

# 不同用水量控制方案下再生粗骨料的水饱和度对混凝土氯离子传输的影响规律

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**摘 要:** 再生粗骨料(RA)具有高吸水特性, 其水饱和度( $S_w$ )波动显著影响再生骨料混凝土(RAC)中氯离子( $Cl^-$ )传输行为。探究 2 种控水方案——拌合用水量固定(S1)、拌合用水与预湿用水总量固定(S2)下 RA 的  $S_w$  变化(0%、50%、80%和 100%)对 RAC 中  $Cl^-$  扩散及结合的影响规律及机理, 结果表明: 在 S1 中, 提高  $S_w$  可增加 RA 释水量, 虽促进水泥水化、降低新界面过渡区(ITZs)中的未水化水泥含量, 但也提高基体实际有效水灰比( $W/C$ ), 使新砂浆和新 ITZs 孔隙率增大、大孔增多、孔隙连通性增强, 导致  $Cl^-$  快速迁移系数、自然侵蚀下的有效和表观  $Cl^-$  扩散系数均增大; 而 S2 中, 由于  $W/C$  较 S1 更低, 因此  $Cl^-$  扩散系数整体偏小, 且随  $S_w$  增大而降低, 但较 S1 波动更小。 $Cl^-$  结合行为也受  $S_w$  与控水方案的共同影响: 在 S1 下提高  $S_w$  可削弱  $Cl^-$  结合能力; S2 下则相反, 且早期未水化水泥在侵蚀过程中持续水化, 使其长期  $Cl^-$  结合能力较 S1 更优。此外, S1 下随  $S_w$  增大, 因侵蚀产物填孔导致  $Cl^-$  扩散系数的变衰减更快, S2 下则反之。

**关键词:** 再生骨料混凝土; 水饱和度; 氯离子传输; 孔结构; 控水方案

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## 1 Introduction

Over the past fifty to sixty years, the rapid growth of the construction industry has generated a substantial amount of construction and demolition waste (C&DW). According to the China Association of Environment Protection Industry, C&DW production in China was projected to reach approximately 3.5 Gt in 2023<sup>[1]</sup>. Projections indicate that the United States will produce nearly 330 Mt annually between 2022 and 2026<sup>[2]</sup>, while European countries generated a total of 807 Mt in 2020<sup>[3]</sup>. However, the recycling rate of C&DW remains relatively low, particularly in developing countries. Recycling coarse aggregate from C&DW to prepare concrete is considered a viable approach to reducing C&DW accumulation.

However, recycled aggregate (RA) contains a significant amount of loose and porous old mortar, with content levels ranging from 14.1% to 86.6%<sup>[4, 5]</sup>, resulting in higher porosity of RA compared to natural aggregate. RA exhibits a significantly higher water

absorption capacity than natural aggregate, with absorption rates that can reach up to 12% for RA, compared to less than 1% for natural aggregate<sup>[6]</sup>. Due to its high water absorption capacity, RA exhibits significant water absorption and release mechanisms during the mixing and curing of recycled aggregate concrete (RAC)<sup>[7]</sup>. Existing research typically classifies RA into four saturation states to investigate its influence on RAC performance: oven dry (OD), air dry (AD), partially saturated (PS), and surface saturated dry (SSD)<sup>[8-10]</sup>. Mefteh *et al.*<sup>[11]</sup> and Khoury *et al.*<sup>[12]</sup> suggested that due to the strong water absorption capacity of RA, it was necessary to treat RA in a PS or SSD state to ensure good workability of fresh concrete. Similarly, Oliveira *et al.*<sup>[8]</sup> demonstrated that, under consistent total water supply conditions, RAC prepared with PS RA exhibited superior compressive strength compared to RAC prepared with OD or SSD RA. However, Etxeberria *et al.*<sup>[13]</sup> cautioned that the reduction in RAC strength associated with SSD RA might be due to the weakening of new interfacial

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transition zones (ITZs) caused by SSD RA. RAC contains multiple types of ITZs compared to natural aggregate concrete. RAC, in addition to the ITZ (ITZ<sub>1</sub>) between virgin aggregate and new mortar, also includes the ITZ (ITZ<sub>2</sub>) between virgin aggregate and old mortar, and the ITZ (ITZ<sub>3</sub>) between old and new mortars<sup>[14, 15]</sup>. It is widely accepted that ITZs are the primary weak phase in concrete<sup>[16]</sup>. The formation of the ITZ originates from the "wall effect", where the packing of cement grains against the larger aggregate particles results in a low concentration of cement grains, a greater volume of voids, and an increased local water-to-cement (W/C) ratio, ultimately leading to higher porosity<sup>[17]</sup>. The varying water saturation degree ( $S_w$ ) of RA may alter the microstructure of the ITZs, thereby influencing the performance of RAC.

In existing literature, the influence of  $S_w$  on the microstructure of the mesoscopic material phases in RAC and its associated mechanism affecting resistance to chloride ion ingress have been examined. Leite *et al.*<sup>[7]</sup> noted that OD RA released gas into fresh cement mortar during the water absorption process, forming a distinct macroporous network around RA particles and thereby increasing the porosity of the new ITZs. Sun *et al.*<sup>[18]</sup> observed that as  $S_w$  increased, the porosity of new mortar and the thickness of the new ITZs (ITZ<sub>1</sub> and ITZ<sub>3</sub>) initially decreased and then increased. They suggested that RA with a pre-saturation degree of 55% was most beneficial for the microstructure of RAC, as it could reduce the  $\text{Cl}^-$  diffusion coefficient by approximately 10%. Wu *et al.*<sup>[19]</sup> suggested avoiding the use of SSD RA and recommended AD RA instead. However, Marchi *et al.*<sup>[20]</sup> reached a different conclusion. They proposed that SSD RA released water into the cement mortar during the curing process, acting as an "internal curing" agent that promoted cement hydration, filled pores with hydration products, and refined the pore structure of cement mortar, thereby reducing pore connectivity. These findings highlighted the ongoing controversy regarding the influence of  $S_w$  on the microstructure of RAC, especially on the ITZ features, which have a significant influence on the chloride diffusivity of concrete. Additionally, the water supply method can influence the relationship between  $S_w$  and water content of cement mortar, making it also a critical factor to consider<sup>[8, 21]</sup>. Zhao *et al.* found that increasing  $S_w$  reduces the compressive strength and chloride ion penetration resistance of RAC under both constant mixing water supply (S1) and constant total water supply (S2)<sup>[22]</sup>. Their study noted distinct influence mechanisms: under S1, increasing  $S_w$  raises the total water content, which in turn increases the porosity of both the new ITZ and the new mortar; in contrast, under S2, the water released by RA with higher  $S_w$  primarily increases the porosity of the new ITZ rather than that of the new mortar. The authors' own published work confirmed the adverse effects of

high  $S_w$  of RA on compressive/flexural strength under S1, which is consistent with the finding of Zhao *et al.*<sup>[23]</sup> However, under S2, different conclusions were drawn, which suggests an optimal  $S_w$  of 80% in terms of mechanical properties of RAC, instead of the use of dry RA. However, it remained unclear how the initial  $S_w$  would affect the chloride transport behavior in RAC when these two different water control schemes are applied.

Therefore, the primary objective of this study is to investigate the influence of RA  $S_w$  on the resistance of RAC to the ingress of external  $\text{Cl}^-$  under varying water control schemes. Under S1 and S2, RAC was prepared with different  $S_w$ . The resistance of RAC to  $\text{Cl}^-$  ingress was macroscopically characterized by the  $\text{Cl}^-$  diffusion test and the chloride binding capacity. Meanwhile, the composition of cement hydration products and the pore structures of new ITZ and the new mortar were investigated by conducting the image processing of Backscattered Electrons (BSE) images and mercury intrusion porosimetry (MIP) experiments, thereby providing an explanation for the influence of  $S_w$  on the chloride transport behavior in RAC by taking varying water control schemes. This research provides guidance for designing RAC with high chloride impermeability in practice, tailored to specific water control schemes and  $S_w$ .

## 2 Materials and methods

### 2.1 Materials

RA used in this study was sourced from the discarded test blocks of a municipal project in Changle, Fuzhou, with particle sizes ranging from 4.8 mm to 31.5 mm. The gradation of RA was adjusted in accordance with the Chinese standard JGJ 52—2006, and its particle size distribution is presented in Fig. 1. The physical properties of RA were determined following GB/T 14685—2022, yielding an apparent density of 2650 kg/m<sup>3</sup>, water absorption of 5.4%, and crushing index of 16.6%. According to GB/T 25177—2010, these property indexes correspond to different classification levels: the apparent density, crushing index, and water absorption fall within the ranges specified for Class I, Class II, and Class III, respectively. Based on the most unfavorable indicator, the RA is therefore classified as Class III. The content of the old cement mortar in RA was quantified using the thermal treatment method proposed by de Juan *et al.*<sup>[24]</sup>, yielding a value of 36.7% by mass. Fine aggregate (FA) consisted of river sand obtained from the Minjiang River, characterized by a fineness modulus of 2.0%, moisture content of 1.0%, and mud content of 0.8%. The particle size distribution of FA, measured in compliance with GB/T 14684—2022, is also illustrated in Fig. 1.

The Portland cement employed in this study was Type P·O 42.5R, with a specific surface area of

$345 \text{ m}^2 \cdot \text{kg}^{-1}$  and a density of  $3.12 \text{ g} \cdot \text{cm}^{-3}$ . The initial and final setting times were recorded as 95 min and 156 min, respectively. Under standard curing conditions, the cement mortar specimens achieved a flexural strength of 6.3 MPa and a compressive strength of 28.0 MPa at 3 d. These values increased to 7.8 MPa (flexural) and 39.5 MPa (compressive) by 7 d. Its principal mineral constituents were  $\text{C}_3\text{S}$  (59.4%),  $\text{C}_2\text{S}$  (15.3%),  $\text{C}_3\text{AF}$  (11.6%), and  $\text{C}_3\text{A}$  (7.8%). A polycarboxylate superplasticizer with a water-reducing rate of 25% and a solid content of 40% produced by Xiamen Kezhijie Company was used when preparing the concrete mixture. The mixing water used was tap water from Fuzhou city, with a  $\text{Cl}^-$  content of  $0.80 \text{ mg} \cdot \text{L}^{-1}$ , meeting the specifications of JGJ 63—2006.

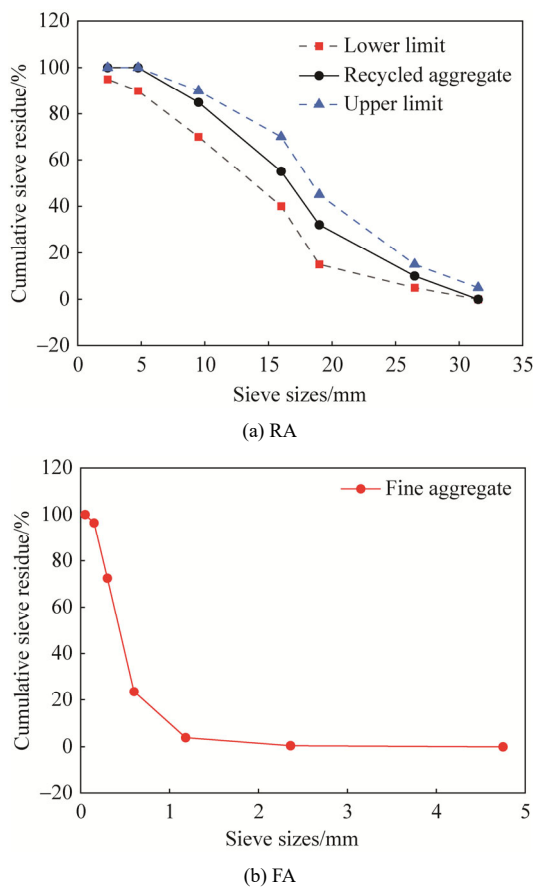


Fig. 1 Particle size distribution of aggregates

## 2.2 Method for the pre-wetting of RA

This study adjusted  $S_w$  by controlling the soaking time of RA. The relationship between the  $S_w$  and the soaking time was obtained through the following procedure: First, RA samples were evenly placed on a sieve tray (mesh size: 2.5 mm). The tray was quickly immersed in a water tank and taken out immediately upon reaching the target soaking time. After rapid drainage, the RA was transferred to a sloped surface ( $\approx 15^\circ$  inclination) to facilitate the quick runoff of free

water. Subsequently, any remaining surface moisture was promptly blotted using a wrung-out wet towel prior to weight measurement. The moisture content and  $S_w$  were calculated according to Eq. (1) and Eq. (2), respectively. Based on this, the variation of the saturation degree of RA with soaking time was determined, and the results are shown in Fig. 2.

$$M = \frac{m_1 - m_2}{m_2} \times 100\% \quad (1)$$

$$S = \frac{M}{W} \times 100\% \quad (2)$$

where  $M$  represents the moisture content of RA (%(mass fraction)) at this certain moisture state, %;  $m_1$  and  $m_2$  represent the mass of RA in a certain moisture state and OD state, respectively, g;  $S$  represents  $S_w$ , %; and  $W$  represents the moisture content of SSD RA.

