Investigation on the transport properties of chlorides in concrete II Numerical simulation

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Abstract. The chloride ions diffusion in concrete is an important problem inducing the corrosion of reinforcement under marine environment. Based on a parallel transmission model, the diffusion coefficient of chloride ions in ITZ was determined. Thereafter, the measured parameters of ITZ were integrated into a numerical model to simulate the chloride ions diffusion and the reliability of the model was verified by comparing the numerical simulation with the surface scanning results collected from the electron microprobe. The test results show that if the concrete is taken as a three-phase composites, the numerical model can reflect the real transmission process of chloride ion more accurately.

1 INTRODUCTION

Shah [1] specified the influence of aggregate on concrete permeability into four effects. Their study revealed that the dilution and tortuosity effects would reduce concrete permeability, while the ITZ and percolation effects could increase permeability. A further investigation conducted by Yang et al.[2] indicated that, among these influential effects, percolation effect had the least impact on chloride diffusion. And ITZ has been proved to be of great importance for the chloride ions diffusion in concrete[3]. However, the diffusivity of ITZ can't be easily measured and its value is always estimated through porosity. But its precise value depends on the shape and type of aggregate, water to cement ratio and other factors which are not easy to be obtained.

In this research, the diffusivity of ITZ was deduced through a one-dimensional transmission test. Based on a two-dimensional mesoscale numerical model, the process of chloride ions transport in concrete was simulated and verified through the electron probe technique.

2 EXPERIMENT PREPARATION

2.1 Materials and specimen preparation

The cement used in this research was normal Portland cement with a grade of PIS2.5. The sand was natural quartz sand with a fineness modulus of 1.6 and water was tap water. For both concrete and mortar, the water to cement ratio was 0.74 and the mass ratio of sand to cement was 2. For concrete, the volume fraction of coarse aggregates was 39.8%. The ITZ was produced by embedding rod-shaped aggregates into mortar matrix.

Rod-shaped aggregates were cored out from a limestone. Three kinds of rod-shaped aggregates were employed in this research with the diameter of 10mm, 7mm and 5mm respectively. The length of the rod-shaped aggregates was 70mm.

Before casting, the distribution diagram was printed from a high accuracy printer on a paper which was stuck on the bottom of the plexiglass plate with the diameter of 50mm. Then the rod-shaped aggregates were glued on the plate exactly according to the designed distribution diagram. Afterwards, the plexiglass plate and the rod-shaped aggregates were placed in a plexiglass mold which was specially produced for this research. The cement mortar was filled in the mold to complete the casting of concrete. While for mortar samples, cement mortar was casted into the plexiglass mold directly. The concrete specimen prepared for test is demonstrated in Fig.1.

After casting, the specimens were cured under the standard curing conditions as the temperature of $20\pm 2^{\circ}\text{C}$ and the relative humidity of 95% for 24h, following the Standard for test method of mechanical properties on ordinary concrete (GB/T 50081-2002)[4]. Then all the specimens were demolded at 1d and cured under standard conditions again until 28d. After 28d, all the specimens were placed under ambient conditions for test. To investigate the influence of ITZ on chloride diffusion in concrete, both one and two-dimensional diffusion tests were carried out utilizing the same kind of specimen prepared in this research. For one dimensional diffusion test, the bottom and side surfaces of the specimens were sealed with epoxy resin whose top surface was left for chlorides transport. For the specimens used for two dimensional diffusion, its top and bottom surfaces were sealed. Once the rod-shape specimens were immersed

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into chloride solution, the chloride ions will transport into concrete through its side surface.

Fig.1 Preparation of cylindrical concrete specimen

2.2 Experiment procedure

2.2.1 Diffusion test and environmental parameters

Based on NT Build 443[5], the NaCl solution with the concentration of 15% (2.8mol/L) was used in this research. And the NaCl solution was maintained under temperature of 30°C during the whole experiment process. All the specimens were immersed in NaCl solution for 30 days. A replacement of the NaCl solution with same concentration was conducted every week to keep the concentration unchanged. At 30d, all the specimens were taken out of the tank and put into an oven dryer, drying at a temperature of 105±2°C for 24h. Then, an abrasive paper was used to remove the vaporized crystalline salt covered on the surface of specimen.

