lead to time-consuming computation. Hence, it is crucial to determine an appropriate number of numerical samples before investigating the influences of each phase in concrete.

For comparison, the chloride diffusivity of RAC is normalized as a ratio between the effective diffusivity of RAC and that of new mortar (D_{eff}/D_{nm}). Figure 6 demonstrates the variations in the average and standard deviations of normalized diffusivity with the number of numerical samples. Four RCA replacement rates, 0, 0.2, 0.5, and 1, are involved, and other parameters are the same as those in a standard case as listed in Table 3. When the number of numerical samples reaches 15, the variations in both the average values and standard deviations of chloride diffusivity of RAC are less than 1%. This sensitive analysis indicates that a minimum geometric trial (15 trails) of the generation and location of

aggregates ensures that the subsequent parametric analyses can capture the representative transport behavior of RAC rather than the mathematical artifacts of the random packing algorithm.

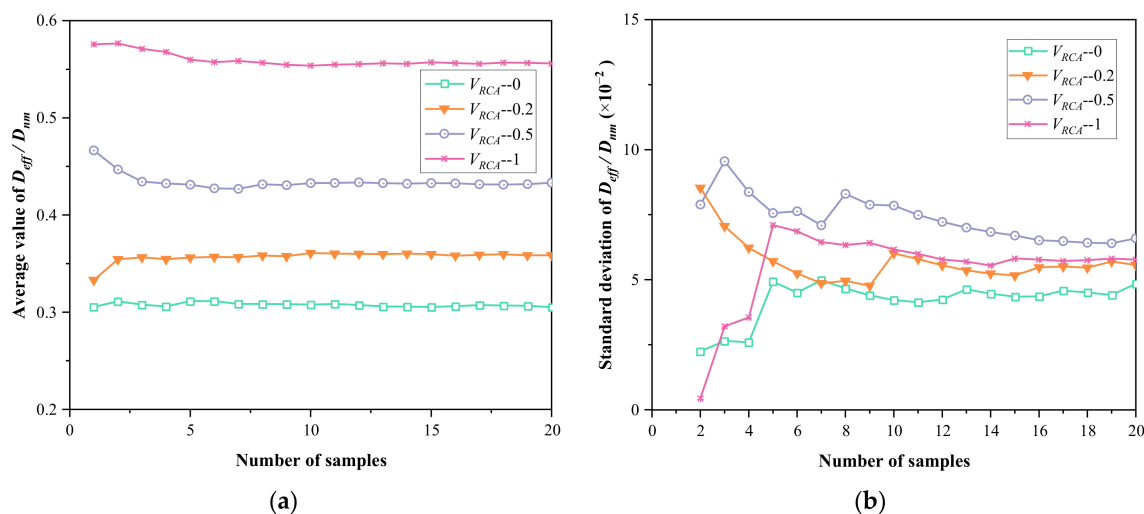


Figure 6. D_{eff}/D_{nm} in NAC and RAC: (a) average value, (b) standard deviation.

The most notable difference between RCA and NA is the presence of old mortar in RCA that cannot be completely removed. A parametric analysis of the effects of old mortar in RCA is conducted with various attached volume fractions, chloride diffusivities and binding capacities of old mortar in RCA. Considering that the chloride-binding capacity of old mortar may vary with carbonation history, AFm composition, and remaining hydration products, three representative values of the parameter ($R = 1, 2, 3$) were selected in this study to conduct a parametric bounding analysis rather than an empirical exact-matching attempt. The lower bound ($R = 1$) represents the lower binding capacity of old mortar, whereas the upper bound ($R = 3$) represents active binder phases with high binding potentials, thereby establishing a quantified evaluation envelope for global chloride diffusivity. Other input parameters are identical to those used in a standard case (Table 3).

Figure 7 illustrates the variation in the normalized chloride diffusivity (D_{eff}/D_{nm}) as a function of the old mortar volume fraction under different chloride binding capacities. It is observed that effective chloride diffusivity exhibits a linear upward trend with the increase in V_{om} , regardless of the binding capacity. This is primarily because the old mortar, compared to the new mortar matrix, typically possesses a more porous structure and micro-cracks, which facilitates ion transport. Interestingly, the chloride binding capacity exerts a significant retardation effect on effective diffusivity. As shown in Figure 7, at a constant V_{om} of 0.5, increasing R from 1 to 3 leads to a reduction in effective diffusivity from 0.460 to 0.416 (a decrease of approximately 10%). Herein, $R = 1$ means the extra binding capacity of old mortar is not considered. This confirms that while the old mortar provides “fast tracks” for diffusion due to its physical defects, its chemical composition, specifically its ability to bind chloride ions, acts as a buffer that compensates for the physical permeability to some extent.