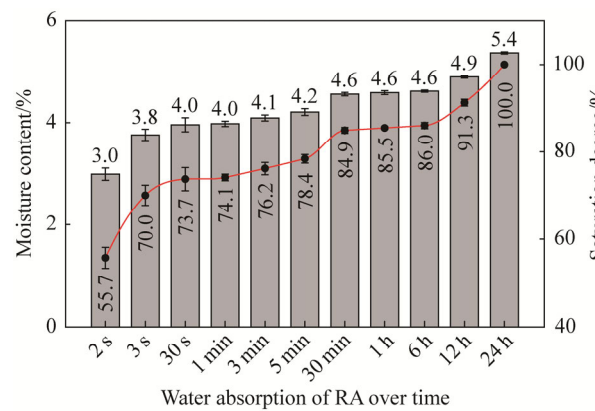


Fig. 2 Evolution of RA over time

According to Fig. 2, it took approximately 2 s, 5 min, and 24 h for the OD RA sample to achieve  $S_w$  values of 56%, 78%, and 100%, respectively, which were quite close to the target  $S_w$  values of 50%, 80%, and 100%.

## 2.3 Water control schemes and mixture proportions

This work established two series of concrete mixtures by controlling the mixing water supply (labelled as S1) and total water supply (labelled as S2). The mixture proportions can be found in Table 1. As presented in Table 1, the calculated effective W/C ( $W_e/C$ ) ratio is defined as the mixing water mass divided by the cement mass, while the total W/C ( $W_t/C$ ) ratio is the total water mass (*i.e.*, the sum of mixing water and pre-absorbed water by RA) divided by the cement mass. It is noteworthy that the  $W_e/C$  ratio present in Table 1 is a calculated values, while the actual  $W_e/C$  is further influenced by the water absorption and desorption of RA during mixing and curing. The influence of this variation on the microstructure and chloride transport behavior of RAC under the two water-control schemes will be discussed later. Both series share a common reference group, designated as 0%S. This group utilized oven-dry RA,

where both its  $W_c/C$  and  $W_f/C$  were 0.55. In the S1 series, the  $W_c/C$  ratio was maintained at 0.55, while the  $W_f/C$  ratio increased with  $S_w$ . Conversely, in the S2 series, the  $W_f/C$  ratio was maintained at 0.55, while the

$W_c/C$  ratio increased with  $S_w$ . The dosage of superplasticizer was 0.2% (mass fraction) of cement in both series, and the water contained in the liquid superplasticizer was included in the mixing water dosage.

**Table 1 RAC mixture proportions of each group**

| Mix ID | Mix constituents/(kg·m <sup>-3</sup> ) |                   |                      |                 |                       |                |                         | $W_c/C$ ratio<br>(calculated values) | $W_f/C$<br>ratio |
|--------|----------------------------------------|-------------------|----------------------|-----------------|-----------------------|----------------|-------------------------|--------------------------------------|------------------|
|        | Cement                                 | Fine<br>aggregate | Pre-saturation<br>RA | Mixing<br>water | Pre-absorbed<br>water | Total<br>water | Water reducing<br>agent |                                      |                  |
| 0%S    | 391.00                                 | 682.00            | 1112.00              | 215.00          | 0.00                  | 215.00         | 0.78                    | 0.55                                 | 0.55             |
| 50%S1  | 391.00                                 | 682.00            | 1141.86              | 215.00          | 29.86                 | 244.86         | 0.78                    | 0.55                                 | 0.63             |
| 80%S1  | 391.00                                 | 682.00            | 1159.77              | 215.00          | 47.77                 | 262.77         | 0.78                    | 0.55                                 | 0.67             |
| SSD1   | 391.00                                 | 682.00            | 1171.71              | 215.00          | 59.71                 | 274.71         | 0.78                    | 0.55                                 | 0.70             |
| 50%S2  | 391.00                                 | 682.00            | 1141.86              | 185.14          | 29.86                 | 215.00         | 0.78                    | 0.47                                 | 0.55             |
| 80%S2  | 391.00                                 | 682.00            | 1159.77              | 167.23          | 47.77                 | 215.00         | 0.78                    | 0.43                                 | 0.55             |
| SSD2   | 391.00                                 | 682.00            | 1171.71              | 155.29          | 59.71                 | 215.00         | 0.78                    | 0.40                                 | 0.55             |

## 2.4 Concrete casting and curing

The fresh concrete mixture was cast into molds to produce 100 mm cubic specimens. During the first 7 d, sealed curing using plastic film wrapping was implemented. This was to prevent moisture loss from the specimens or ingress of external water, which could cause the total internal water content of RAC to fall outside the controllable range. Therefore, it ensures that the water absorption and desorption behavior of RA at different  $S_w$  levels, along with the initial  $W_c/C$  ratio of the RAC, is the primary factors influencing microstructural development. After the curing age of 7 d, the microstructure of the RAC has largely stabilized and is less susceptible to external moisture influences. At this point, the film was removed, and the specimens were placed indoors for natural curing until 28 d.

## 2.5 Test methods

### 2.5.1 Microstructural features before chloride ingress

#### 1) Porosity distribution across ITZs and the content of unhydrated cement clinkers

In this study, the porosity distribution and the unhydrated cement content in the vicinity of the ITZ after 28-day curing were studied by BSE image analysis. Referring to the study of Zhang *et al.*<sup>[25]</sup>, the BSE samples were processed by following a procedure with cutting, hydration termination, epoxy resin, grinding, and polishing. The microstructural data for each type of ITZ in the concrete groups were obtained by averaging the grayscale data from 9 BSE images. In the obtained BSE images, the gray-white phases represent unhydrated cement (UH), while the black dots indicate pores that were infiltrated and filled with epoxy resin during the vacuum impregnation process<sup>[14]</sup>. In this way, the porosity and content of UH in the vicinity of ITZs can be obtained for analysis.

#### 2) Pore structure of mortar

The pore structure of mortar after 28 d of curing was analyzed using MIP. The MIP analysis was conducted using a Quanta Poremaster-60 instrument, capable of measuring pores within the range of

0.003–1800.000  $\mu\text{m}$ .

### 2.5.2 Transport of chloride ion in RAC

#### 1) Rapid chloride migration (RCM) test

The resistance to chloride ingress of each RAC group after 28-day curing was evaluated based on the chloride diffusion coefficient ( $D_{RCM}$ ), as specified in GB/T 50082—2024.

#### 2) Chloride transport under natural exposure

RAC specimens were immersed in a 5% (mass fraction) NaCl solution after 28-day curing, and chloride transport was tested via one-directional diffusion. After immersion periods of 60, 120, 180 d, and 240 d, free chloride ion content ( $C_f$ ) and total chloride ion content ( $C_t$ ) at varying depths from the exposure surface were determined via titration. At each target age, one concrete cube from each group was used for measurement. The cubes were removed from the NaCl solution, and the paraffin coating was scraped off before drying in an oven at 45 °C. Powder samples for chloride content testing were obtained by drilling the dried cubes at incremental depths: the first layer within 1 mm, the second between 1–3 mm, the third between 3–5 mm, subsequent layers at 5 mm intervals until reaching a total depth of 25 mm. The collected powder was sieved using a 0.08 mm mesh to remove coarse particles and stored in sealed zip-lock bags.

The concentrations of both  $C_f$  and  $C_t$  were measured using a Mettler Toledo G20S titrator in accordance with the Chinese standard JGJ/T 322—2013. Deionized water was used as the solvent for  $C_f$  determination, whereas for  $C_t$ , the samples were dissolved in 1 mol·L<sup>-1</sup> nitric acid with heating to ensure complete chloride extraction.

## 3 Results and discussion

### 3.1 Microstructural features before chloride ingress

#### 3.1.1 Porosity distribution and UH contents across ITZs

The BSE images of the new ITZs of RAC prepared with RA at varying  $S_w$  at the age of 28 d are demonstrated in Fig. 3 and Fig. 4.

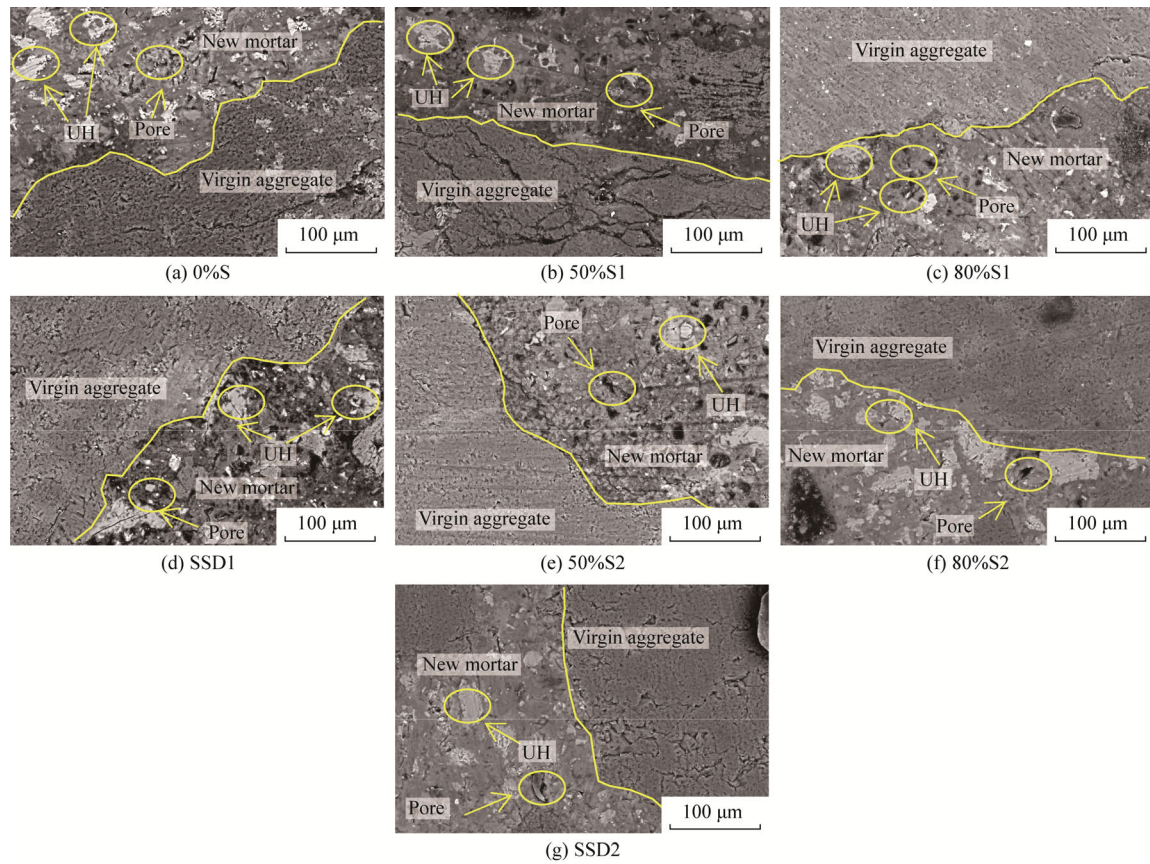


Fig. 3 BSE images of ITZ<sub>1</sub> in RAC prepared with RA at varying  $S_w$  after 28 d

