A study on effects of water-cement ratio and crack width on chloride ion transmission rate in concrete

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Abstract. To study the effects of water-cement ratio changes and cracks on chloride ion transmission rate in cracked concrete, RCM method was adopted to accelerate the diffusion of chloride ion in cracked concrete, and the changes in chloride ion concentration and around the cracks are inferred by finite-element method. The test results show that as far as prefabricated cracks on concrete components are concerned, the width thresholds of two cracks on the concrete specimens with a water-cement ratio of 0.5 and 0.6 are 0.05 mm and 0.1 mm respectively, the width threshold of two cracks on the concrete specimens with a water-cement ratio of 0.4 is 0.05 mm and 0.2 mm respectively; and the results of numerical simulation show that the smaller the water-cement ratio is, the more significant effects of cracks on chloride ion transmission rate are. As a result, more attention shall be paid to the crack prevention, repairing and strengthening for high-strength concrete.

Keywords: water-cement ratio; cracks; concrete; chloride ion; numerical simulation

1. Introduction

Reinforced concrete cracking is one of the common damages of concrete structure, and in effect, most structural members in the structure are working with cracks. However, many current analyses on chloride ion penetration are made on the basis of intact concrete, i.e., modeling concrete as an intact porous media for transmission characteristics analysis (Song et al. 2016, Tsao et al. 2015). Nonetheless, due to the existence of cracks in actual concrete material, the simplification in this way can result in big errors (Ye 2013). Cracks as short and easy channels for chloride ions and other external corrosive substances enabled them to approach the reinforcing bar surface more rapidly to expedite depassivation and rustiness of reinforcing bars, leading to structure failures (Pijaudier-Cabot et al. 2013, Sangoju et al. 2011, Picandet et al. 2009). Therefore, studying the influence of cracks on chloride ion transmission rate has very important significance.

According to the existing researches on durability of cracked concrete with different water-cement ratios, there are basically two views: 1) the crack width is the only factor affecting the chloride ion transmission rate in cracked concrete. The presence of cracks has an important influence on the chloride ion transmission in concrete, with upper and lower thresholds of crack width. When the crack width was below the lower threshold w_1 , thanks to the "self-repairing effects" inherent in concrete (Baradaran Shoraka et al. 2013) and other factors, the crack existence had little or no impact on the diffusion of chloride ions. When the crack width was between the upper and lower thresholds, the diffusion coefficient of chloride ions in cracked concrete increased rapidly with the increase of crack width. When the crack width is bigger than the upper threshold w_2 , the roughness and tortuosity of cracks had no influence on the chloride ion transmission, equivalent to the transmission of chloride ions in free solutions. According to the steady-state migration experiment on cracked concrete specimens with a water-cement ratio of 0.49 (ordinary concrete), 0.38 (high performance concrete) and 0.32 (high performance concrete with silica fume) respectively made by Djerbi et al. (2008), the change in water-cement ratio had no influence on the chloride ion transmission in cracks which was only related to the crack width, the obtained crack width thresholds were w₁=0.03 mm, w₂=0.08 mm. Park et al. (2012) carried out tests on the concrete specimens with a water-cement ratio of 0.44 and obtained $w_2=0.2$ mm. Jang *et al.* (2011) carried out tests on the concrete specimens with a water-cement ratio of 0.44, 0.64, 0.53 and 0.40 respectively and obtained $w_1=0.08$ mm, $w_2=0.2$ mm. Kwon et al. (2009), Zhang et al. (2011), Sahmaran (2007) provided the diffusion coefficient of chloride ions in cracked concrete and the relation between the diffusion coefficient of chloride ions in cracks and the crack width changes, and found that when the crack width was between the upper and lower thresholds, the bigger the crack width was, the more rapidly the chloride ions transferred in cracks, and the higher diffusion coefficient of chloride ions in cracked concrete was.