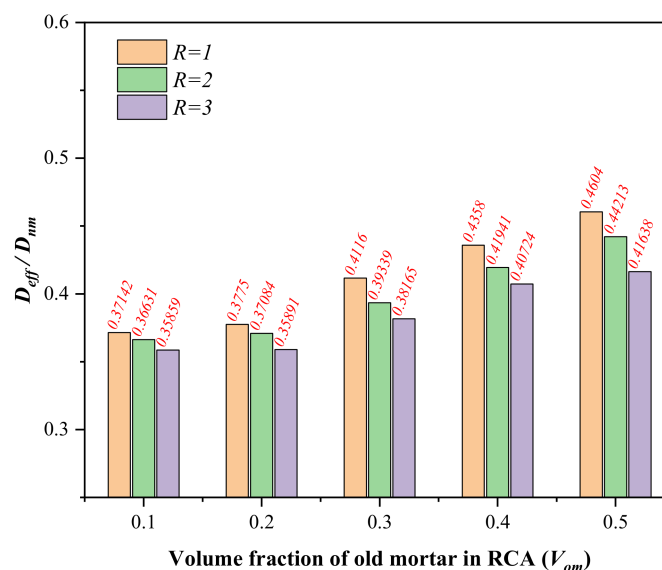


Figure 7. Normalized chloride diffusivity of RAC with various volume fractions and binding capacities of old mortar.

The influence of the quality of old mortar, represented by the diffusivity ratio k_{om} , is further elucidated in Figure 8. The results indicate that chloride resistance of old mortar is the most sensitive parameter affecting the chloride resistance of RAC. When $k_{om} = 0.5$ (representing a high-quality, dense old mortar), the effective diffusivity of the concrete remains at a relatively low level (<0.36) and increases only marginally with V_{om} . However, when the old mortar is of poor quality ($k_{om} = 2.5$), the normalized chloride diffusivity surges significantly, reaching 0.521 at $V_{om} = 0.5$. This dramatic increase suggests that the detrimental effect of old mortar volume is amplified by its intrinsic diffusivity. From a practical standpoint, this implies that the “quality” of the source concrete (parent concrete) is more critical than the “quantity” of the adhered mortar in determining the durability of the resulting RAC.

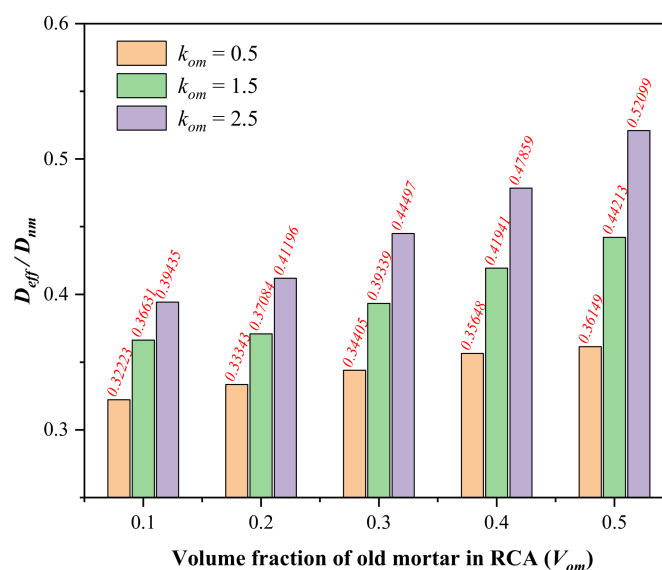


Figure 8. Normalized chloride diffusivity of RAC with various volume fractions and chloride diffusivities of old mortar.

