

Research Article

Influence of Pore Structure on Chloride Penetration in Cement Pastes Subject to Wetting-Drying Cycles

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Copious studies have discovered a phenomenon that a chloride concentration peak appears on the surface of concrete under cyclic drying-wetting environments. In such cases, the chloride diffusion coefficient (D) obtained through directly fitting the standard error function of Fick's second law is no longer accurate. The more reliable D obtained by the method proposed by Andrade is employed in this research to investigate the influence of pore structure on chloride penetration rate of pastes. The results show that both the effective coefficient (D_{eff}) and the apparent coefficient (D_{app}) increase with total porosity, the most probable pore size, and water absorption porosity, suggesting that the increase of the three pore structure parameters accelerates chloride penetration rate under cyclic wetting-drying condition. The increase of the three parameters makes more room available and eases the difficulty for salt solution to enter the matrix and thus leads to the augmentation of chloride transporting in matrix.

1. Introduction

Steel corrosion induced by chloride attack is a major causation for the deterioration of concrete structures. Therefore, the exploration of chloride penetration rate is of great significance for the safety and durability of concrete structures. The chloride penetration rate of concrete can be represented by the chloride diffusion coefficient, which is usually obtained through fitting the chloride profile. However, the chloride profile is very complicated under cyclic wet-dry environments. Instead of chloride decreasing monotonously with distance from the exposed surface increasing, a chloride concentration peak (as shown in Figure 1 [1]) was first discovered in 1993 [2, 3] and was reported in other studies [4-8] successively. According to the recent researches [1, 9, 10], the chloride concentration peak is induced by the coupling effect of moisture hysteresis caused by alternate wet-dry and bound chloride releasing due to carbonation.

Obviously, the diffusion coefficient (*D*) obtained through directly fitting standard error function solution of Fick's

second law (equation (1)) is no longer accurate after chloride concentration peak appears since the phase of chloride content increasing with depth ($0 \sim \Delta x$, shown in Figure 1) does not conform to the diffusion law. An accurate *D* is vital for evaluating the chloride penetration rate under cyclic wetting and drying precisely:

$$C_{(x,t)} = C_0 + (C_s - C_0) \left(1 - \operatorname{erf}\left[\frac{x}{2\sqrt{Dt}}\right] \right),$$
 (1)

where *D* is the chloride diffusion coefficient, C_0 is the initial chloride content, C_s is the surface chloride content, *t* is the exposure time, and *x* is the depth from exposed surface.

There are several methods to obtain *D* after chloride peak occurs according to the summary of Othmen et al. [11], among which one of the relatively reliable methods was proposed by Andrade et al. [12]. The operating procedure is as follows: rescale the horizontal axis by setting the depth Δx as zero point, and fit the decreasing part of the chloride profile to get *D* through equation (1) (as shown in Figure 1, fitting the chloride data in the range of $\Delta x \sim x$). Actually, this



FIGURE 1: Illustration of chloride profile with the appearance of a chloride concentration peak (C_{max} is the peak value of chloride content or the maximum chloride content, and Δx is the depth at which C_{max} appears) [1].

method does not rigorously fulfill the boundary conditions for a correct solution of Fick's second law of diffusion [13, 14], but it is a practical procedure that nearly gives the same values as those of concrete in practice instead of treating concrete as a composite material with two layers with different diffusivities from the surface. Therefore, this procedure respects more the diffusion process because it considers the maximum as an apparent surface concentration, which has been clearly illustrated in the literature [12].

The pore structure is one of intrinsic features of matrix, and its influence on chloride penetration rate has been widely investigated [15–23]. The total porosity, the most probable pore size, water absorption porosity, etc., are some important parameters that reflect the compactness of pore structure [17, 21, 22]. The experiment results of Roman [13] show that the finer pores lead to lower chloride penetration rate of concrete. Furthermore, it was also found that pore aperture and connectivity played more important roles than porosity in affecting concrete transportability [17, 19]. Besides, Liu et al. [18] investigated the absorbability of concrete surface and found that it was the function of pore structure. Zhang and Li [23] got the similar conclusion; that is, pore structure parameters are linearly correlated with chloride permeability.