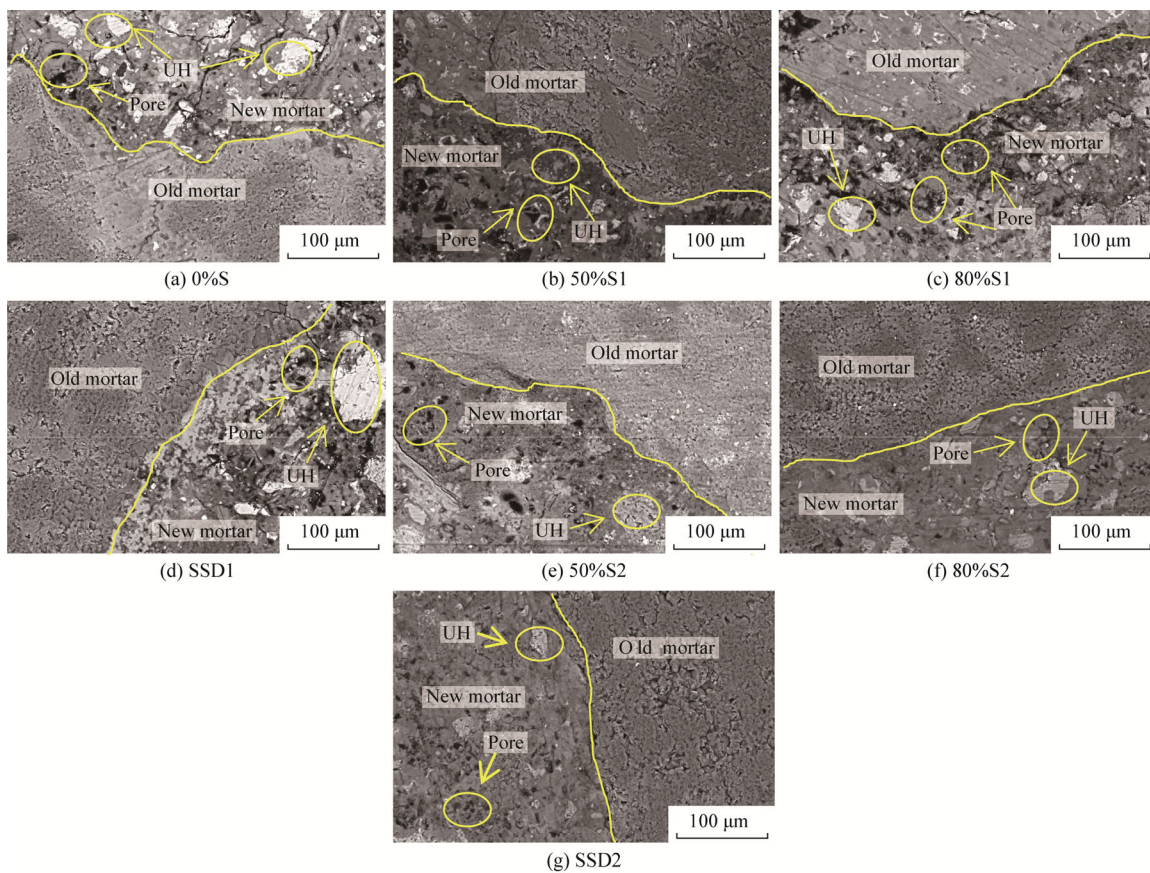
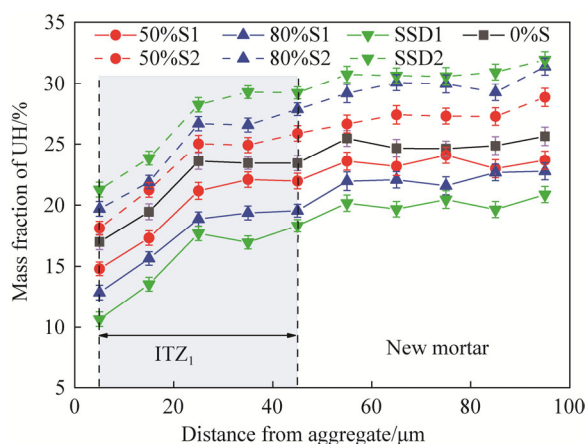
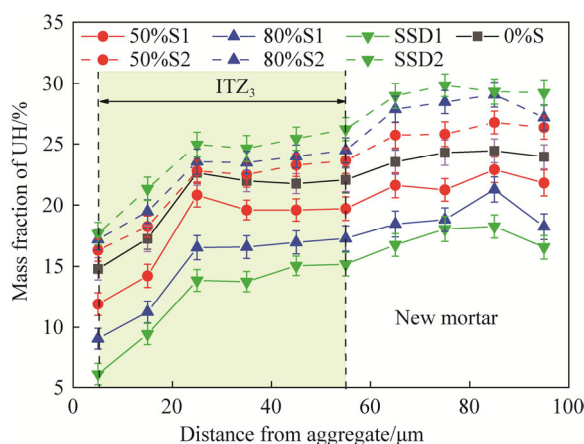


Fig. 4 BSE images of ITZ<sub>3</sub> in RAC prepared with RA at varying  $S_w$  after 28 d

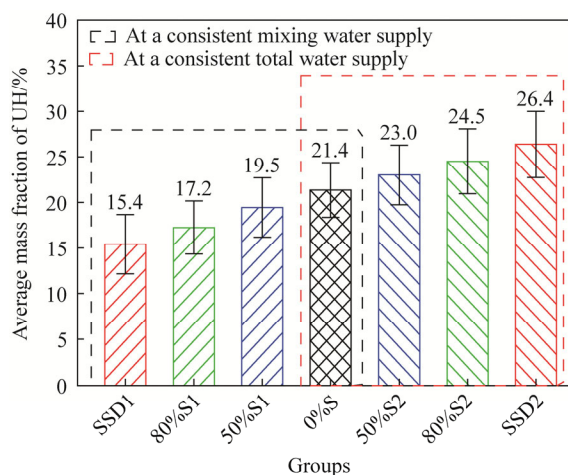
As shown in Fig. 3, under S1, as the  $S_w$  increased, the content of the gray-white phase in ITZ<sub>1</sub> and ITZ<sub>3</sub> decreased, whereas the black dots became more prevalent. This suggested a reduction in UH content and an increase in porosity within new ITZs under S1. In contrast, under S2 (Fig. 4), the opposite trend was observed.



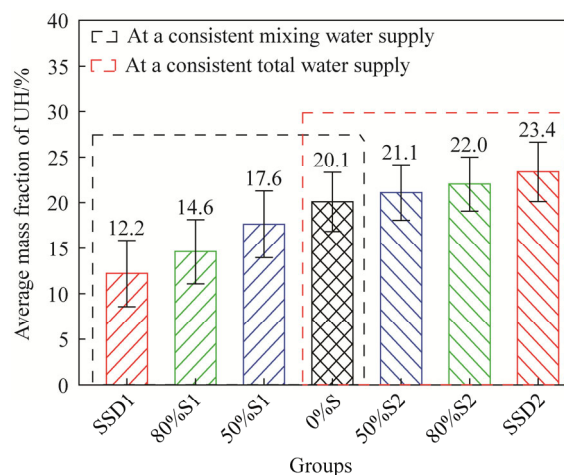
(a) UH mass fraction of ITZ<sub>1</sub>



(b) UH mass fraction of ITZ<sub>3</sub>



(c) Average UH mass fraction of ITZ<sub>1</sub>



(d) Average UH mass fraction of ITZ<sub>3</sub>

Fig. 5 UH mass fraction and the average UH mass fraction of ITZ<sub>1</sub> and ITZ<sub>3</sub> in RAC prepared with RA at varying  $S_w$  after 28 d

Fig. 5 demonstrates that, under S1, the UH content of new ITZ decreased with increasing  $S_w$ . This trend could be explained by the reduced water absorption capacity of RA during concrete mixing as  $S_w$  increased, with highly saturated RA even releasing water into fresh concrete<sup>[14]</sup>. The consequent increase in the actual  $W_c/C$  ratio around the RA enhanced the degree of cement hydration in the new ITZ, thus lowering its UH content. Elsharief *et al.*<sup>[26]</sup> similarly reported that as the  $W/C$  ratio of concrete increased from 0.4 to 0.5, the UH content in ITZ decreased significantly. The study by Zhou *et al.*<sup>[27]</sup> showed that a larger  $W/C$  ratio increased the water content around each cement particle, leading to faster early hydration reactions. However, under S2, the trend was reversed. Specifically, compared to 0%S,

## 1) UH contents

Fig. 5a–Fig. 5b illustrates the distribution of UH content as a function of distance from the virgin aggregate/old mortar interface. Additionally, the average UH content of new ITZs in RAC prepared with RA at varying  $S_w$  at the age of 28 d is detailed in Fig. 5c–Fig. 5d.

a notable increase in average UH content was observed in ITZ<sub>1</sub> (23.4%) and ITZ<sub>3</sub> (16.4%) at SSD2. This phenomenon may be attributed to the fact that under S2, the  $W_c/C$  ratio of RAC decreases with increasing  $S_w$ . As shown in Table 1, the calculated  $W_c/C$  ratio of SSD2 is 0.40, representing a 27.3% reduction compared with that of 0%S. Although RA with higher  $S_w$  releases moisture into the cement matrix, this supplementary water may not be sufficient to compensate for the hindered cement hydration in the vicinity of new ITZs<sup>[28]</sup>.

## 2) Porosity distribution across ITZs

Fig. 6a–Fig. 6b illustrates the porosity distribution relative to the distance from the virgin aggregate/old mortar interface. Accordingly, the average porosity across ITZs with RA at different  $S_w$  is shown in Fig. 6c–Fig. 6d.

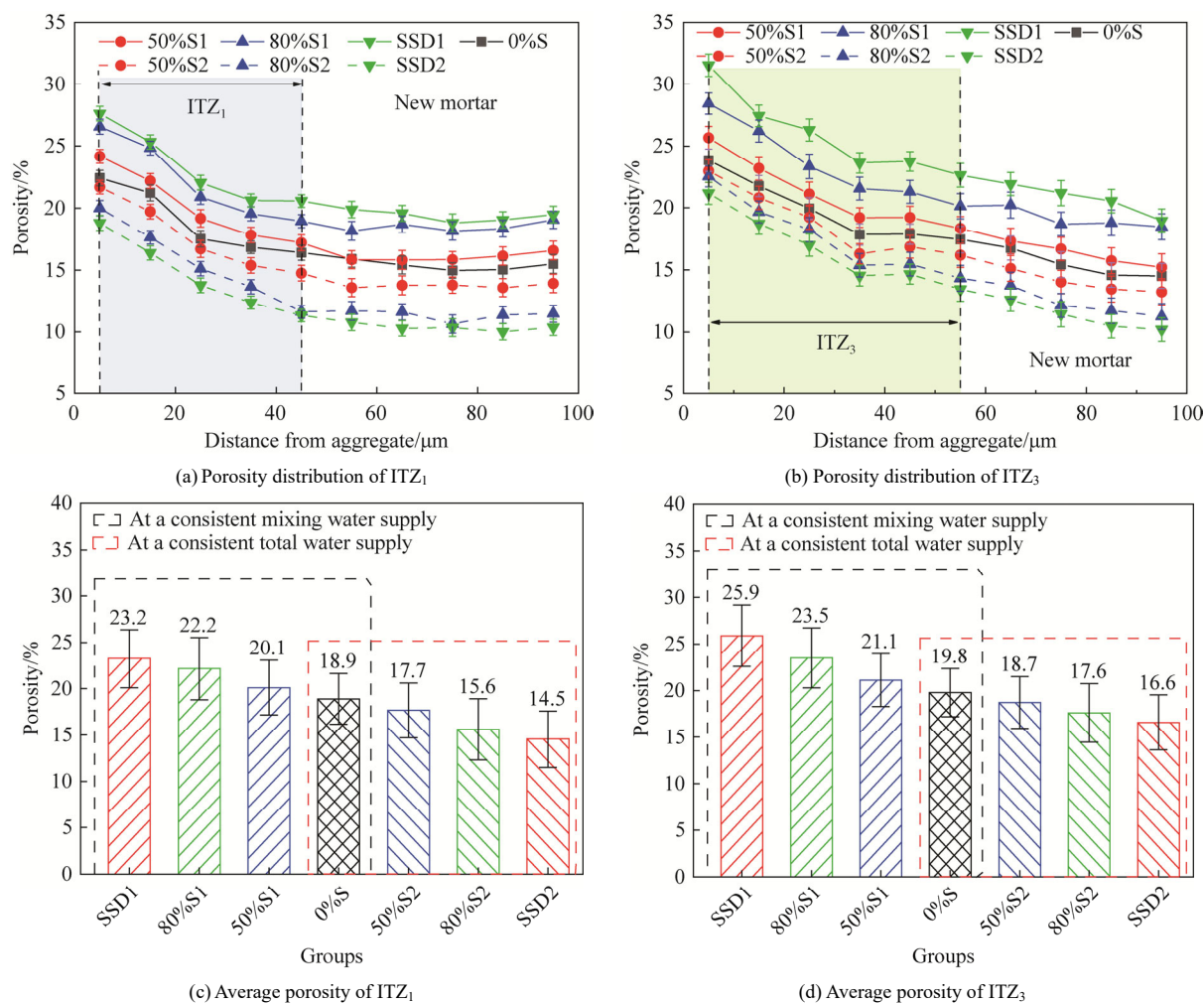


Fig. 6 Porosity distribution and the average porosity of ITZ<sub>1</sub> and ITZ<sub>3</sub> in RAC prepared with RA at varying  $S_w$  after 28 d

Fig. 6a and Fig. 6b show that the porosity was higher on the surface of virgin aggregate/old mortar and decreased gradually at further positions. Scrivener *et al.*<sup>[17]</sup> observed the same phenomenon and attributed it to the "wall" effect, which results in a steep gradient of the actual  $W_c/C$  that decreases with distance from the RA surface and eventually stabilizes at a characteristic distance.