2) Not only the crack width, but also the water-cement ratio affects the transmission rate of chloride ions in

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Table 1 Physical and chemical properties of cement

Cement	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	CaO (%)	MgO (%)	SO ₃ (%)	Specific surface area/ (m ² /kg)	3d compression strength/MPa	28d compression strength/MPa
P.O 32.5	21.36	3.21	4.92	62.33	3.41	1.92	326	17	35.2

cracked concrete. According to the tests on reinforced concrete beams with a water-cement ratio of 0.25, 0.45 and 0.65 respectively made by Win et al. (2004), as the watercement ratio went up, the erosion rate of chloride ions increased. When the crack in concrete was 0.2 mm wide, the increase of water-cement ratio resulted in the increase of penetration depth of chloride ions. Zhuang (2010) prepared concrete specimens with a water-cement ratio of 0.69, 0.53 and 0.35 respectively, obtaining different crack widths via split tensile test, and based on the derived chloride ion concentration distribution in and around cracks and the comparison of diffusion coefficient of chloride ions in cracks, it is concluded that for the cracked concrete specimens in the underwater area in ocean, when the watercement ratio was 0.69, the critical crack width w_1 affecting the chloride ion transmission in concrete was 0.03 mm. When the water-cement ratio was 0.53 and 0.35, the critical crack width w_1 was 0.05 mm. For the cracked concrete specimens in the ocean tidal zone, when the water-cement ratio was 0.69 and 0.53, the critical crack width w_1 was 0.05 mm. When the water-cement ratio was 0.35, the critical crack width w_1 was 0.03. Jiang *et al.* (2011), Xie *et al.* (2004) and Zhao et al. (2010) studied the influence of water-cement ration changes on erosion performance of chloride ions in transversely cracked concrete and the results showed that the changes in water-cement ratio affected the penetration speed of chloride ions into concrete which outweighed the influence of crack width, and as increasing the water-cement ratio, the chloride ion concentration on surface and the accumulative rate went up gradually.

In light of this, in this paper, the experiments on cracked concrete specimens with different water-cement ratios were carried out. Based on the research results of chloride ion transmission rate in cracks from previous references, the diffusion coefficient value D_{cr} in cracks was determined. Then the numerical simulation of chloride ion transfer behavior was made to analyze and discuss the effects of water-cement ratio, crack width and other factors.

2. Experimental study

2.1 Raw materials and mix design of concrete

Cement: ordinary Portland cement P.C 32.5, Table 1 shows the key ingredients and physical and mechanical properties. Coarse aggregate: 5-12.5 mm continuous graded macadam, density: 2650 kg/m³, silt content <0.3%. Fine aggregate: river sand, fineness modulus: 2.52, silt content <1.0%. Superplasticizer: polycarboxylate superplasticizer, water reducing rate: 20%. Table 2 shows the mix proportion and physical and mechanical properties of concrete.

Table 2 Mix proportion and physical properties of concrete

No.	Cement /kg/m ³	Water /kg/m ³	Sand /kg/m ³	Stone /kg/m ³	Superplasticizer /Kg/m ³	28d compression strength/MPa	Water-cement ratio
А	306	163	752	1160	0	24.5	0.6
В	333	163	654	1270	2	32.5	0.5
С	400	163	528	1310	2	41.5	0.4
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Fig. 1 The diagram of RCM test

2.2 Test method

Cylindrical concrete specimen: diameter-100 mm, height-50 mm. Cracks in concrete were prepared by prefabricated crack method, i.e., thin copper sheets (Marsavina*et al.* 2009, Poursaee and Hansson 2008) with a thickness of 0.05 mm, 0.08 mm, 0.1 mm and 0.2 mm respectively were embedded in fresh concrete, crack depth-20 mm. The copper sheets were removed about 4-5 h after concrete was poured to obtain the specimens with corresponding crack width. 3 groups of specimens were prepared for each experiment conditions. The form was removed 24 h after final setting of specimens, and the specimens were placed under standard conditions (temperature-20 \pm 2°C, relative humidity-above 95%) for curing for 28 d.

The specimens were placed in the RCM test device (GB/T 50082 2009) for accelerated test, as shown in Fig. 1, with the crack side exposing downward. After the test device was stable, a 35 V voltage was applied to the specimens with a water-cement ratio of 0.6, a 50 V voltage to the specimens with a water-cement ratio of 0.5 and a 60 V voltage to the specimens with a water-cement ratio of 0.4.

The test time for uncracked concrete specimens was 24 h. With regard to specimens with cracks, to prevent chloride ions penetrating the specimens through cracks, when the test ran for 4 h, 8 h and 12 h respectively, the specimens were taken out with the power turned off. Then the splitting test was performed along the vertical cracks on the specimens, the 0.1 mol/LAgNO₃ solution was sprayed to every splitting plane and after 15 min measured the penetration depth. The chloride ion concentration was measured by rapid detection method of chloride ion concentration. The chloride concentration was measured according to the GB/T 50476-2008 (similar as BS1881-124, ASTM C 1218M-99).