2.2.2 Measurement of chloride content

Chloride content in concrete specimens under one dimensional diffusion was measured using rapid chloride test (RCT) method. For one dimensional diffusion specimens, only the top surface was exposed to chloride solution. So chloride ions will diffuse into concrete specimen vertically from its exposed surface. To evaluate the influence of aggregate on chloride diffusion, thin concrete plates parallel to the top surface were collected from specimen to measure chloride content on behavior of the whole cross section. The chloride content was measured from penetration depths at 1mm, 3mm, 5mm, 7mm, 10mm, 15mm, 20mm, 25mm, 30mm, 35mm, 40mm and 50mm.

At the target depths, a fine grinding was performed on the cross section to produce concrete powder within a thickness no more than 0.5mm. Then the concrete powder was collected and dewatered in an oven dryer at the temperature of 105±2°C for 2h. Afterwards, all the powder samples were cooled down to room temperature. Then the powder sample was extracted with 10 ml distilled water. A RCT electrode was immersed in the mixture to record a corresponding voltage. And the

chloride content was determined through a comparison between the measured result and a calibration chart.

2.2.3 Electron microprobe analysis

The electron microprobe (EMP) is an analytical tool used to non-destructively determine the chemical composition of solid materials. In electron microprobe analysis, a beam of electrons is fired at a sample. The beam causes each element in the sample to emit X-rays at a characteristic frequency; the X-rays can then be detected by the electron microprobe[6]. The size and current density of the electron beam determines the trade-off between resolution and scan time. Chemical composition is determined by comparing the intensities of characteristic X-rays from the sample material with intensities from known composition or standards.

3 DIFFUSIVITY OF ITZ

The chloride ion concentration measured with RCT method, for both concrete and cement mortar samples, are plotted in Fig.2. For one dimensional diffusion applied in this research, the analytical solution for Fick's second law is:

$$C(x,t) = C_0[1 - \operatorname{erf}(\frac{x}{2\sqrt{D_c t}})] \quad (1)$$

where C_0 is the surface concentration of chloride ions which is determined by surficial porosity of the sample and concentration of solution, in %; x is the penetration depth, in mm; erf is a complementary error function. Based on the measured chloride ion distribution in concrete and cement mortar, the diffusivities can be obtained from a fitting analysis. According to Eq.(1), the diffusivities for concrete and cement mortar are 3.13×10^{-11} and $3.69 \times 10^{-11} \text{m}^2/\text{s}$, respectively.

Fig.2 Chloride ion distribution in concrete and cement mortar

In this research, a parallel model is used to calculate the diffusivity of ITZ. As mentioned previously, the effective diffusivity of concrete can be specified in terms of diffusivity and volume fraction of each phase. The diffusivity of aggregate is naturally assumed to be zero. Then the diffusivity of ITZ can be deduced as[7]:

$$D_{ITZ} = \frac{D_c - D_m (1 - V_{agg} - V_{ITZ})}{V_{ITZ}} \quad (2)$$

where D_m and is the diffusivity of cement mortar; D_{ITZ} is the diffusivity of ITZ; V_{agg} is the volume fraction of aggregate; V_{ITZ} is the volume fraction of ITZ.

Deduced from Eq.(2), the diffusivity of ITZ can finally be obtained as $1.48 \times 10^{-9} \text{m}^2/\text{s}$ for concrete employed in this research. According to the measured results, the diffusivity of ITZ is 40.13 times higher than that of cement mortar. In 2002, Yang and Su has reported that the approximate chloride migration coefficient of ITZ is about 2.83 times of the matrix based on experimental and regression analytical results. A further investigation of Yang has revealed that the approximate ITZ migration coefficient can be 5.84, and 3.62 times of the matrix[8]. But it should be pointed out that these ratios correspond to the ITZ thickness for 20 or 30 μm . For a higher ITZ thickness, the ratio for diffusivity of ITZ and mortar matrix tends to be a higher value. Yang has also admitted that this ratio can exceed 100 times in some studies which may be attributed to the experiment technologies[9]. The experiment results conducted in this research is consistent to the findings of Yang et al. and Yu et al[10-11]. It should also be emphasized that ITZ and cement mortar are all suggested to be isotropic materials and the diffusivities for them can be applied in two-dimensional diffusion.