Fig. 6 also shows that under S1, the porosity of the new ITZ increased with the rise in  $S_w$ , while under S2, the opposite trend was observed. Under S1, the calculated  $W_c/C$  of the concrete remained constant, but the water desorption behavior of the RA led to an increase in the actual  $W_c/C$  ratio in the local region around the RA. As indicated in Table 1, compared with 0%S, the  $W_t/C$  of the cement matrix in the SSD1 increased by 27.3%. The theoretical  $W/C$  ratio required for complete cement hydration is approximately 0.24<sup>[29]</sup>; thus, any additional water beyond this range contributes to pore formation within the cement matrix<sup>[30]</sup>. As  $S_w$  increased, the local water content rose accordingly, resulting in more pores in the hardened new ITZ. Under S2, the  $W_t/C$  remained constant, while the  $W_c/C$  decreased with increasing  $S_w$ . Clearly, during the early

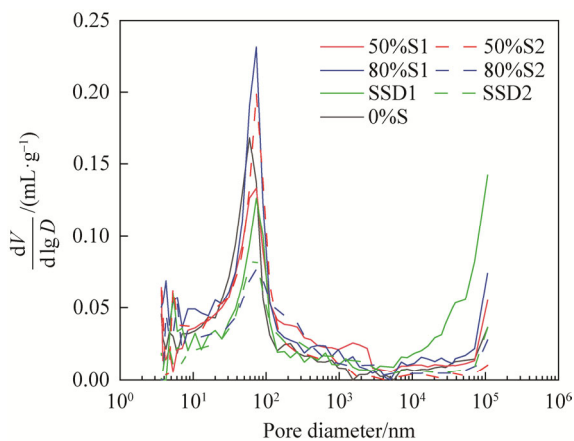
stages of hydration, the water released by the RA was insufficient to counteract the lower porosity in the new ITZ, as the  $W_c/C$  had been reduced.

Furthermore, as illustrated in Fig. 6c and Fig. 6d, the average porosity of ITZ<sub>1</sub> was consistently less than that of ITZ<sub>3</sub>. This may be attributed to the more pronounced water desorption from the old mortar than from the virgin aggregate, resulting in a higher local water content in ITZ<sub>3</sub> than in ITZ<sub>1</sub>. This explanation is further corroborated by the consistently higher average UH content observed in ITZ<sub>1</sub> than in ITZ<sub>3</sub>.

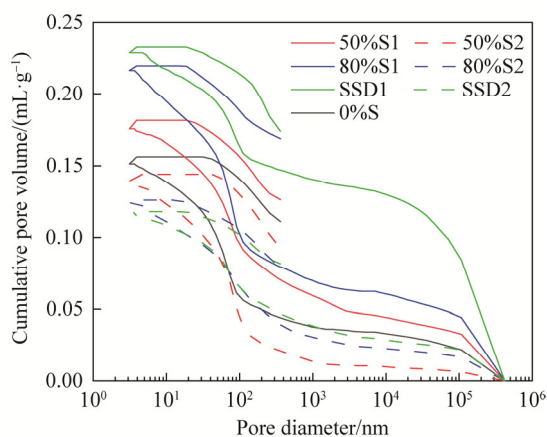
**3.1.2 Pore structure of new mortar** The pore size distribution curves and cumulative pore size distribution curves for new mortar in the 7 groups of RAC after cured for 28 d are shown in Fig. 7. The representative pore structure parameters, *i.e.*, total porosity and effective porosity derived from Fig. 7 are shown in Table 2.

As illustrated in Fig. 7 and Table 2, under S1, the total porosity of new mortar exhibited an increasing trend with the augmentation of  $S_w$ . Conversely, under S2, an opposite trend was observed. The explanation is similar to that stated in Section 3.1.1, Item 1). Additionally, Table 2 shows that effective porosity

increased as  $S_w$  increased under S1, but decreased under S2. It is widely accepted that the effective porosity can reflect the connectivity of pores and the tortuosity of permeation paths and has a significant impact on ion transport in concrete, *i.e.*, the larger the effective porosity, the larger the connectivity of pores and the smaller the tortuosity of permeation paths, which negatively impacts the impermeability and durability of the material<sup>[31]</sup>. Therefore, the results in Table 2 imply that under S1, the increase in actual  $W_c/C$  ratio with higher  $S_w$  may lead to enhanced pore connectivity, while the opposite occurs under S2.



(a) Pore size distribution



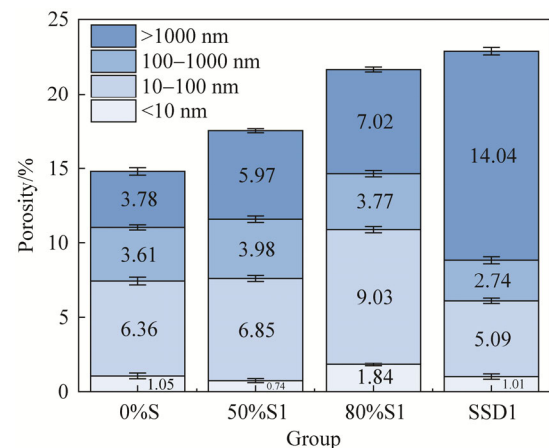
(b) Cumulative pore size distribution

Fig. 7 Pore size distribution of new mortar in RAC prepared with RA at varying  $S_w$  after 28 d

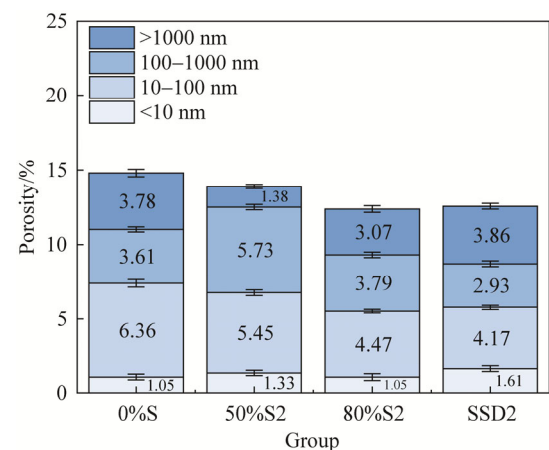
**Table 2** Typical pore diameter of new mortar in RAC prepared with RA at varying  $S_w$  after 28 d

| Mix ID | Typical pore parameters/% |                    |
|--------|---------------------------|--------------------|
|        | Total porosity            | Effective porosity |
| 0%S    | 15.13                     | 4.04               |
| 50%S1  | 17.54                     | 4.92               |
| 80%S1  | 21.65                     | 4.79               |
| SSD1   | 22.88                     | 5.36               |
| 50%S2  | 13.89                     | 4.62               |
| 80%S2  | 12.39                     | 4.46               |
| SSD2   | 11.57                     | 3.40               |

The pore structure, particularly the pore size distribution rather than porosity, plays a decisive role in controlling the permeability of concrete<sup>[32]</sup>. Based on pore size, the pores in cement-based materials can be broadly categorized into four types<sup>[33]</sup>: gel pores (<10 nm), transition pores (10–100 nm), capillary pores (100–1000 nm), and macropores (>1000 nm), as illustrated in Fig. 8.



(a) At S1



(b) At S2

Fig. 8 Pore classification diagram of new mortar in RAC prepared with RA at varying  $S_w$  after 28 d

Fig. 8 shows that under S1, increasing  $S_w$  led to a significant rise in the fraction of pores larger than 100 nm in RAC, with the most notable changes occurring in macropores. Compared to the 0%S reference group, the fractions of macropores in 50%S1, 80%S1, and SSD1 increased by 57.9%, 85.7%, and 271.4%, respectively. The investigation conducted by Zhou *et al.*<sup>[27]</sup> demonstrated that an increase in free water promoted the formation of capillary pores, causing smaller adjacent pores to interconnect and coalesce into larger pores. While the calculated  $W_c/C$  ratio in the S1 series concrete remains at 0.55, the  $W_c/C$  ratio rises to 0.70 when  $S_w$  reaches 100%. Furthermore, even though the pre-absorbed water by RA would not be completely released, the increased free water content at higher  $S_w$

of RA could still benefit the large pore formation, leading to a rise in large pore fraction. In contrast, under S2, the fraction of pores larger than 100 nm gradually decreased with higher  $S_W$ , which was mainly attributed to the significantly reduced free water content in the fresh mixture, hindering the formation of large pores during hardening. Even though RA with higher  $S_W$  may release water during curing, the effects on pore size or its distribution could be quite limited. The fraction of pores larger than 100 nm in concrete is often associated with improved chloride resistance<sup>[34]</sup>, which will be discussed in detail in the following parts.

### 3.2 Transport of chloride ions

#### 3.2.1 Chloride ion diffusion coefficient

##### 1) Rapid chloride migration test

The rapid chloride migration coefficient  $D_{RCM}$  of RAC tested by the RCM method is shown in Fig. 9.

Fig. 9 shows that the  $D_{RCM}$  of RAC increased as  $S_W$  increased from 0% to 100% at S1. The  $D_{RCM}$  of the 50%S1, 80%S1 and SSD1 groups was 36.6%, 59.3% and 67.5% higher than that of the reference 0%S, respectively. This may be because the increased  $S_W$  elevated the porosity and large pore fraction in both new ITZs and new mortar, particularly in the fraction of macropores, as already confirmed by Sections 3.1.1 and 3.1.2. Previous studies also reported that the chloride diffusion coefficient of concrete is largely dependent on

porosity, especially the proportion of pores larger than 100 nm<sup>[34, 35]</sup>.

Fig. 9 also indicates that the behavior under S2 is more stable over the fluctuation of the RA saturation degree, which is likely related to the overall lower  $W/C$  level under S2, resulting in a lower diffusion coefficient and reducing its sensitivity to variations in  $S_W$ .

##### 2) Chloride profile under natural exposure

Fig. 10 and Fig. 11 illustrate the distribution of  $C_f$  and  $C_i$  along the depth of the exposed surface in RAC prepared with RA at varying  $S_W$ , respectively.