It should be noted that under the presence of peaks on the chloride concentration profiles of pastes and mortars, especially of real concrete structures, it is needed to know the influence of pore structure along the matrix depth of the material. This will allow development of technology to control that peak through manipulation of the pore structure with some specific products and then to obtain more reliable service life prediction models. To look for such a pore structure, it is necessary not only to reproduce the situation at laboratory and at a basic level (i.e., cement pastes) but to follow a reliable procedure to make reasonable calculations. In this way, although with the proper nature and limitations provided by the rescaling procedure, the method of obtaining D proposed by Andrade et al. [12] can be a reliable way to do it. However, few researches have investigated the influence of pore structure on the chloride penetration rate using this method when a chloride concentration peak occurs under cyclic wet-dry condition.

To investigate the influence of pore structure on the chloride penetration rate in cases that chloride concentration peaks appear, paste specimens with different water-to-cement ratio (w/c) were exposed to cyclic wetting and drying conditions. After exposure, free and total chloride content was tested, and their profiles were plotted to reveal chloride distribution features. Besides, the chloride diffusion coefficient was obtained with the method proposed by Andrade. Meanwhile, pore structure and moisture distribution of different specimens were also tested, and their influence on chloride diffusion coefficient was explored.

2. Experiments

2.1. Raw Materials and Mix Proportions. Portland cement P.II. 52.5, produced by Nanjing Jiangnan Xiaoyetian Co, Ltd., was used. Its chemical composition is shown in Table 1. The mixing water is deionized water. Besides, paste specimens of five different w/c (0.30, 0.35, 0.40, 0.45, and 0.50) were cast in this research.

2.2. Specimen Preparation. The molding size of paste specimens is $70 \text{ mm} \times 70 \text{ mm} \times 70 \text{ mm}$. To prevent moisture evaporation, the mold free surface was sealed with thin film and taped immediately after casting. Specimens were demolded after 24 h and cured in saturated calcium hydroxide solution at $20 \pm 1^{\circ}$ C for 60 d. After curing, the mold free surface was cut away 20 mm with a high-precision cutting machine, and the cut surface was used as the exposed surface. The processing of specimens and the adopted size guaranteed the homogeneity of matrixes. Moreover, the five other surfaces except the exposed surface were sealed with epoxy resin before being subjected to the cyclic wet-dry condition.

It should be noted that the external surfaces of specimens are connected to mold in the casting process, and the oil coated in the mold for easier demolding may be left on them, which can affect chloride transport and is not an ideal exposure surface. Therefore, the cut mold free surface with homogeneous surface was chosen. Moreover, these specimens are hardened cement pastes, and the distribution of pores with depth can be deemed as homogeneous. Thus, it is probably the best choice to use the cut surface as the exposed surface to investigate chloride transport.

2.3. Cyclic Wetting and Drying Condition. The details of the cyclic wetting and drying condition are presented in Table 2. Note that all specimens were fully saturated with water in a vacuum tank before exposure to guarantee the same initial conditions.

TABLE 1: Chemical composition (%) of cement P.II. 52.5.

SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂
20.0	4.46	2.99	63.8	0.510	2.44	0.110	0.660	0.262

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TABLE	2:	Cyc	пc	wetting-u	ii yiiig	condition.

Wetting condition	Wetting time/cycle	Drying condition	Drying time/cycle	Exposure time
3.5% NaCl solution; $20 \pm 1^{\circ}$ C	12 h	45°C in oven	36h	18 cycles

2.4. Chloride Content. In this research, a silver nitration titration method was employed to test free chloride and total chloride based on the operations of *Testing Code of Concrete for Port and Waterway Engineering* (JTJ 270-98) [24].