4 NUMERICAL SIMULATION AND DISCUSSION

4.1 Finite element model

A numerical simulation on the two-dimensional chloride ion diffusion in concrete was carried out with a commercial software, COMSOL. The finite element model was exactly created according to the arrangement of aggregate, mortar matrix and ITZ for concrete sample. The 2D triangle element was used in the meshing. The elements around each aggregate sufficiently represented ITZ with the thickness of $40.7 \mu\text{m}$. And the elements on both sides of ITZ were refined gradually to match the geometrical characters of ITZ. The aggregate was still taken as impenetrable in the model. The diffusivities of ITZ and cement mortar were considered as $1.48 \times 10^{-9} \text{m}^2/\text{s}$ and $3.69 \times 10^{-11} \text{m}^2/\text{s}$ respectively, following the experiment observations.

Boundary conditions the same as the experimental setup were applied to the model. The sample surface was exposed to the chloride solution with the concentration of 0.78% after conversion in considering the surface porosity of concrete sample. Before the simulation, the concrete sample was entirely chloride free. After applying boundary conditions to the model, the finite element method was used to numerically solve Fick's second equation for two-dimensional chloride diffusion. For the whole experiment procedure, 720 equally-sized time intervals of 1 hour were chosen for temporal discretization.

4.2 Simulation results

As a multi-phase material, concrete permeability is controlled by the permeability of its constituent phases and their geometric arrangement[1]. The area scan conducted by electron microprobe analysis proves that chloride ion diffusion is remarkably affected by the aggregate intrusion. As shown in Fig.3(a), although the boundary conditions are equally applied on the surface of the sample, but the chloride ions don't uniformly diffuse into the sample due to the aggregate arrangement. It can be attributed to the tortuosity effect as the aggregates block the migration of chloride ions and extend the diffusion path. Inversely, at the outer side of an aggregate, the inward concave on the level isoline indicates that more chloride ions move towards aggregate as the ITZ has a much higher diffusivity. The ITZ effect leads to a higher concentration gradient around the aggregate. Generally, the rod-shape aggregates retard the diffusion of chloride ions into concrete. So the tortuosity effect shows more significant influence on chloride ions diffusion than ITZ effect in this experiment.

The numerical simulation results, as shown in Fig.3(b), are in good agreement with the experiment results. The measured chloride ions distribution visually matches the simulation results very well. Five points along a linear measuring path, as shown in Fig.3(a), are selected to verify the finite element model. The simulation result and the measured data at each point are both plotted in Fig.4. In view of the absolute error, the simulated chloride ion concentration is close to the measured results. And the absolute error descends from surface to the inside of the sample. But it should also be noticed that the chloride ion concentration drops quickly along the penetration depth, and the relative error actually increases reversely. A detailed error analysis is conducted through a calculation of relative errors of 2500 equally spaced measuring points on the cross section of the sample. As a result, a two-dimensional error distribution is obtained in Fig.5. As indicated in Fig.5, the relative error at the centric part of the sample is higher than that at the peripheral part. And the highest relative errors are prone to appearing around aggregate, especially in the zone between two rod-shape aggregates. This phenomenon implies that the accuracy of chloride ion diffusion analysis mainly depends on the modeling of ITZ. Eliminating the points within aggregate from calculation, the average relative error of all the measuring points is 10.4% in this research. Generally, the simulation results agree well with the measured data.

(a) Experiment results

Fig.5 Relative error distribution and simulation results

(b) Simulation results

Fig.3 Comparison between experiment results and simulation results

Fig.4 Comparison of measured data

5. CONCLUSIONS

In this research, an electron microprobe technique was applied to quantitatively characterize the chloride ions diffusion in concrete. To guarantee the consistency between the numerical model and the experiment specimen, the geometric arrangement of ITZ in concrete was controlled by predesigned template outlining the aggregate distribution. A two-dimensional diffusion experiment was conducted to evaluate the influence of ITZ on chloride ions diffusion. Taking the diffusivity and thickness of ITZ into consideration, the numerical simulation of chloride ions diffusion in concrete agrees well with the experimental results. The ITZ effect can not be ignored in the chloride ions diffusion investigation.

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