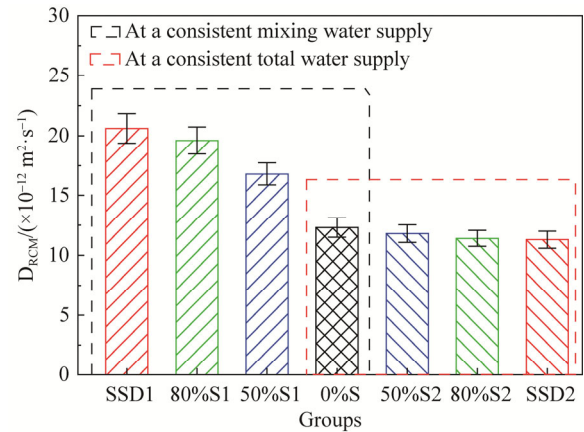


Fig. 9  $D_{RCM}$  of RAC prepared with RA at varying  $S_W$  after 28 d

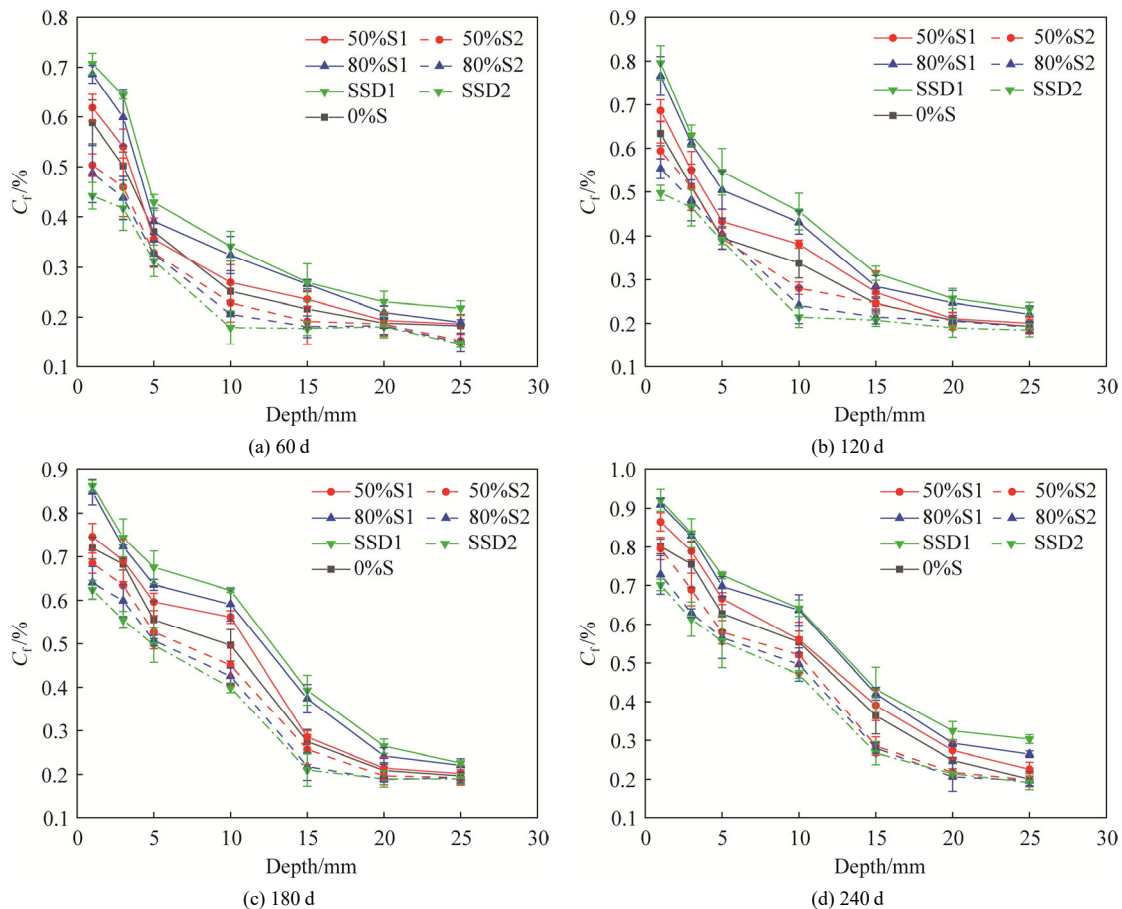


Fig. 10 Distribution of  $C_f$  in RAC prepared with RA at varying  $S_W$  under different exposure ages

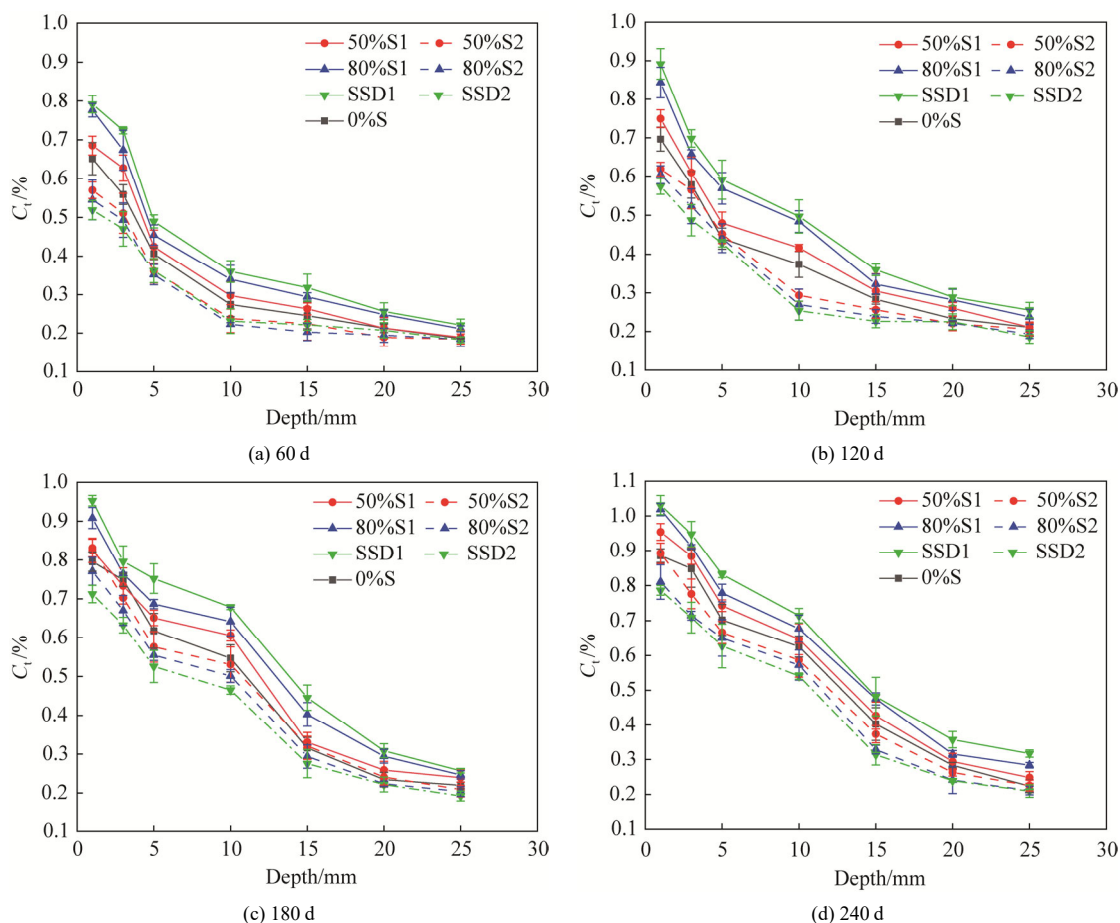


Fig. 11 Distribution of  $C_t$  in RAC prepared with RA at varying  $S_w$  under different exposure ages

To better quantify the impact of  $S_w$  on the chloride resistance of RAC under S1 and S2 in natural exposure conditions, this study employed 1stOpt software to analyze the data presented in Fig. 10 and Fig. 11. The data were fitted according to Fick's second law (Eq. (3)), obtaining effective chloride diffusion coefficient ( $D_e$ ) and apparent chloride diffusion coefficient ( $D_a$ )<sup>[36]</sup>, which are illustrated in Fig. 12.

$$C(x, t) = C_0 + (C_s - C_0) \cdot \left[ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{D \cdot t}} \right) \right] \quad (3)$$

where  $C(x, t)$  represents the  $\text{Cl}^-$  concentration (%(mass fraction)) at depth  $x$  after chloride exposure time  $t$ , %;  $x$  is the depth from exposed surface, m;  $t$  is the chloride exposure time, s;  $C_0$  and  $C_s$  are the initial chloride concentration and the surface chloride concentration, %, respectively;  $C_0$  was determined by chloride titration on powder samples drilled from RAC after curing was completed, and the average value was about 0.124%.  $D$  represents the  $\text{Cl}^-$  diffusion coefficient,  $\text{m}^2 \cdot \text{s}^{-1}$ ; and the  $\operatorname{erf}(z)$  is the Gauss error function.

Fig. 12 shows that both  $D_e$  and  $D_a$  of RAC increased with an increase in  $S_w$  under S1, while they showed an opposite trend under S2. This finding is consistent with the RCM test results, indicating that the influence of  $S_w$  on the  $\text{Cl}^-$  diffusivity of RAC is similar between accelerated migration conditions and natural

exposure. Furthermore, both  $D_e$  and  $D_a$  were more stable under S2. For S1, RAC with saturated surface dry aggregate exhibited 35.5%–59.0% higher  $D_e$  and 24.2%–57.5% higher  $D_a$  compared to oven-dry RAC during the testing period. In contrast, S2 resulted in decreases of 15.6%–28.8% in  $D_e$  and 8.3%–25.6% in  $D_a$ .

In addition, both  $D_a$  and  $D_e$  decreased with increasing exposure age. Previous studies have indicated that  $\text{Cl}^-$  penetrates the interior of concrete, where it reacts with cement hydration products, such as  $\text{Ca}(\text{OH})_2$  and unhydrated aluminum salts ( $\text{C}_3\text{A}$ ), to form expansive substances like Friedel's salt<sup>[37]</sup>. These substances fill the pores within the concrete, densifying its microstructure and enhancing its resistance to chloride ingress. Notably, under identical conditions of depth and exposure time,  $D_a$  consistently remained higher than  $D_e$ . This phenomenon results from not only the chemical bonding of  $\text{Cl}^-$  with hydration products but also its physical adsorption onto C-S-H<sup>[38]</sup>. Under the combined effects of these mechanisms,  $D_e$  was significantly reduced. The influence of  $S_w$  on the  $\text{Cl}^-$  binding capacity of RAC under the two water-control schemes will be further analyzed and discussed in the following sections.

**3.2.2 Chloride binding capacity** Fig. 13 illustrates the microstructure morphologies of the SSD1 new mortar after 1 d of curing and 240 d of exposure, with

corresponding EDS results are presented in Fig. 14. Fig. 15 presents the XRD pattern of new mortar of SSD1 after 240 d of exposure.

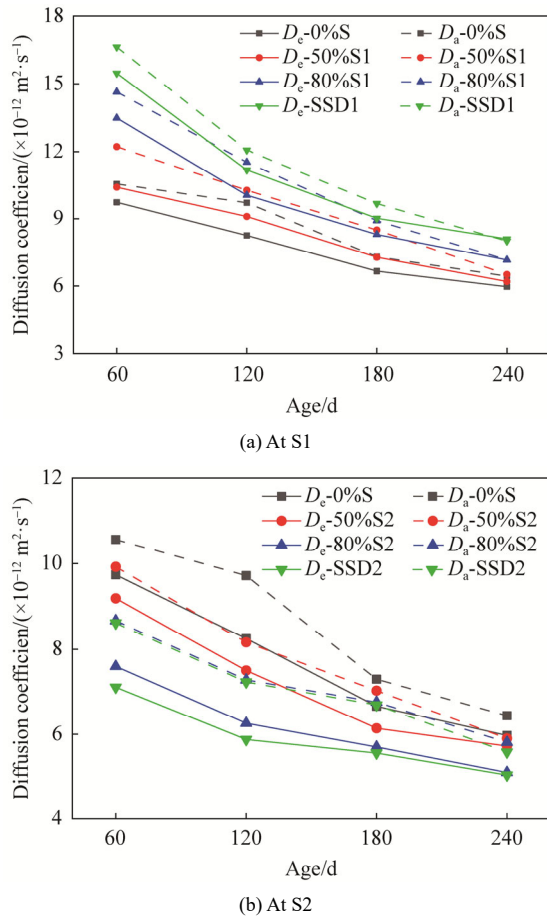


Fig. 12  $\text{Cl}^-$  diffusion coefficient in RAC prepared with RA at varying  $S_W$  under different exposure ages

It should be noted that samples from the 5–10 mm depth region (rather than the surface-nearby region) of SSD1 after 240 d of exposure were selected for SEM/EDS analysis, to avoid interference from surface carbonation which can lead to the decomposition of Friedel's salt<sup>[39]</sup>. Besides, the SSD1 group was selected because  $C_f$  and  $C_t$  in SSD1 were significantly higher than those of other groups as seen from Fig. 10 and Fig. 11. The samples were soaked in isopropanol to arrest hydration and subsequently dried under vacuum before use.

As shown in Fig. 13, clustered fibrous gels were observed in SSD1 after 1 d of standard curing. EDS analysis of areas A-1 to A-3 (Fig. 14) indicated that these formations primarily consisted of O, Ca, and Si, with no detectable Cl, identifying them as C-S-H gel. After 240 d of chloride exposure, the SSD1 matrix appeared denser and more compact, with numerous layered crystals present. EDS analysis of points B-1 to B-3 revealed that O, Ca, and Si remained the dominant elements, while Cl was also detected, with atomic percentages ranging from 0.2% to 4.6%, suggesting the

formation of chloride-bearing phases. XRD analysis (Fig. 15) further confirmed that part of these phases were Friedel's salt, evidenced by characteristic diffraction peaks at  $2\theta = 11.3^\circ$ ,  $22.1^\circ$ , and  $39.5^\circ$ <sup>[40, 41]</sup>. The presence of Friedel's salt indicates the chemical binding of  $\text{Cl}^-$ , while some other chloride ions detected by EDS should be physically adsorbed by the C-S-H gel, as widely reported<sup>[42]</sup>.