Figure 9 provides a cross-comparison between k_{om} and R . The data shows that the diffusivity increment decreases as R increases, suggesting that enhanced chloride binding

can partially mitigate the negative impact of high-diffusivity old mortar. The competition between the “facilitation effect” (due to micro-cracks and porosity) and the “retardation effect” (due to chloride binding) is evident throughout the simulated cases. In these present five-phase models, the effective normalized diffusivity is consistently lower than 0.6, which is attributed to the dilution effect of the impenetrable natural aggregates and the RCA cores. However, the synergistic effect of a high V_{om} and a high k_{om} can lead to a significant loss in chloride resistance. Therefore, improving the chemical binding capacity R of the new matrix (e.g., through physical–chemical treatment) is an effective strategy to compensate for the inherent weaknesses of recycled aggregates.

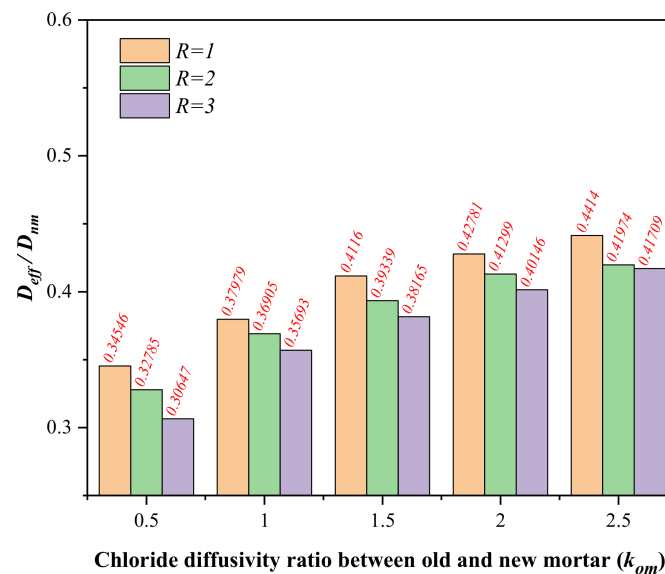


Figure 9. Normalized chloride diffusivity of RAC with various chloride diffusivities and binding capacities of old mortar.

The old mortar attached to RCA is identified as the key phase controlling chloride transport. On one hand, the old mortar usually contains higher porosity and micro-cracks generated during crushing, which increase the connectivity of pore networks and facilitate chloride migration. On the other hand, the old mortar also contains additional chloride-binding phases, including C-S-H surface sites and AFm phases, which can immobilize free chloride ions and retard transport. Therefore, the influence of old mortar is not unidirectional but reflects the competition between physical facilitation and chemical retardation [31,32]. The results show that increasing the old mortar content always increases effective diffusivity, indicating that the adverse effect of additional porous phases dominates at the mesoscopic scale. Nevertheless, the reduction in diffusivity caused by increasing binding capacity demonstrates that the physicochemical adsorption in old mortar provides a non-negligible compensation effect. This dual role explains why RAC may exhibit significantly different chloride resistance even at similar replacement rates.

Figure 10 illustrates the impact of the RCA replacement rate (V_{RCA}) on the normalized effective diffusivity under various old mortar qualities (k_{om}). It is evident that the normalized effective diffusivity increases monotonically with the elevation of V_{RCA} , regardless of the k_{om} value. However, the sensitivity of the concrete’s chloride resistance to the replacement rate is significantly dictated by the quality of the old mortar. When the old mortar is of high quality ($k_{om} = 0.5$), the effective diffusivity increases only slightly from 0.309 to 0.396 as V_{RCA} rises from 0.2 to 1.0. In sharp contrast, for poor-quality old mortar ($k_{om} = 2.5$), the diffusivity surges from 0.358 to 0.641. This trend indicates a strong synergistic effect between the quantity and quality of RCA. Specifically, the slope of the normalized effective

diffusivity curve becomes much steeper at higher k_{om} values, suggesting that the detrimental impact of increasing RCA content is disproportionately amplified when the adhered old mortar is highly porous. This further indicates the necessity of selecting high-quality parent concrete when high replacement rates are required in engineering practice.