3. Experiment results and discussion

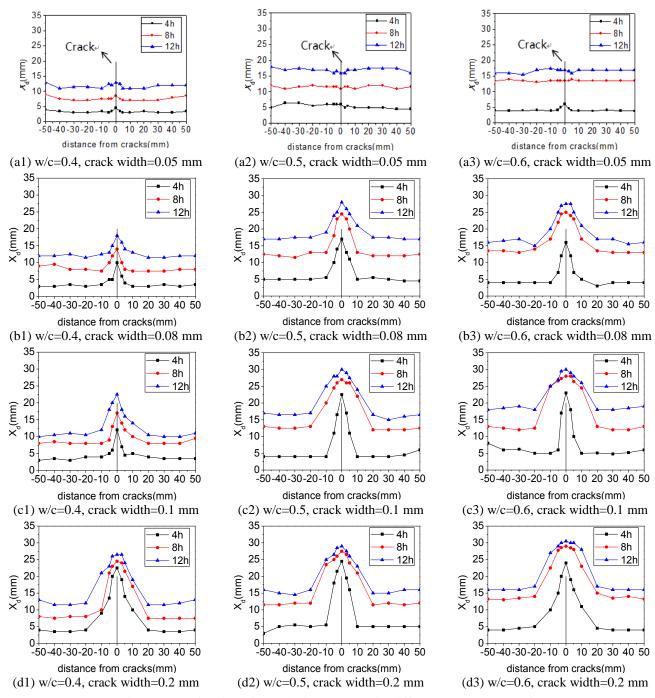


Fig. 2 Penetration depth in cracked concrete under different water cement ratio

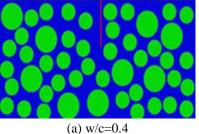
3.1 Influence of water-cement ratio changes on uncracked concrete

RCM test was carried out on three groups of uncracked specimens, Group A, B & C, power-on time: 24 h. After the test, the average penetration depth of Group A, B and C specimens measured by $AgNO_3$ color developing method was 30.17 mm, 33.5 mm, 21.5 mm respectively. According to Eq. (1) (McGrath and Hooton 1996),

$$D_{RCM} = \frac{0.0239(273+T)L}{(E-2)} \left(x_d - 0.0238 \sqrt{\frac{(273+T)Lx_d}{E-2}} \right)$$
(1)

Wherein, x_d -color rendering depth of concrete specimen with 0.1 mol/L silver nitrate solution spray; *E*-applied voltage; *T*-average temperature of solution; *L*-thickness of specimen; *t*-test time.

The diffusion coefficient of chloride ions was calculated: $D_A=1.34\times10^{-11}$, $D_B=1.02\times10^{-11}$, $D_C=5.46\times10^{-12}$ respectively. According to the above results, for the uncracked concrete specimens, the diffusion coefficient of chloride ions decreased gradually as the water-cement ratio decreased. For the concrete specimens with a curing period of 28d, when the water-cement ratio decreased from 0.6 to 0.5, 0.4, the diffusion coefficient of chloride ions was reduced by 23.9% and 59.3% respectively. It means that the



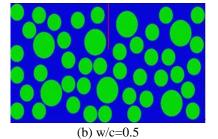
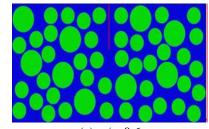


Fig. 3 Aggregate distribution model



(c) w/c=0.6

water-cement ratio changes have a strong influence on the chloride ion diffusion in uncracked concrete specimens, of which the primary cause is that with the same curing period, as the water-cement ratio of concrete changes, the porosity of concrete and type, shape, distribution of pores even the nanopore of C-S-H gel affect the chloride transport (Li et al. 2011, Zhou et al. 2016).

3.2 Influence of water-cement ratio changes on cracked concrete

To investigate the influence of water-cement ratio changes on chloride ion transmission in concrete with different crack widths, the penetration depth of chloride ions in cracked concrete with acceleration time of 4 h, 8 h and 12 h respectively were measured by AgNO3 color method. In Fig. 2 showing the results, the X-axis represents the distance from cracks and the Y-axis represents the penetration depth X_d .