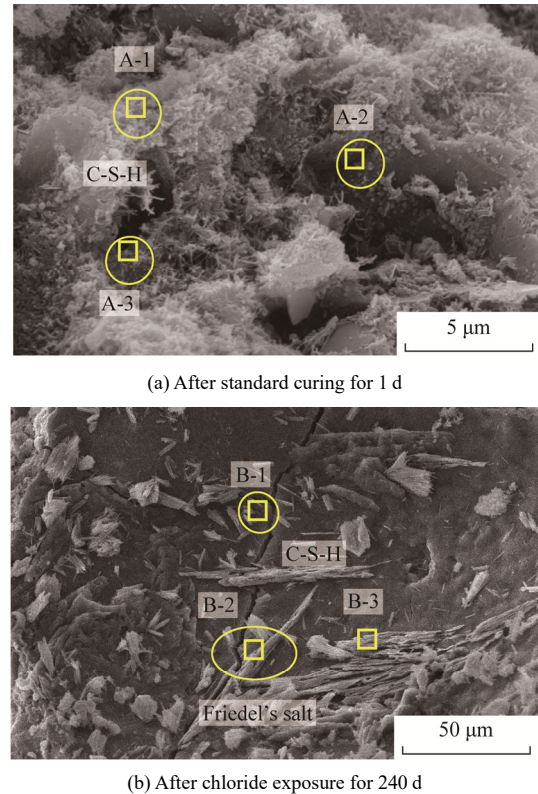


Fig. 13 SEM images of SSD1 after standard curing for 1 d and after chloride exposure for 240 d

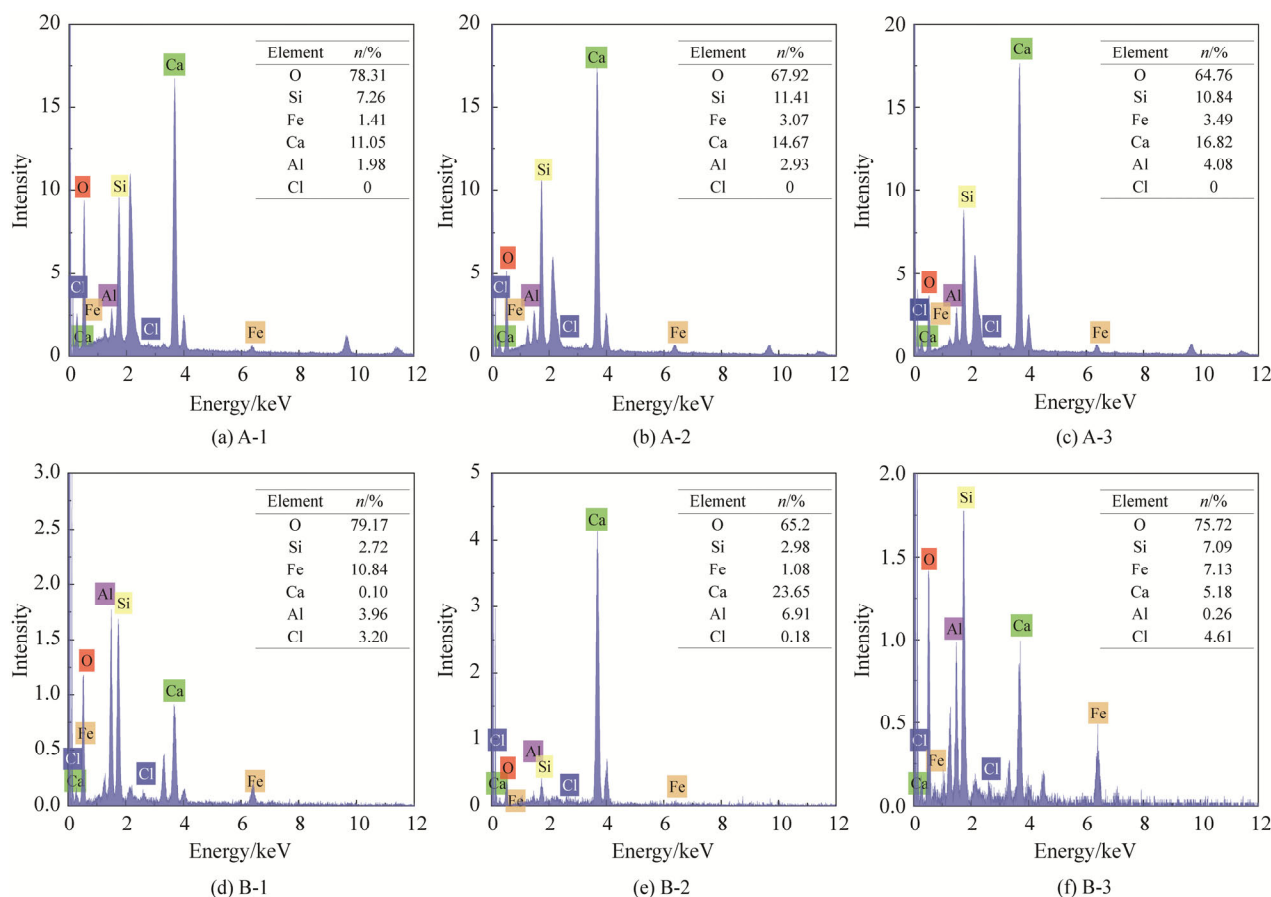
Previous studies have demonstrated a significant linear correlation between  $C_f$  and  $C_t$ <sup>[43, 44]</sup>, as well as between  $D_e$  and  $D_a$ <sup>[45]</sup>, which can be mathematically expressed through Eq. (4) and Eq. (5).

$$C_t = K_1 \cdot C_f \quad (4)$$

$$D_a = K_2 \cdot D_e \quad (5)$$

where  $K_1$  and  $K_2$  represent the chloride binding capacity of RAC,  $K_1$  is derived from the fitting of  $C_f$  and  $C_t$ , while  $K_2$  is obtained from the fitting of  $D_e$  and  $D_a$ . A higher  $K_1$  and  $K_2$  value indicates a stronger chloride binding capacity.

This study utilizes Origin software to fit the data in Fig. 10 and Fig. 11 based on Eq. (4), as well as to fit the data in Fig. 12 according to Eq. (5). Fig. 16a–Fig. 16b present the fitting plots of the chloride ion concentration parameter  $K_1$  under S1 and S2 conditions after 240 d of chloride exposure. Fig. 16c–Fig. 16d display the fitting plots of the diffusion coefficient  $K_2$  at different stages of the exposure process. The fitting results shown in Fig. 16 are further summarized and presented in Fig. 17.



$n$  is mole fraction.

Fig. 14 EDS spectrum of SSD1 after standard curing for 1 d and after chloride exposure for 240 d

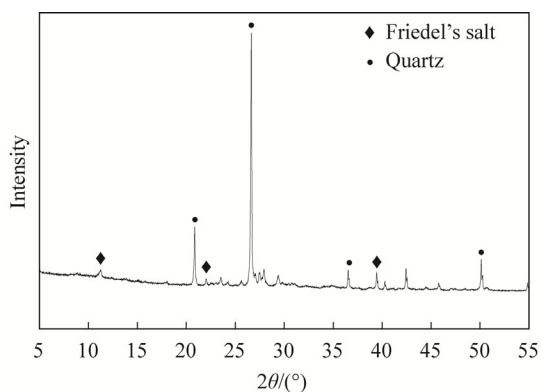


Fig. 15 XRD analysis of new mortar in SSD1 after chloride exposure for 240 d

As illustrated in Fig. 17, the  $K_1$  values of RAC exhibited distinct patterns under S1 and S2 during different exposure times. At 60 and 120 d of exposure, the  $K_1$  value was significantly higher in S1 than in S2. However, this trend completely reversed with prolonged exposure. This phenomenon suggested that during the early exposure stage (60–120 d), RAC demonstrated a stronger  $\text{Cl}^-$  binding capacity under S1 than S2. Conversely, after exposure beyond 180 d, the  $\text{Cl}^-$  binding capacity of RAC under S1 became weaker than that under S2. This transition in  $\text{Cl}^-$  binding capacity

may be attributed to the differential hydration rates influenced by  $S_w$  under S1 and S2. During the standard curing stage, RAC under S1 exhibited a higher actual  $W/C$  ratio than under S2, which enhanced the hydration degree of cement mortar. This resulted in the generation of a greater amount of cement hydration products, including C-S-H and AFm. These hydration products were capable of both physical adsorption and chemical binding of  $\text{Cl}^-$ , thereby augmenting the  $\text{Cl}^-$  binding capacity of RAC at earlier exposure ages. As the immersion experiment progressed, sufficient moisture facilitated the hydration of UH particles. With increasing exposure age, compared to S1, more UH content in RAC was transformed into new hydration products under S2. This enhanced production of hydration products subsequently improved the  $\text{Cl}^-$  binding capacity of RAC under S2.

Fig. 17 illustrates the influence of  $S_w$  on  $K_1$ , which remained within a 5% variation margin. This limited variation suggests that  $K_1$  was not a sensitive indicator for evaluating the impact of  $S_w$  on the  $\text{Cl}^-$  binding capacity of RAC. In contrast,  $K_2$  responded more distinctly to  $S_w$ : it decreased with increasing  $S_w$  under S1, whereas under S2 it increased. This suggests that the chloride-binding capacity of RAC weakens with increasing  $S_w$  under S1, while an opposite behavior is

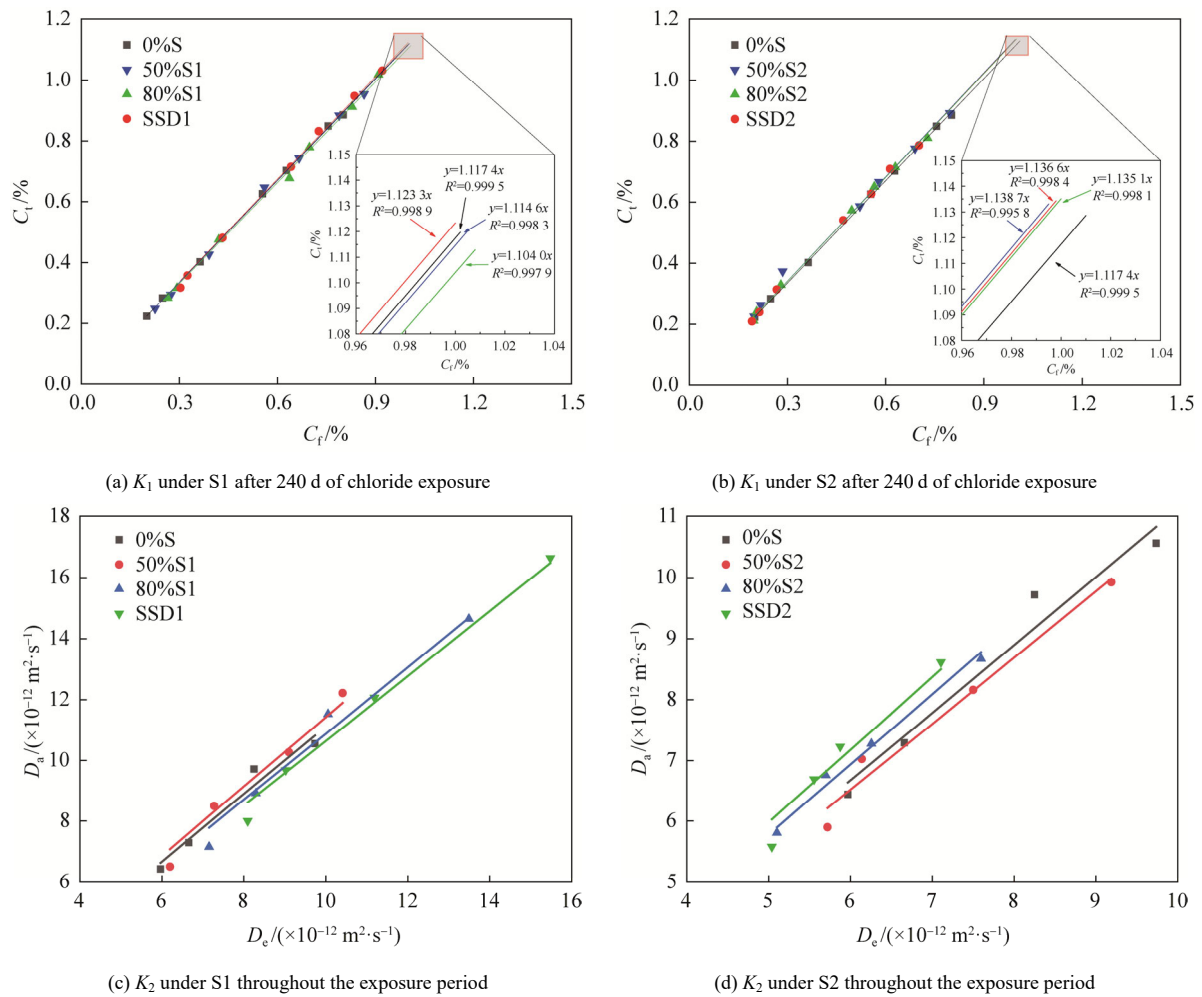


Fig. 16 Fitting plot of  $\text{Cl}^-$  concentration parameter  $K_1$  and diffusion coefficient  $K_2$  in RAC