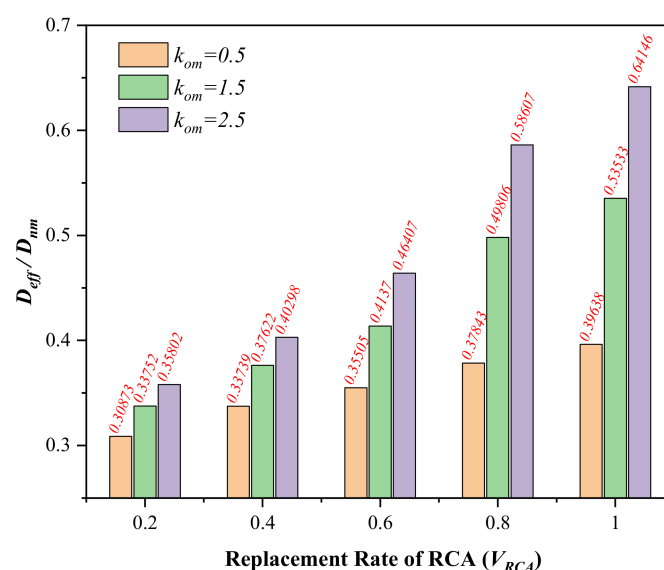


Figure 10. Normalized chloride diffusivity of RAC with various replacement rates of RCA and chloride diffusivities of old mortar.

Figure 11 further explores how the chloride binding capacity of the old mortar influences the transport properties across different replacement rates of RCA levels. As expected, higher R values consistently lead to improved chloride resistance, acting as a buffer against ion penetration. A key finding from Figure 11 is that the absolute reduction in normalized chloride diffusivity attributed to chloride binding becomes more pronounced at higher RCA replacement rates. For instance, when $V_{RCA} = 0.2$, the difference in diffusivity between $R = 1$ and $R = 3$ is relatively marginal. However, at $V_{RCA} = 1.0$, the retardation effect is enhanced by approximately 10.6% when distinct binding capacity between old and new mortar increases from $R = 1$ to $R = 3$. This phenomenon occurs because a higher V_{RCA} introduces a greater volume of old mortar into the system, thereby increasing the total number of available binding sites. This result again highlights the importance of considering the binding capacity of old mortar. The results suggest that the chemical binding potential inherent in the old mortar phase is a critical self-defense mechanism of RAC that must be accounted for to achieve accurate durability predictions.

Among all the parameters considered, the initial quality of old mortar, represented by the diffusivity ratio between new and old mortars, shows the highest sensitivity, which is consistent with the numerical results conducted by Hu et al. [10]. The results indicate that the chloride resistance of RAC is more strongly controlled by the quality of parent concrete than by the absolute amount of attached old mortar. When old mortar has low diffusivity, the increase in replacement rate of RCA causes only limited deterioration. In contrast, poor-quality (high-chloride diffusivity) old mortar amplifies the negative influence of both old mortar content and RCA replacement rate. This suggests that the source quality of recycled aggregates is a critical factor for durability-oriented RAC design.

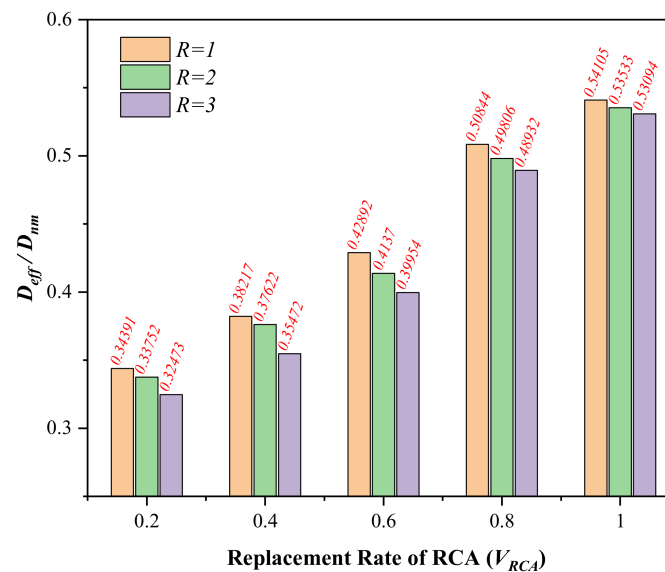


Figure 11. Normalized chloride diffusivity of RAC with various replacement rates of RCA and binding capacities of old mortar.