Chloride content in two specimens of each w/c was detected, and the mean values at different depths were adopted to plot chloride profiles. Noted that the "free" and "total" chloride measured by the above method is actually water-soluble and acid-soluble chloride separately, which is deemed as free and total chloride in this research. Besides, a high-precision numerical controlled milling machine was used to grind powder layer by layer automatically [25], and its grinding thickness is 0.5 mm with error controlled within 0.04 mm [8], which highly improves the accuracy of chloride distribution along with depth.

2.5. Pore Structure

2.5.1. Mercury Intrusion Porosimetry (MIP). Samples with grain size of $1.0 \sim 3.0$ mm were obtained from specimens, immersed in absolute ethyl alcohol for 7 d to cutoff hydration and then dried in a 45°C vacuum oven for another 7 d. The equipment DV 2000 was used for the MIP test. The surface tension is 480 mN/m, the contact angle is 140°, and the pressure range is $0.50 \sim 46800.00$ psi.

2.5.2. Water Absorption Porosity (P_c). The water absorption porosity (P_c) was tested through the vacuum saturating method. The detailed operations were listed in reference [8]. By converting the mass difference between complete dry and full saturation of specimens into volume, the volume of capillary pores, that is, P_c , can be obtained with equation (2). Three specimens of each w/c were tested, and the mean value was adopted:

$$P_{\rm c} = \frac{m_{\rm s} - m_0}{\rho},\tag{2}$$

where P_c is the water absorption porosity, cm³; m_s is the mass of fully saturated specimens, g; m_0 is the mass of completely dried specimens, g; and ρ is the water density, g/ cm³.

2.6. Moisture Distribution. After curing and cutting treatment, m_s and m_0 of specimens were first tested before they were exposed to the cyclic wetting-drying condition. In the following wet-dry cycles, all specimens were tested weight $M_{\rm wi}$ after 12 h of wetting and weight $M_{\rm di}$ after 36 h of drying in a 45°C oven and cooling down to the room temperature. In such circles, the weight of specimens was examined after each drying and wetting. Two specimens of each w/c were tested, and the mean value was adopted. The unit mass $(M_{\rm abs})$ of absorbed solution during each wetting and its mean value $(M_{\rm mean})$ in the whole exposure process can be calculated through equations (3) and (4) separately. Meanwhile, the saturation degree (S) of specimens after each drying and its mean value $(S_{\rm mean})$ in the whole exposure process can be obtained with equations (5) and (6) separately:

$$M_{\rm abs} = \frac{M_{\rm wi} - M_{\rm di}}{m_0},\tag{3}$$

$$M_{\rm mean} = \frac{\sum_{1}^{n} M_{\rm abs}}{n \cdot m_0},\tag{4}$$

$$S = \frac{M_{\rm di} - m_0}{m_{\rm s} - m_0} \times 100\%,\tag{5}$$

$$S_{\text{mean}} = \frac{\sum_{1}^{n} S}{n},\tag{6}$$

where M_{wi} is the mass of specimens after the *i*th wetting, g; M_{di} is the mass of specimens after the *i*th drying, g; M_{abs} is the mass of the adsorbed salt solution per unit paste during each wetting, g/g paste; M_{mean} is the mean value of M_{abs} in the whole exposure process, g/g paste; S is the saturation degree of specimens after each drying, %; S_{mean} is the mean value of S in the whole exposure process, %; and n is the times of wetting and drying cycles.

3. Results and Discussion

3.1. Chloride Distribution under Cyclic Wetting-Drying Condition

3.1.1. Chloride Profiles. Figure 2 presents free chloride profiles of paste specimens with different w/c. It can be seen that a chloride concentration peak appears in the chloride profiles of all w/c, and the chloride content after the peak decreases to near zero gradually with the depth increasing. With w/c elevating, free chloride content increases. Moreover, chloride concentration peak becomes more prominent with w/c increasing, and the peaks move to the right with the increase of the w/c ratio. The above findings were also



FIGURE 2: Free chloride profiles of paste specimens with different w/c.

observed in reference [5], as shown in Figure 3. It is worthy to be noted that the data of this study were obtained with paste specimens under the laboratory condition, while the data of reference [5] were obtained from concrete structures in natural marine environments. The similar rule discovered from them suggests that the findings of this study can be extrapolated to natural marine environment and have significant reference value for the chloride distribution in the real situation.