observed under S2. This result appears to contradict the conclusion drawn in Section 3.1.1, where a higher  $S_w$  under S1 was found to promote cement hydration by supplying additional water *via* desorption from RA. In theory, this enhanced hydration should produce more C-S-H gel, thereby increasing the physical adsorption of chloride ions and improving the overall binding capacity. However, the chloride-binding capacity is predominantly governed by chemical binding, specifically through the reaction between  $\text{Cl}^-$  and AFm phases to form Friedel's salt, rather than by physical adsorption onto C-S-H gels<sup>[46]</sup>. Previous studies have reported that the proportion of  $\text{Cl}^-$  chemically bound by AFm phases can reach between 67.0% and 69.0%, while the content of chlorides physically adsorbed by C-S-H is only 28.0%–28.5%, and the amount of chlorides chemically bound by AFt is essentially negligible<sup>[46, 47]</sup>. As discussed earlier, the extra water released from RA with higher  $S_w$  under S1 increases the  $W_c/C$  in the new mortar and the ITZ, which may influence the AFm content in RAC. Chen *et al.* demonstrated, using in-situ powder X-ray diffraction, that a higher  $W/C$  retards the formation of AFt and slows its conversion to AFm<sup>[48]</sup>. They attributed this

delay to the lower concentrations of key ions (*e.g.*,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ) in the pore solution at elevated  $W/C$  ratios. Under S1, the increase in the  $W_c/C$  ratio resulting from water desorption of high- $S_w$  RA reduces the pH of the pore solution<sup>[49]</sup>, and the lower pH environment can inhibit the formation of the AFm phase. This inference is supported by the research of Sánchez-Herrero *et al.*, who demonstrated that a high-pH environment ( $\text{pH} > 13.4$ ) promotes the formation of the AFm phase in high-purity tricalcium aluminate, while the opposite is observed under a low-pH condition<sup>[50]</sup>. Since AFm phases are primarily responsible for chemical chloride binding, their retardation leads to a degradation of the overall binding capacity. Similar adverse effects of increasing  $W/C$  on the chemical binding capacity of cement paste have been reported by Kim *et al.*<sup>[51]</sup>. In contrast, under S2, an increase in  $S_w$  of RA reduces the  $W_c/C$ . This reduction elevates the concentrations of  $\text{OH}^-$ , calcium, and sulfate ions in the pore solution, which in turn promotes the formation of AFm phases. Consequently, the chemical chloride-binding capacity is enhanced.

### 3.2.3 Time-dependence of the chloride diffusivity

In this study, both  $D_e$  and  $D_a$  exhibited time-

dependent attenuation characteristics (see Section 3.2.1, Item 2)). To quantify this attenuation rate for each RAC group, the power-law relationship model proposed by Thomas *et al.*<sup>[52]</sup> was adopted. This model describes the relationship between the chloride diffusion coefficient ( $D_t$ ) at time  $t$  and the exposure duration, as expressed in Eq. (6):

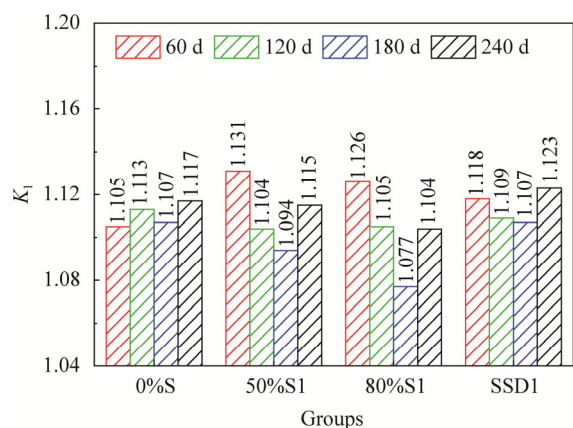
$$D_t = D_0 \left( \frac{t_0}{t} \right)^m \quad (6)$$

where  $D_t$  is the diffusion coefficient (*i.e.*,  $D_e$  or  $D_a$ ) at exposure time  $t$ ,  $\text{m}^2 \cdot \text{s}^{-1}$ ;  $D_0$  is the diffusion coefficient at

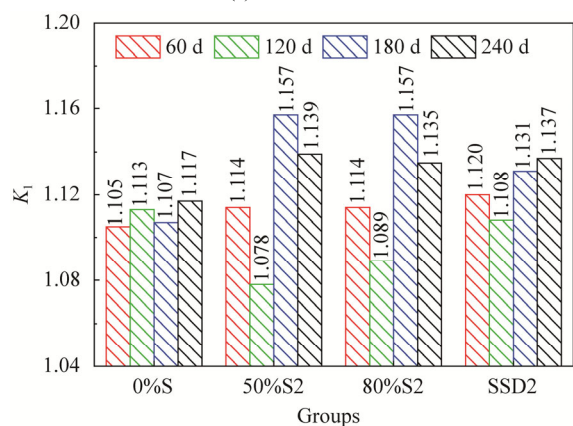
a reference age (the  $D_0$  used in this study refers to the  $\text{Cl}^-$  diffusion coefficient at 60 d of exposure),  $\text{m}^2 \cdot \text{s}^{-1}$ ; and  $m$  is the diffusion attenuation index.

Based on Eq. (6), the data in Fig. 12 were fitted, where  $m_e$  and  $m_a$  represent the decay coefficients for  $D_e$  and  $D_a$ , respectively. The fitting results are presented in Fig. 18.

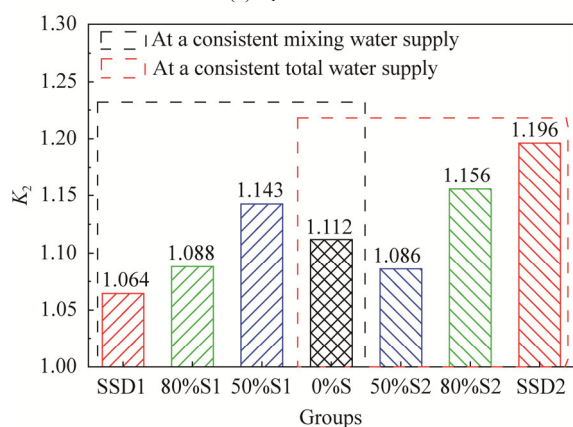
Fig. 18 shows that both  $m_e$  and  $m_a$  of RAC increased with rising  $S_w$  under S1. In contrast, under S2, the relationship of  $m_e$ ,  $m_a$ , and  $S_w$  followed an opposite trend. This indicated that under S1, the decay rates of  $\text{Cl}^-$  diffusion coefficient in RAC accelerated with increasing  $S_w$ , whereas under S2, the decay rates exhibited an inverse pattern. This phenomenon could be attributed to the fact that, under S1, increasing  $S_w$  resulted in higher porosity in new mortar. More pores, especially capillary pores and macropores, could facilitate the transport of  $\text{Cl}^-$ , resulting in a higher chloride diffusion coefficient in RAC during the early exposure period. Higher  $\text{Cl}^-$  content in RAC also led to the generation of more chloride-binding products, which further refined the pore structure to a greater extent, and in turn led to more obvious attenuation of the chloride diffusion coefficient over time. In contrast, under S2, the increased  $S_w$  led to reduced initial porosity,



(a)  $K_1$  under S1

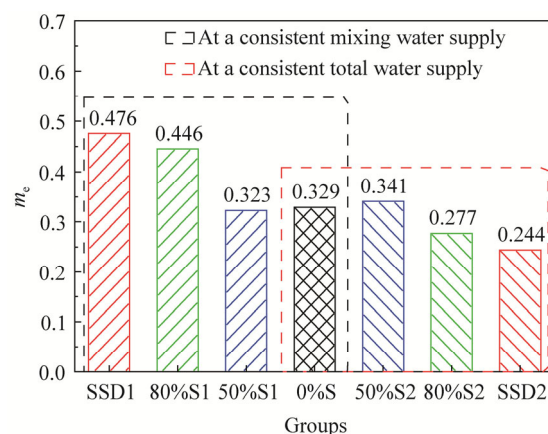


(b)  $K_1$  under S2

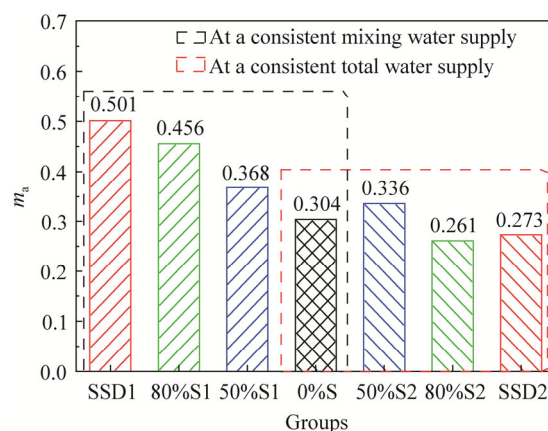


(c)  $K_2$

Fig. 17 Fitting results of  $\text{Cl}^-$  concentration parameter  $K_1$  and diffusion coefficient  $K_2$  in RAC



(a)  $m_e$



(b)  $m_a$

Fig. 18 Attenuation index of  $\text{Cl}^-$  diffusion coefficient in RAC prepared with RA at varying  $S_w$

which consequently decreased early-stage chloride penetration. Reduced quantities of these reaction products formed in high- $S_W$  RAC over time, diminishing these products pore-refining effect on cement mortar. Consequently, under S2, higher  $S_W$  caused a slower decay rate of chloride diffusion coefficient in RAC.

### 3.3 Further discussion on the influence of $S_W$ on chloride transport in RAC

The results of this study indicated that  $S_W$  had a significant impact on  $\text{Cl}^-$  transport characteristics of RAC under different water-control schemes. Under S1, the chloride diffusion coefficients ( $D_{\text{RCM}}$ ,  $D_e$ , and  $D_a$ ) of RAC increased with increasing  $S_W$ , while the chloride binding capacity decreases accordingly. Under S2, the opposite trend was observed.

According to the discussion above, the divergence in  $D_{\text{RCM}}$  and  $D_e$  should be primarily attributed to the combined effects of the  $W_e/C$  ratio and the water absorption-desorption behavior of RA on the RAC microstructure. Under S1, the calculated  $W_e/C$  ratio of RAC was consistent. However, RA with higher  $S_W$  released water into the cement matrix, thereby increasing the actual  $W_e/C$  ratio. In a related published work, the authors proposed a water absorption-desorption model for RA in RAC (as shown in Fig. 19), in which unsaturated RA in concrete underwent four distinct water exchange processes: initial RA water absorption, first water exchange equilibrium, RA water release, and second water exchange equilibrium<sup>[23]</sup>. In this model, RA with higher  $S_W$  completed the water absorption earlier compared to drier RA. As shown in Fig. 19a, under S1, RA entered the water release stage before the curing age of 12 h. Furthermore, the water release curve becomes steeper and the amount of released water increases with higher  $S_W$ . This resulted in a decrease in the UH content of the new ITZ under S1 with increasing  $S_W$  within the first 12 h. For SSD1, RA might directly enter the third stage during the mixing process, leading to an increase in the actual  $W_e/C$  ratio of the matrix. Consequently, under S1, higher  $S_W$  made it more likely for excess moisture in the cement matrix during early hydration to occupy space and form additional pores. This is proven by the porosity results discussed in Sections 3.1.2 and 3.1.3, where increasing  $S_W$  under S1 led to enhanced porosity in the new ITZs and new mortar, particularly increasing the effective porosity and the fraction of pores larger than 100 nm in new mortar. The increasing effective porosity and fraction of large pores could enhance pore connectivity and decrease the tortuosity of the chloride permeation path<sup>[53]</sup>, explaining the higher  $D_{\text{RCM}}$  and  $D_e$  at higher  $S_W$  under S1. Furthermore, the experimental result of decreasing UH content in the new ITZs with increasing  $S_W$  under S1 further supports the interpretation of this water release mechanism: higher  $S_W$  promoted more water participation in the hydration reactions within the

new ITZ, thereby reducing the UH content. These micro-level observations confirm the impact of RA water release behavior on the hydration progress and pore structure of the matrix, which cannot be ignored when designing the chloride permeability of RAC in real practice.