From Fig. 2, regardless of what the water-cement ratio was, the specimen permeability raised with the increase of crack width, and for Group A, B and C specimens with 0.05 mm crack width, the color rendering depth of chloride ions in cracks was generally the same as that in the uncracked parts. Thus the lower threshold of crack width w_1 of these three groups of specimens was 0.05 mm. From Figs. 2(a2), (b2), (c2), (d2), (a3), (b3), (c3) and (d3), when the watercement ratio is 0.5 or 0.6, for the cracked concrete specimens, crack width=0.1 mm, the chloride ions penetrate the cracks directly into the concrete, thus the upper threshold of crack width w_2 is 0.1 mm. When the watercement ratio is 0.4, as shown in Fig. 2(c1), the chloride ions do not penetrate the cracks to the crack top at early penetration stage, indicating that the upper threshold of crack width here is no longer 0.1 mm. As shown in Fig. 2(d1), the upper threshold of crack width here is 0.2 mm. To sum up, for prefabricated cracks, the critical crack threshold of cracked concrete specimens is not a fixed value, varying with the water-cement ratio.

4. Finite-element analysis

4.1 Finite-element model & parameters

To further look into the diffusion behavior of chloride ions in cracked concrete with different water-cement ratio, the meso-scale random aggregate model of chloride ion

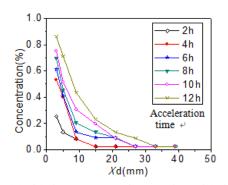


Fig. 4 Chloride ion concentration varying with depth in area unaffected by cracks (w/c=0.6)

diffusion in concrete built by Du et al. (2015) was used to make finite-element simulation for the experiment. The volume fraction of coarse aggregate in the model was determined based on the experiment in this paper, i.e., the volume fraction of coarse aggregate for Group A, B and C specimens was 43.8%, 47.7% and 49.4% respectively. For simplicity, the aggregate was set to round and the size of coarse aggregate was set to 7 mm and 11 mm according to Fuller's grading curve. The specimens were 100 mm long and 50 mm high and the crack width was 20 mm. Fig. 3 shows the two-dimensional models of aggregate distribution of Group A, B and C specimens. Concrete age, Cl⁻ binding capacity, temperature and other factors' impacts on diffusion behavior were ignored. In addition, the approximate global mesh size used was 0.05 mm.

The transmission time used for simulation was determined by fitting the curve of chloride ion concentration varying with penetration depth in the area unaffected by cracks measured in the experiment (see Fig. 4).

Since the test environment, materials, test method, test age are different, the boundary conditions always vary. In this paper, the boundary chloride ion content was obtained by fitting Fig. 4, $C_0=1\%$ (percentage of concrete mass). Because the test time was less than 12 h, the boundary conditions were considered as constant in the experiment. In addition, the chloride ions penetrated only from the upper surface and no chloride ion penetration occurred on other three sides, equivalent to one-dimensional diffusion. Therefore, according to Fick's second law, it can be obtained that the free transmission time corresponding to 12 h RCM acceleration was t_A =37.0d. Similarly, t_B =59.93d, t_{C} =48.28d.

The chloride ion transmission in cracked concrete is generally divided into two parts: chloride ion transmission

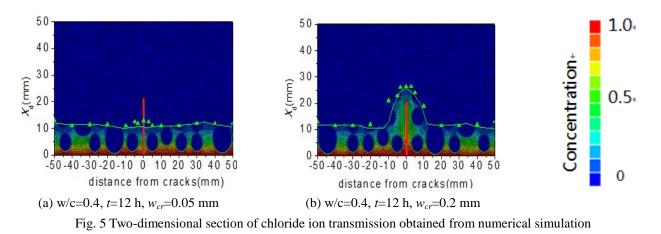


Table 3 Diffusion coefficient of chloride ions in cracks

w/c	$D_{\rm m}({\rm m}^2/{\rm s})$	<i>w</i> ₁ (mm)	<i>w</i> ₂ (mm)	$D_{0.05}(\text{m}^2/\text{s})$	D _{0.08} (m ² /s)	$D_{0.1}({\rm m}^2/{\rm s})$	$D_{0.2}({\rm m}^2/{\rm s})$
0.6	1.34×10 ⁻¹¹	0.05	0.1	1.34×10^{-11}	1.64×10 ⁻⁹	2.03×10-9	2.03×10 ⁻⁹
0.5	1.02×10 ⁻¹¹	0.05	0.1	1.02×10^{-11}	1.33×10 ⁻⁹	2.03×10-9	2.03×10 ⁻⁹
0.4	5.46×10 ⁻¹²	0.05	0.2	5.46×10^{-12}	2.0×10^{-10}	5.12×10^{-10}	2.03×10 ⁻⁹

