Numerical Simulations of Chloride Transport in Concrete Considering Connectivity of Chloride Migration Channels in Unsaturated Pores

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Abstract

This study aimed to develop a method for the reasonable prediction of chloride ingress into concrete under unsaturated conditions. To achieve this, the connectivity of both the pore networks and the water paths in hardened cement paste were investigated and modeled in the existing numerical analytical system. Previous measurement results for the continuous porosity in hardened cement paste were reorganized, and the relationship between the total porosity and continuous porosity was clarified and formulated as the pore connectivity. In addition, the connectivity of the liquid water in unsaturated pore structures was formulated referring to previous numerical studies, suggesting that the connectivity of the liquid water decreases at a lower degree of saturation. Furthermore, by calculating the chloride transport considering the pore connectivity and the liquid water connectivity under unsaturated conditions, the chloride penetration into unsaturated concrete, including an airborne chloride environment, could be reproduced more realistically than was previously possible.

1. Introduction

In the performance-based durability design of chloride attacks on concrete structures, the chloride ingress during the in-service period is typically estimated based on a simple diffusion law utilizing the apparent diffusion coefficient of chloride ions (fib 2010; JSCE 2017). Various phenomena related to the chloride transport and equilibrium in cementitious materials, such as chloride ion ingress with diffusion and advection, and chloride binding in the hardened cement paste were generally attributed only to the diffusion phenomenon in the design method; therefore, the diffusion coefficient in the design is referred to as the “apparent diffusion coefficient”. However, for concrete structures suffering from chloride attack in a real environment, it is not always possible to make effective predictions based solely on the simple diffusion law because there are various environmental actions, such as tides and rainfall. Chloride attacks tend to become severe under such conditions as repeated cycles of drying and wetting by salt water and/or where chloride is supplied under unsaturated conditions, because water, chloride and oxygen are adequately supplied. It is more important to consider the various phenomena and predict the chloride ingress into concrete structures in seashore or coastal areas.

Numerous experimental and numerical studies have been conducted regarding the chloride ion penetration into hardened cement paste. Many of the studies focused on the chloride ingress under saturated conditions, resulting in improved accuracy of the chloride penetration predictions for saturated conditions, which was addressed by the porosity of continuous pores or the connectivity of the pores, considering that the pore size for the chloride transport ranges widely from nanometer to millimeter. Patel et al. (2016) reviewed enormous experimental and modelling approaches to determine effective diffusion coefficients of water saturated ordinary Portland cement-based materials. Patel discussed that Experimental data of mortar and concrete reveals predominant influence of increasing tortuosity due to aggregates and limited influence of interface transition zone. Ye et al. (2003) simulated the microstructure by using the cement hydration model which using some algorithms utilized to determine the local geometrical information, such as gravity center's coordinate, perimeter and area of each individual pore. Some model verifications have also pointed out issues remaining for the future, such as the necessity to introduce time-dependent diffusion coefficients, and the need to identify the pores that do not contribute to the chloride transport (Patel et al. 2018; Liu et al. 2018; Stroven et al. 2012; Ye et al. 2003). On the other hand, there have been few experimental and numerical studies on chloride penetration under unsaturated conditions. Chloride penetration tests under unsaturated conditions have been attempted in only a few studies (Vera et al. 2007; Erik et al. 2003; Guimarães et al. 2011), so procedures have not yet been established and the available data are limited. Although the airborne chloride environment is a typical environment where chloride penetration occurs under unsaturated conditions, the existing related measurement data are not sufficient. As a result, the phenomena are not adequately understood; therefore, when evaluating the