In contrast, under S2, the  $W_e/C$  ratio of RAC decreased with increasing  $S_W$ . As shown in Fig. 19b, RA also entered the water release stage before the curing age of 12 h. Compared to S1, the free water content of RAC under S2 was significantly lower. At the same  $S_W$  level, RA under S2 should enter the water release stage earlier than under S1. Moreover, as already discussed above, although RA with high  $S_W$  also released water into the cement matrix during early curing under S2, this process occurred at a slower rate (as shown in Fig. 19), and the released water was insufficient to counteract the dense microstructure formed by the initially low  $W_e/C$  ratio (as calculated). The increased matrix compactness and likely reduced pore connectivity collectively led to the decrease in  $D_{\text{RCM}}$  and  $D_e$ , as discussed in Section 3.2.1 Simultaneously, the lower  $W_e/C$  ratio also resulted in an increase in the UH content of the new ITZs.

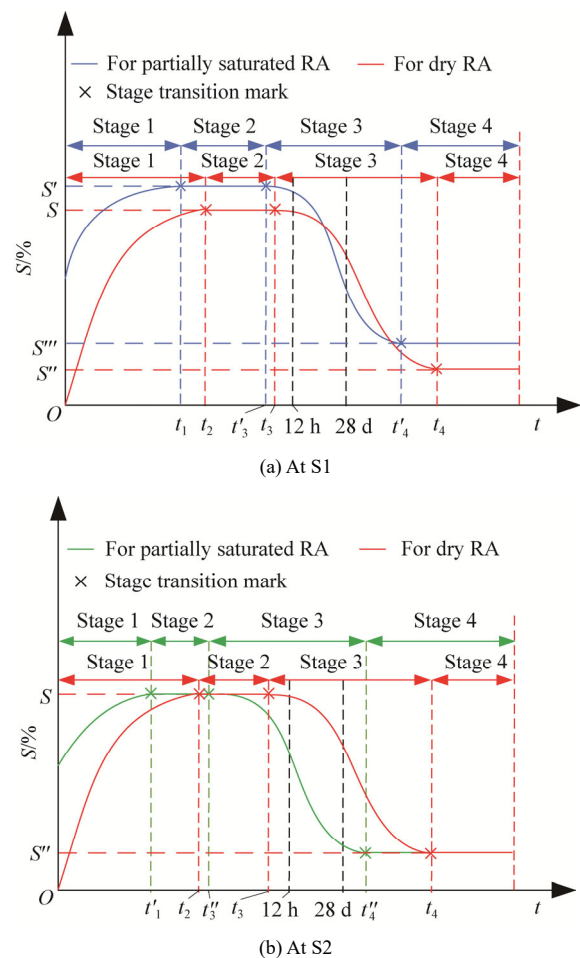


Fig. 19 Model of water absorption and desorption of dry and partially saturated RA in the RAC mixture<sup>[23]</sup>

The chloride binding capacity is governed by both the degree of hydration and the specific content of AFm phases in the matrix; the former dictates the physical binding capacity, whereas the latter determines the chemical binding capacity. As discussed in Section 3.2.2, the  $S_w$  of RA under the two different water-control schemes may create distinct conditions for AFm formation by altering the W/C ratio and the alkalinity of the matrix. Further research work should take thermogravimetric analysis or quantitative X-ray diffraction techniques to provide quantitative information on the content of AFm phases, thereby establishing a quantitative relationship among  $S_w$ , AFm content, and chloride binding capacity at different water control schemes.

In summary, this work confirms that the  $S_w$  of RA significantly influences the chloride resistance of RAC, and this influence is largely determined by the water control scheme adopted. Under S2, in which the total water is kept constant, the  $W_c/C$  ratio of the RAC matrix remains lower than that under the S1 scheme—where only the mixing water is fixed—regardless of variations in  $S_w$ . This results in a more compact ITZ and mortar matrix, characterized by lower porosity and reduced pore connectivity, thereby leading to correspondingly lower values of  $D_{RCM}$ ,  $D_e$ , and  $D_a$ . Furthermore, compared with S1, the chloride diffusion coefficients of RAC under S2 are less sensitive to fluctuations in  $S_w$ , contributing to more stable and predictable chloride diffusion performance. The S2 scheme can preferably be implemented in combination with the pre-wetting treatment of RA, considering that the high  $S_w$  of RA under this condition can further enhance the chloride impermeability. In contrast, using RA with low  $S_w$  or in a dry state is preferred under S1 to enhance RAC's chloride impermeability as well as the chloride binding capacity.

## 4 Conclusions

1) Under S1, a higher  $S_w$  of RA increases its moisture release during early hydration, elevating  $W_c/C$  ratio in the ITZs and new mortar. This results in lower UH content but higher porosity, including an increased proportion of macropores ( $>100$  nm). Conversely, under S2, a higher  $S_w$  lowers the  $W_c/C$  ratio, leading to reduced porosity and higher UH content, despite the additional moisture supplied by the RA.

2)  $D_{RCM}$  obtained by rapid migration tests,  $D_e$  and  $D_a$  obtained under natural exposure all increase with  $S_w$  under S1, indicating higher chloride permeability. Under S2, they show a decreasing trend. This divergence is attributed to the opposing effects of  $S_w$  on pore structure and connectivity under the two water-control schemes.

3) Both XRD and EDS results confirm physical chloride binding by C-S-H gel and chemical binding as Friedel's salt in RAC. A higher  $S_w$  reduces binding

capacity under S1, but enhances it under S2. While the specimens under S1 exhibited stronger binding at early exposure stages (60–120 d), those under S2 exhibited greater long-term binding capacity after 180 d, owing to continued hydration of the more abundant residual cement particles in the latter.

4) The decrease in  $D_e$  and  $D_a$  over time, caused by pore filling from chloride-bearing phases, occurs at a rate that accelerates with  $S_w$  under S1 but decelerates under S2. This demonstrates the competing influences of the initial  $W_c/C$  ratio-governed pore structure and the subsequent pore refinement during chloride ingress on long-term transport behavior.

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## Effects of Aggregate Water Saturation Degree on Chloride Diffusion in Recycled Aggregate Concrete

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### Extended Abstract

**Introduction** Due to the large amount of old mortar attached to the surface of recycled coarse aggregate (RA), its water absorption capacity is significantly higher than that of natural coarse aggregate. Consequently, the water saturation degree ( $S_w$ ) of RA plays a crucial role in influencing the microstructure and resistance to  $\text{Cl}^-$  erosion of recycled aggregate concrete (RAC). However, the specific effects of different saturation states on RAC performance remain controversial. Some studies suggest that water released from surface-saturated RA weakens the newly formed interfacial transition zone (ITZ), reducing resistance to chloride penetration, whereas others argue that its desorption behavior acts as an internal curing agent that enhances RAC durability. Furthermore, the influence of  $S_w$  on the microstructure under different water control schemes—namely, constant mixing water supply (labelled as S1) and constant total water supply (labelled as S2)—has yet to be fully elucidated. Therefore, this study aims to systematically investigate the effects of varying  $S_w$  of RA on chloride diffusion and binding behavior in RAC under different control schemes, and to elucidate the underlying microscopic mechanisms.

**Methods** The RA used in this study had a particle size range of 4.8–31.5 mm, an apparent density of  $2650 \text{ kg/m}^3$ , a water absorption rate of 5.4%, a crushing index of 16.6%, and an old mortar content of 36.7%. The fine aggregate was river sand with a fineness modulus of 2.0, a moisture content of 1.0%, and a mud content of 0.8%. Ordinary Portland cement 42.5 R with a specific surface area of  $345 \text{ m}^2/\text{kg}$  and a density of  $3.12 \text{ g/cm}^3$  was used. A polycarboxylate superplasticizer with a solid content of 40% and a water reduction rate of 25% was added to control the workability of fresh concrete. Under both S1 and S2, the effective water-to-cement ratio ( $W_e/C$ ) and the total water-to-cement ratio of RAC were maintained at 0.55. The  $S_w$  of RA was adjusted to 0%, 50%, 80%, and 100% by controlling the soaking time.

After curing for 28 d, the rapid chloride migration coefficient ( $D_{RCM}$ ) of RAC was determined using the rapid chloride migration method. Cubic specimens were then immersed in a 5% NaCl solution for one-dimensional natural chloride ingress tests. At exposure durations of 60, 120, 180 d, and 240 d, the concentration profiles of free  $\text{Cl}^-$  and total  $\text{Cl}^-$  were measured using potentiometric titration. Based on Fick's second law of diffusion, the effective and apparent chloride diffusion coefficients ( $D_a$  and  $D_e$ ) were calculated. In addition, after 28 d of curing, the distribution of unhydrated cement content and the porosity in the new ITZ were analyzed using backscattered electron imaging (BSE), while the pore size distribution of the new mortar was determined by mercury intrusion porosimetry (MIP). Furthermore, scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD) were employed to characterize the microstructure and phase composition of chloride-binding products on the concrete surface layer after 240 d of exposure.

**Results and discussion** Under S1, as  $S_w$  of RA increases, the content of unhydrated cement content in the new ITZ decreases, while porosity increases. In contrast, under S2, the opposite trend is observed. MIP results further indicate that under S1, total porosity, effective porosity, and the proportion of macropores ( $>100 \text{ nm}$ ) in the new mortar all increase significantly with increasing  $S_w$ , whereas under S2, these parameters decrease. Under S1, the water absorption capacity of RA decreases with increasing  $S_w$ ; moreover, RA with high  $S_w$  may release water into the fresh mixture, resulting in an increase in the actual  $W_e/C$  ratio of the cement matrix.

Conversely, under S2, higher  $S_w$  corresponds to a lower effective  $W_e/C$  ratio during the early hydration stage, thereby suppressing both hydration and pore development.

Since higher porosity and improved pore connectivity lead to increased chloride diffusivity, under S1, the values of  $D_{RCM}$ ,  $D_e$ , and  $D_a$  all increase with increasing  $S_w$ . In contrast, under S2, the chloride diffusion coefficients decrease as  $S_w$  increases. SEM/EDS and XRD analyses confirm the occurrence of chloride binding in RAC, revealing the presence of chloride-bearing C-S-H gel and Friedel's salt after chloride ingress. During the early exposure stage (60–120 d), RAC under S1 exhibits a stronger chloride-binding capacity due to a higher initial degree of hydration. Under S2, however, a larger amount of residual unhydrated cement continues to hydrate during prolonged immersion, resulting in superior long-term chloride binding capacity. Moreover, under S1, the chloride binding capacity decreases with increasing  $S_w$ , whereas under S2, the opposite trend is observed. The decay rate of the chloride diffusion coefficient increases with  $S_w$  under S1 but decreases under S2. This may be attributed to the fact that, compared with S2, higher  $S_w$  under S1 leads to a larger early-age chloride diffusion coefficient, which promotes the formation of more corrosion products and significantly refines the pore structure, thereby accelerating the time-dependent reduction in chloride diffusivity.

**Conclusions** Under S1, increasing  $S_w$  reduces the water absorption capacity of RA, and highly saturated RA may release water into the fresh mixture. This results in an increased  $W_e/C$  ratio in the new ITZ and mortar, leading to higher porosity and a greater proportion of macropores, and consequently higher chloride diffusion coefficients. In addition, the extra moisture promotes the hydration reaction, reducing the content of unhydrated cement particles in the new mortar and the new ITZ. In contrast, under S2, higher  $S_w$  corresponds to a lower effective  $W_e/C$  ratio during early hydration, which significantly suppresses hydration, pore development and chloride diffusion. SEM/EDS and XRD analyses confirm that chloride binding in RAC involves both physical adsorption and chemical binding. During the exposure period of 60–120 d, RAC under S1 exhibits a stronger chloride-binding capacity due to a higher initial degree of hydration. Under S2, however, the continued hydration of residual unhydrated cement during long-term immersion provides superior chloride binding capacity after 180 d. Furthermore, under S1, increasing  $S_w$  is detrimental to chloride binding capacity, whereas under S2, it is beneficial. The decay rate of the chloride diffusion coefficient increases with  $S_w$  under S1 but decreases under S2. This behavior is attributed to the larger initial diffusion coefficient under S1, which promotes the formation of more corrosion products and leads to progressive refinement of the pore structure over time.

**Keywords** recycled aggregate concrete; water saturation degree; chloride ion transport; pore structure; water control schemes