in intact concrete and transmission in cracks. From the experiment results in Section 3.1, in intact concrete with a water-cement ratio of 0.6, 0.5 and 0.4 respectively, the diffusion coefficient of chloride ions was $D_{mA}=1.34\times10^{-1}$ $^{11}{\rm m}^2/{\rm s}$, $D_{\rm mB} = 1.02 \times 10^{-11} {\rm m}^2/{\rm s},$ $D_{\rm mC}=5.46\times10^{-12}{\rm m}^2{\rm /s},$ respectively. Thus, the diffusion coefficient of chloride ions in the interfacial transition zone (Du et al. 2015) was set to $D_{\rm iA} = 8D_{\rm mA} = 1.07 \times 10^{-10} {\rm m}^2/{\rm s},$ $D_{\rm iB} = 8D_{\rm mB} = 8.16 \times 10^{-11} {\rm m}^2/{\rm s},$ $D_{\rm iC}=8D_{\rm mC}=4.37\times10^{-11}{\rm m}^2/{\rm s}$ respectively. Due to the extremely low permeability of coarse aggregate, assuming the diffusion coefficient of chloride ions in coarse aggregate $D_a=0$ (Oh et al. 2004, Nilenius et al. 2015, Sun et al. 2011); the chloride ion transmission in cracks was often the core problem of chloride ion transmission in cracked concrete. Jin et al. (2016) regarded that for concrete specimen with only one crack, the diffusion behavior of chloride ions in crack can be divided into three stages, and the quantitative relation between D_{cr} and crack width w_{cr} was

$$D_{cr} = \begin{cases} D_{m} & w_{cr} \le w_{1} \\ \frac{D_{m} + D_{0}}{2} + \frac{D_{0} - D_{m}}{2} \sin\left[\frac{\pi}{w_{2} - w_{1}}\left(w_{cr} - \frac{w_{2} + w_{1}}{2}\right)\right] & w_{1} \le w_{cr} \le w_{2} \end{cases}$$
(2)

Wherein: Dm-diffusion coefficient of chloride ions in undamaged concrete around cracks (m²/s); D_0 -diffusion coefficient of chloride ions in free solution (m²/s).

According to the investigation made by Jin *et al.* (2016), $D_0=2.03\times10^{-9}$ m²/s, the diffusion coefficient of chloride ions in various specimens was calculated according to Eq. (2). Table 3 shows the calculation results.

4.2 Finite-element and experiment results

The finite-element model was built and the results in Section 4.1 were substituted into the model to obtain the chloride ion penetration depth diagram after 4 h, 8 h and 12 h acceleration. Then a comparison between the finiteelement results and experiment results was made. Figs. 5 and 6 show the results, in which the X-axis represents the distance from cracks and the Y-axis represents the penetration depth X_d .

Taking Fig. 5 for example, water-cement ratio=0.4, acceleration time=12 h, for the specimens with crack width of 0.05 mm and 0.2 mm respectively, the two-dimensional section of chloride ion penetration obtained from numerical simulation and the color rendering depth diagram of chloride ions obtained from the experiment are shown, in which, \blacktriangle represents the experimental value, — represents the simulated value.

As shown in Fig. 6, for Group A, B and C specimens with different crack width, acceleration time=4 h, 8 h & 12 h, the numerical simulation results and experiment results of chloride ion transmission depth agree well with each other, indicating that this numerical simulation method can be used to calculate the chloride ion transmission in cracked concrete specimens with different water-cement ratio and different crack width. Because the coarse aggregate distribution is different, when simulating the chloride ion corrosion erosion depth, artificial method was used to take a point from a distance. Then these points were connected to form a curve, so the location of the point and the density of the points have a little influence on the curve shape of the transmission depth.