Figure 4 shows total chloride profiles of paste specimens with different w/c. It can be observed that the change trend of total chloride is basically consistent with that of free chloride, except that the chloride content of the former is higher. Besides, it is also discovered that the chloride content difference between w/c = 0.30 and w/c = 0.40 is significant, no matter for free chloride or total chloride, which could probably be resulted from the pore structure of w/c = 0.30.

Moreover, it can be seen from Figures 2 and 4 that the error bar of chloride content at peak position is large compared with that at deeper position. This may be because the peak position is within the influence range of the capillary suction. The pore structure of different samples cannot be totally the same, even though those specimens are with the same mix and were prepared under the identical process. Considering that chloride ions carried by capillary suction are much more than that caused by diffusion, the even tiny difference in pore structure can lead to large difference in chloride content in capillary suction influenced area.

3.1.2. Chloride Diffusion Coefficient. The chloride diffusion coefficient obtained with the method proposed by Andrade et al. [12] mentioned above, corresponding surface chloride concentration (C_s), and the correlation coefficient (R^2) are presented in Table 3. It can be seen that R^2 of chloride profiles almost all exceed 0.99, suggesting that the fitted curve and the chloride content data are highly correlated. It



FIGURE 3: Concentration profiles of concrete with different w/c ratios exposed to natural marine environments [5].



FIGURE 4: Total chloride profiles of paste specimens with different w/c.

TABLE 3: Surface chloride content (C_s), chloride diffusion coefficient (D), and correlation coefficient (R^2).

	w/c	0.30	0.35	0.40	0.45	0.50
Free	$C_{s,f}$ (%)	1.142	1.738	1.772	1.791	1.936
	$D_{\rm eff} ({\rm mm^2/a})$	150.9	343.9	423.5	432.0	685.8
chioride	R^2	0.9897	0.9979	0.9975	0.9959	0.9961
Total	$C_{s,t}$ (%)	1.082	1.863	1.944	1.836	1.990
	$D_{\rm app} ({\rm mm}^2/{\rm a})$	222.6	554.1	857.3	921.4	1365
chioride	R^2	0.9911	0.9935	0.9935	0.9949	0.99087

 $D_{\rm eff}$ means the effective diffusion coefficient; $D_{\rm app}$ means the apparent diffusion coefficient.

can also be observed that the surface chloride content, whatever free or total chloride, increases with w/c and so does the chloride diffusion coefficient except C_s of total chloride of w/c = 0.45.

The relation between effective diffusion coefficient (D_{eff}), apparent diffusion coefficient (D_{app}) , and w/c is presented in Figure 5. It can be found that both D_{eff} and D_{app} are linearly related to w/c. And D_{app} is significantly greater than D_{eff} with the same w/c. During wetting and drying cycles, the chloride ions in external solution will also react with the hydration products like calcium silicate hydrate (C-S-H) or AFm in the process of entering matrix and form some bound chlorides [26–31]. The forming of bound chloride is a constant course, and its total content will increase with chloride penetration depth and exposure time, which inevitably will reduce free chlorides in pore solution that moves into matrix, retard chloride penetration rate, and render $D_{\rm eff}$ much less than $D_{\rm app}$. Besides, the difference between $D_{\rm app}$ and $D_{\rm eff}$ at the same w/c increases with w/c, and it is related to the content of bound chloride formed during specimens of different w/ccontacting with salt solution, which is discussed in Section 3.2.