The distinction between new and old ITZs and cement matrix is fundamental to understanding the transport heterogeneities in RAC. From a microstructural perspective, the new ITZ is formed during the fresh mixing stage, where the “wall effect” of the aggregates leads to a higher porosity. In contrast, the old ITZ, which originally existed in RCAs, has undergone long-term hydration and potentially carbonation, making its pore structure and mineral composition distinct from the newly formed matrix. Based on the existing literature suggesting a diffusivity ratio between ITZ and mortar (k_{itz}) between 1.3 and 18.5 [10], five discrete ratios ($k_{itz} = 1, 5, 10, 15, 20$) were selected to evaluate the sensitivity of chloride transport to both new and old ITZs quality. The RCA replacement rate varied from 0 to 1.0, while the old mortar content was maintained at a constant $V_{om} = 0.3$.

Figures 12 and 13 show the evolution of the normalized chloride diffusivity of concrete as a function of new and old ITZs’ properties. Interestingly, the impact of new ITZ diffusivity on the global chloride resistance appears independent of the RCA replacement rate. For instance, as k_{itz} of the new ITZ increases from 1 to 20, the effective diffusivity of concrete rises by 19.6%, 26.4%, 24.8%, and 18.2% for $V_{RCA} = 0, 0.2, 0.5, 1$, respectively, showing no clear trend correlated with V_{RCA} . This is because new ITZ encapsulates all aggregate particles (both NA and RCA) in the five-phase model; it creates a continuous percolating network throughout the mortar matrix. Consequently, variations in its diffusivity lead to a significant proportional increase in the effective diffusion coefficient, regardless of the RCA replacement rate. This suggests that in terms of chloride penetration, the quality of the new interfacial bond is a decisive factor for any grade of V_{RCA} .

In contrast, the influence of old ITZ diffusivity is highly sensitive to the RCA replacement rate. Specifically, the same increase in k_{itz} (1 to 20) for the old ITZ results in a diffusivity increment of 0%, 2.8%, 8.7%, and 16.8% for $V_{RCA} = 0, 0.2, 0.5, 1$, respectively. This is because the old ITZ total volume fraction and spatial connectivity are directly restricted by the RCA replacement rate. Thus, the influence of the old ITZ is highly sensitive to the RCA content applied in RAC. This disproportionate sensitivity highlights that for high-performance RAC, the pre-treatment of RCA (e.g., removing or strengthening the old attached mortar and its ITZ) is just as critical as optimizing the new mix proportions.

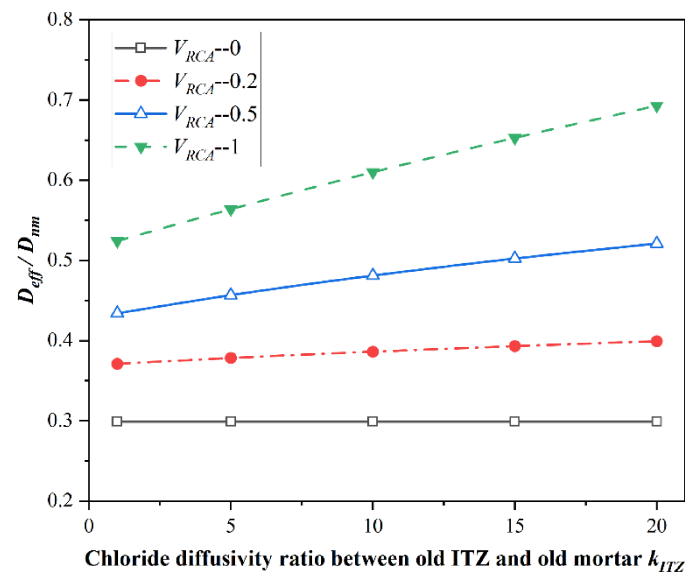


Figure 12. Normalized chloride diffusivity in NAC and RAC with various diffusivities of old ITZ.