According to the simulated results, the chloride ion concentration was collected. Fig. 7 shows the chloride ion concentration change curve, acceleration time=12 h, distance from the surface=9 mm, perpendicular to crack direction, in which, the X-axis represents the distance from cracks and the Y-axis represents the mass concentration of chloride ions (percentage of concrete mass)

From Fig. 7, for Group A, B and C specimens, the chloride ion concentration in cracks are obviously higher than that in the uncracked zone. As the crack width increases, the impact of crack on accelerated diffusion of chloride ions enhances. Comparing Figs. 7(a), (b) and (c), it's not difficult to find that the chloride ion transmission in and around cracks was very rapid. For crack width=0.08 mm ($<w_2$), for Group A, B and C specimens, the highest concentration in cracks increase by 34%, 33% and 39% respectively compared with the concentration in average zone. Thus, for crack width below the upper threshold, the

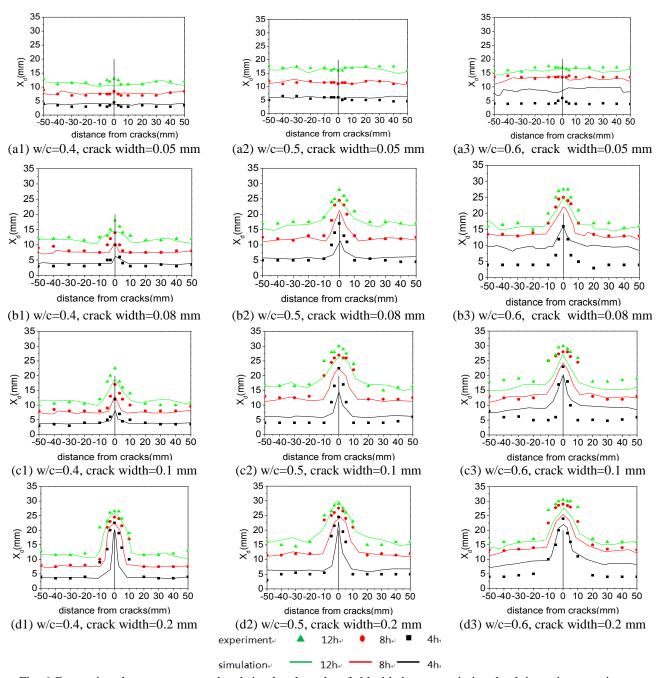


Fig. 6 Comparison between measured and simulated results of chloride ion transmission depth in various specimens

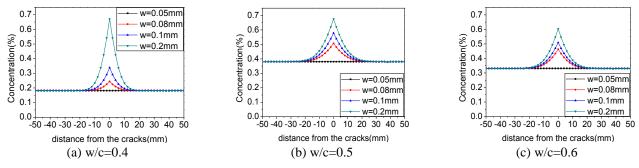


Fig. 7 Chloride ion concentration change curve

influence of water-cement ratio changes on chloride ion transmission is relatively small. For crack width=0.2 mm

 $(\geq w_2)$, for Group A, B and C specimens, the highest concentration in cracks increases by 78%, 82% and 280%

respectively, compared with the concentration in average zone. Thus, for crack width above w_2 , the less the watercement ratio, the greater the influence of crack width on chloride ion transmission rate in cracked specimen. It's mainly because the decrease of water-cement ration would reduce the porosity within concrete matrix to prevent penetration of chloride ions. However, the cracks would provide a convenient path to accelerate the chloride ion penetration into concrete, and the acceleration would be more significant for lower water-cement ratio. In the engineering structure, the crack width is always bigger than 0.2 mm. The less the water-cement ratio, the more significant the acceleration effects of cracks on chloride ion transmission. Therefore, more attention shall be paid to the crack prevention, repairing and strengthening for highstrength concrete.

5. Conclusions

• Under the experiment conditions, the critical crack threshold of cracked concrete specimens is not a fixed value, varying with the water-cement ratio. When the water-cement is 0.5 and 0.6, the lower and upper thresholds of crack width of concrete specimen are w_1 =0.05 mm, w_2 =0.1mm; When the water-cement is 0.4, the lower and upper thresholds of crack width of concrete specimen are w_1 =0.05 mm, w_2 =0.2 mm.

• The finite-element method can be used to simulate the transmission behavior of chloride ions in cracked concrete specimens with different water-cement ratio and different crack width threshold. The simulated results agree well with the experiment results.

• The smaller the water-cement ratio of concrete specimen, the more significant the effects of cracks on acceleration of chloride ion transmission. Therefore, more attention shall be paid to the crack prevention, repairing and strengthening for high-strength concrete.

In the future work, more attention should be paid to the influences of the chloride binding capacity, age of concrete, the tortuosity of the crack, and temperature variation on chloride penetration. In addition, in order to make the simulation more realistic, the voids and pores should be taken into account, so there is still much work to be done.

Acknowledgments

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