3.2. Pore Structure and Humidity Distribution

3.2.1. Pore Structure. Figure 6 shows the MIP results of different w/c specimens. It can be observed that the peak of differential pore volume curve generally increases and moves to the direction of aperture increasing, suggesting that the total porosity and the most probable pore size increase with w/c. The total porosity and the most probable pore size of different w/c are listed in Table 4, and it can be found that the evolution trend of these two is consistent with that of the differential pore volume curve. Besides, it can also be seen that the peak height of the curve of w/c = 0.30, the corresponding aperture, and the area enclosed by the curve are all significantly smaller than those of the other three w/c, which implies that the pore structure of w/c = 0.30 is very dense and probably leads to the much lower chloride content of it than that of the other w/c in Figures 2 and 4.

The water absorption porosity results are also presented in Table 4. It can be observed that water absorption porosity also increases with w/c.

3.2.2. Moisture Distribution. Figure 7 shows the evolution law of S of different w/c specimens during the whole exposure. It can be observed that *S* is generally more than 55% at the beginning of exposure; S decreases gradually with time increasing; S decreases less than 40% at the end of exposure; and S of some higher w/c, such as 0.50 and 0.45, can reach less than 20%. Moreover, S decreases with w/c increasing within the same exposure time. And S of w/c = 0.30 being significantly higher than that of other w/c is probably caused by its denser pore structure. In addition, it should be noted that there is a decrease in saturation degree around 200 h. The exact reason is unclear, and it is probably due to the misoperation during experiment. However, the decrease is within the fluctuation range and does not change the general evolution law of saturation degree in the whole exposure duration.

After 18 times of wetting and drying, only one set of pore structure parameters can be obtained. However, *S* and M_{abs}



FIGURE 5: The relation between w/c and chloride diffusion coefficient.



FIGURE 6: MIP testing results of specimens with different w/c.

TABLE 4: Parameters of pore structure

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Parameters	0.30	0.35	0.40	0.45	0.50		
Total porosity (%)	14.2	15.6	15.8	22.0	24.4		
The most probable pore size (nm)	30.6	31.1	34.3	42.4	49.0		
Water absorption porosity (%)	18.3	23.5	29.9	36.8	37.7		

can be obtained after each drying and wetting cycle. Since it is impossible to characterize the pore structure of samples after each wetting and drying cycle, therefore, to investigate the relation between S and $M_{\rm abs}$ and pore structure, $S_{\rm mean}$ and $M_{\rm mean}$ are adopted, which represent the saturation degree and the weight of absorbed salt solution of specimens in the whole exposure duration, respectively. This method of data processing is believed to be feasible because the change



FIGURE 7: The change law of saturation degree (*S*) with exposure time.

law of S_{mean} with w/c is basically consistent with that of S with w/c, which can be seen in Figure 7 and Table 5. The calculated S_{mean} and M_{mean} are shown in Table 5. It can be seen that the higher the w/c is, the lower the S_{mean} is and the greater the M_{mean} is. In addition, the absorbed salt solution mass (M_{mean}) of w/c = 0.30 is significantly lower than that of other w/c, which accords with the lower chloride content of it in Figures 2 and 4.

Figure 8(a) shows the relation between total porosity and S_{mean} and M_{mean} , Figure 8(b) the relation between the most probable size and S_{mean} and M_{mean} , and Figure 8(c) the relation between water absorption porosity and S_{mean} and M_{mean} . It can be seen that, with the raise in total porosity, the most probable pore size, and water absorption porosity, S_{mean} increases while M_{mean} decreases. It is caused by the fact that moisture evaporation is easier after total porosity, the most probable pore size, and water absorption porosity increase, leading to the decrease of S_{mean} . Moreover, since the saturation of matrix is closely related to its absorption capacity, that is, the lower that former is, the greater the latter is [8, 32], more salt solution will be absorbed into the matrix in the following wetting and M_{mean} will be promoted consequently.