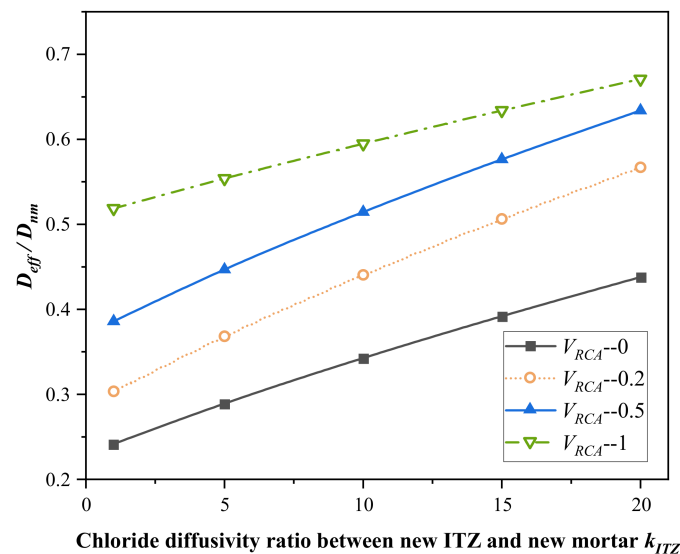


Figure 13. Normalized chloride diffusivity in NAC and RAC with various diffusivities of new ITZ.

From an engineering perspective, these results suggest that improving RAC durability requires both the optimization of new matrix properties and the pre-treatment of recycled aggregates to reduce the permeability and enhance the binding capacity of adhered old mortar and old ITZ. To further validate the originality and clear the boundary of the developed multi-species thermodynamic framework for multi-phase RAC, a comprehensive comparison is presented in Table 4. Unlike earlier models that ignore the ion–ion and ion–hydrate interactions or use empirical binding isotherms, the present model incorporates distinct thermodynamic binding capacities between new and old mortar and quantifies the competing effects between the high permeability of old mortar and the physicochemical chloride binding on AFm and C–S–H phases. The comparison indicates that the proposed model provides a useful tool for high-precision durability assessment of RAC and for optimizing the balance between permeability reduction and chloride-binding enhancement of adhered old mortar.

Table 4. Comparison of the present model with previous empirical and mesoscopic models for chloride transport in RAC.

	Empirical Models [11,21]	Existing Mesoscopic Models [10,24,31,32]	Present Model
RAC mesostructure	2~5 phases	2~5 phases	5 phases
Chloride binding	No binding	Empirical isotherms or no binding	Distinct thermodynamic binding between new and old mortar
Main novelty	Heterogenous effects	Capable of simulating the tortuosity effects of RCA	Coupled facilitation and retardation mechanism
Advantage	Simple implementation	Simple implementation	More mechanistic prediction
Limitation	Limited precision	Ignoresg interactions between different ions and hydrates	Large computational burden
Applicability	Rapid estimation of chloride resistance for RAC with stable-quality RCA	Effective diffusivity estimation with simple chloride binding	High-precision modeling and optimization of old mortar properties

5. Conclusions

In this study, the proposed thermodynamic multi-species framework provides a more mechanistic understanding of chloride transport in RAC by simultaneously considering ionic transport and physicochemical chloride binding in different mortar phases. Compared with effective diffusivity evaluated only from transport properties, the present model captures the competing effects of old mortar permeability and chloride binding. The primary conclusions are summarized as follows:

1. The presence of old mortars exerts a dual effect on chloride transport. While its inherent porosity and micro-cracks provide accelerated pathways for ion penetration, its chloride binding capacity significantly retards the diffusion process. Neglecting distinct binding effects between old and new mortar may lead to a substantial overestimation of chloride diffusivity, particularly at high RCA replacement rates.
2. The negative impact of increasing the RCA replacement rate is disproportionately amplified by poor-quality old mortar. The simulation results indicate that the quality (diffusivity) of the source concrete (parent concrete) is more critical than the absolute quantity of adhered mortar. Furthermore, the use of RCA shows a more pronounced negative influence on the chloride resistance of concrete with a lower water-to-binder ratio.
3. The impact of interfacial transition zones is non-symmetric. The new ITZ presents a global effect, consistently influencing chloride resistance regardless of the RCA replacement rate. Conversely, the influence of the old ITZ is highly sensitive to the RCA content.
4. The developed multi-phase model effectively captures the “dilution” and “tortuosity” effects of impermeable aggregates, consistently predicting that the effective diffusivity remains lower than that of the mortar matrix. The findings suggest that for high-performance RAC, prioritizing the pre-treatment of RCA to enhance the old ITZ and optimizing the chemical binding potential of the new matrix are essential strategies for durability design.
5. In the future, the proposed model will be extended to couple carbonation, sulfate attacks, wet–dry cycles, and so on. This development will provide a more comprehensive and accurate tool, successfully bridging the gap between numerical simulations

and the practical durability design and service life prediction of recycled aggregate concrete structures in real-world engineering.

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