3.3. Relation between D and Pore Structure

3.3.1. Influence of Total Porosity on D. Figure 9 presents the relation between total porosity and D_{eff} and D_{app} . It can be observed that both D_{eff} and D_{app} generally increase with total porosity, suggesting that the increase of total porosity accelerates the chloride penetration rate under cyclic wetting and drying. When total porosity increases, it means that there are more pores in matrix, which provides more space for salt solution to enter into during wetting and for salt crystal to deposit during drying and benefits more chlorides transporting easier in matrix consequently. As reflected in Figure 8(a), the absorbed salt solution in specimens increases

TABLE 5: The values of S_{mean} and M_{mean} at different w/c.

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w/c	0.30	0.35	0.40	0.45	0.50
S _{mean} (%)	57.5	44.9	42.3	37.8	34.6
$M_{\rm mean}~(10^{-3}{\rm g/g}~{\rm paste})$	4.05	7.87	10.6	13.2	13.8

significantly after total porosity goes up. In consequence, the chloride diffusion coefficient of the corresponding specimen increases. However, it should be noted that total porosity and D_{eff} and D_{app} do not grow linearly with each other. When the total porosity is around 16%, *D* increases drastically even at points where total porosity is very close; while *D* just increases slightly when the total porosity increases from 16% to 22%.

It can also be observed from Figure 9 that $D_{\rm app}$ is significantly higher than $D_{\rm eff}$ when total porosity is the same, which is clearly caused by the formation of bound chloride in the process and has been explained in Section 3.1.2. Besides, it is obvious that the difference between $D_{\rm app}$ and $D_{\rm eff}$ with the same total porosity increases with total porosity. When total porosity increases, it provides more opportunities for chloride in pore solution to contact with AFm and C-S-H, and correspondingly more chemically and physically bound chloride will be formed [30, 33–35]. As a result, free chloride in pore solution will be reduced [36] and their penetration rate will be retarded, leading to the result that the gap between $D_{\rm eff}$ and $D_{\rm app}$ increases with total porosity.

3.3.2. Influence of the Most Probable Pore Size on D. Figure 10 presents the relation between the most probable pore size and D_{eff} and D_{app} . It can be found that both D_{eff} and $D_{\rm app}$ increase with the most probable pore size. Compared with porosity, the most probable pore size is more important for chloride transport [17, 37]. The greater the most probable pore size is, the higher the connectivity of matrix is and the lower the tortuosity is [18]. Thereby, the increase of the most probable pore size makes it easier for salt solution to enter and enter deeper into matrix (Figure 8(b) reveals that the absorbed solution increases significantly with the most probable pore size). Meanwhile, moisture in deeper places of matrix also evaporates easily (Figure 8(b) shows that the increase of the most probable pore size significantly decreases S), which prepares for the next wetting and quick influx of solution and leads to the acceleration of the chloride penetration rate.

It can also be observed in Figure 10 that the increase rate of D_{eff} and D_{app} is the rapidest when the most probable pore size is 30.0~35.0 nm; when the most probable pore size increases from 35.0 nm to 50 nm, the growth rate of D_{eff} and D_{app} is fast in the beginning and slows down afterwards, which can be ascribed to the pore distribution of matrix. According to equation (7), the greater the pore diameter is, the weaker the capillary suction is. Hence, the increase of the most probable pore size will lead to the weakening of capillary suction. Given that, the actual promotion of solution influx by the increase of the most probable pore size alleviates in the later stage and so does the penetration rate of D_{eff} and D_{app} :



FIGURE 8: Relation between pore structure parameters and S_{mean} , M_{mean} : (a) total porosity; (b) the most probable pore size; (c) water absorption porosity.





FIGURE 9: Relation between chloride diffusion coefficient and total porosity.

FIGURE 10: Relation between diffusion coefficient and the most probable pore size.

$$\Delta p = \frac{2\gamma\cos\theta}{r},\tag{7}$$

where *r* is the radius of the capillary pore, θ is the contact angel, γ is the gas-solution interfacial tension, and Δp is the pressure difference between the gas and liquid phases in the curved liquid surface of capillary pores.

Furthermore, D_{app} is significantly higher than D_{eff} when the most probable pore size is the same, which is also caused by forming of bound chloride. From Figure 10, it can also be found that the difference between D_{eff} and D_{app} of the same most probable pore size increases with the growth of the most probable pore size. The increase of the most probable pore size means the extension of pore surface area, presenting a good linear correlation as shown in Figure 11. Therefore, the increase of the most probable pore size signifies that the chlorides in pore solution will have more chances to contact with the wall and react with C-S-H and AFm. Consequently, it will form more bound chloride, decrease free chloride content in pore solution, retard free chloride transport, and enlarge the gap between D_{eff} and D_{app} .

3.3.3. Influence of Water Absorption Porosity on D. Figure 12 shows the relation between water absorption porosity and $D_{\rm eff}$ and $D_{\rm app}$. It can be found that the former increases with the latter two, presenting a good linear correlation. Water absorption porosity represents the volume of capillary pores, and studies discover that capillary pores are of great significance for the transmissibility of matrix surface [37, 38]. The increase of water absorption porosity provides more channels for the influx of external salt solution and the evaporation of moisture. In consequence, more solution will enter matrix (Figure 8(c) also shows that the influx of salt solution into matrix increases with water absorption porosity.), and correspondingly more salt crystals will deposit. Therefore, chloride penetration will be accelerated. Furthermore, Neithalath [39-41] discovered that water absorption porosity is closely related to connectivity, as portrayed by equation (8). It is obvious that they two are linearly correlated. As has been explained in Section 3.3.2, the increase of connectivity also can speed up the chloride penetration rate. Moreover, D_{app} is also greater than D_{eff} when water absorption porosity is the same, and the reason that the gap between D_{eff} and D_{app} increases with water adsorption porosity is the same as that of total porosity:

$$\beta = \frac{\sigma_{\rm eff}}{\sigma_{\rm pore}} P_c, \tag{8}$$

where β is the connectivity factor, σ_{pore} is the conductivity of pore solution, and σ_{eff} is the effective conductivity.

The above analysis about how the difference between $D_{\rm app}$ and $D_{\rm eff}$ of the same pore structure parameter increases with the pore structure parameter increasing can also shed light on the explanation of why the difference between $D_{\rm app}$ and $D_{\rm eff}$ of the same w/c increases with w/c in Figure 5. The higher the w/c is, the greater the corresponding pore structure parameters are, including total porosity, the most



FIGURE 11: Relation between the most probable pore size and total surface area of pores.



FIGURE 12: Relation between diffusion coefficient and water absorption porosity.

probable pore size, and water absorption porosity. As a result, specimens of higher w/c will adsorb and form more bound chlorides during wetting and drying cycles, which significantly retards chloride transport and enlarges the gap between $D_{\rm app}$ and $D_{\rm eff}$ of specimens with the same w/c.

4. Conclusions

- (1) Chloride concentration peaks appears on the surface of all specimens subjected to the cyclic wettingdrying condition, and these peaks become higher and move deeper with the increase of w/c. These findings are consistent with the reported results obtained from natural marine environments and confirm the mechanism by which the peak appears in concrete under field condition.
- (2) Both D_{eff} and D_{app} increase with total porosity, the most probable pore size, and water absorption

porosity, suggesting that the increase of the three pore structure parameters accelerate chloride penetration under cyclic wet-dry condition. The increase of the three parameters makes more room available and eases the difficulty for salt solution to enter the matrix and thus leads to the augmentation of chloride transporting.

(3) The difference between D_{app} and D_{eff} is probably caused by the forming of bound chloride. Furthermore, the increase of total porosity, the most probable pore size, and water absorption porosity provides more opportunities for chlorides in pore solution to contact with C-S-H and AFm, and correspondingly more bound chlorides will be formed, leading to the result that the gap between D_{eff} and D_{app} increases with the three parameters.

Data Availability

All the data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflict of interest.

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