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chloride penetration under unsaturated conditions, relatively simple prediction methods are often employed, such as using the ratios of the apparent diffusion coefficient under saturated and unsaturated conditions, which are indirectly calculated from the electrical resistivities, etc. (Mendoza et al. 2014; Olsson et al. 2013). However, these prediction approaches are fraught with challenges. In hardened cement paste under unsaturated conditions, the liquid water is unevenly distributed over the complex pore networks, and so it is necessary to understand not only the connectivity of the pores but also the continuity of the liquid water. In addition, because the pore sizes in the vapor/liquid interface based on Kelvin’s law tend to be on the order of nanometers under ambient relative humidity, chloride penetration under unsaturated conditions is dominant in nanometer-sized pores. To predict the chloride penetration into concrete structures under unsaturated conditions with a high degree of versatility and accuracy, a simple expression with the relative diffusion coefficient for saturated conditions is not sufficient; it is necessary to formulate the complicated behavior of the liquid water and chloride ions based on the pore structure, in line with various materials, mix proportions, and environmental conditions.

To investigate the connectivity of the pores in hardened cement paste, a two-step measurement process using a mercury intrusion porosimetry (MIP) has been widely used (Zhaoqing et al. 2018). This process makes it possible to detect the continuous porosity, excluding ink-bottle pores and dead-end pores, by conducting decompression after the initial intrusion and subsequent re-intrusion. The resolution of MIP, or the minimum pore size measurable by MIP, is about 3 to 10 nm (Yoshida et al. 2007). Meanwhile, x-ray computed tomography (XCT) has been used in recent studies to detect the three-dimensional structure of pores and identify the mass transfer channels in the pores (Zhang et al. 2012; Promentilla et al. 2008). XCT enables the detailed analysis of pore connectivity, as well as the total porosity and continuous porosity, which are also measurable by MIP. However, the resolution of XCT is about 0.5 µm, which makes it difficult to obtain information on pore networks at the nanometer scale.

The authors have developed a multiscale thermodynamic analysis system, named DuCOM, which can predict the chemical reaction and equilibrium processes in cement hydrates from the initiation of the hydration of concrete over its long-term degradation. The system has successfully reproduced the cement solidification process including heat generation due to hydration, pore structure development and water equilibrium transport, and is used to predict chloride transport and material degradation phenomena including chloride-induced steel corrosion (Maekawa et al. 2003, 2008; Ishida et al. 2009). The analytical system takes into account the hydration development, which varies depending on the mix proportions and environmental conditions. In addition, the time-dependent pore size distributions have been formulated considering the porosity and the peak radius as major variables. The chloride ions that migrate within the liquid water in the pores are calculated based on the diffusion and advection models, and the model can handle various water-cement ratios (W/C) and cement types by adjusting the reduction parameters including the conductivit parameter (Nakarai et al. 2006; Ishida et al. 2009). Takahashi and Ishida (2016) introduced a model that considers the threshold pore radius focusing on the chloride ion transport in nanometer-sized pores, and the applicable range of the model has been expanded to hardened cement paste with relatively dense pore structures such as one with a low water-cement ratio. This chloride transport model has been extensively verified through experiments under saturated and/or cyclic wetting-drying conditions, and its excellent accuracy has been confirmed. However, the model’s applicability to unsaturated conditions is still unclear, including the airborne chloride environment, which is a main focus of the present study. In the existing model, the pore connectivity and the electrical properties of the pore walls are indirectly reflected in the reduction parameters; however, the authors believe that more explicit modeling is possible by understanding the phenomena, which would improve the applicability of the system for predicting chloride penetration under unsaturated conditions.

Table 1 compares the differences between the existing model and the modified model.

|                        | Existing model | Modified model |
|------------------------|----------------|----------------|
| Pore connectivity     | Including the threshold radius indirectly | Considered directly |
| Water connectivity     | Not considered | Considered directly |
| Degree of precision in unsaturated and airborne chloride environment | Low accuracy | Accuracy |

Based on the background of the present study, the authors first investigated the applicability of the existing model using the experimental values obtained from previous exposure tests under an airborne chloride environment. Second, the results of previous studies focusing on the pore connectivity and the water connectivity in pores were reorganized, and chloride diffusion tests were
conducted under unsaturated conditions. Next, the pore connectivity and the water connectivity were formulated based on the results of previous experiments and the unsaturated chloride transport experiments conducted in this study. Finally, the applicability of the modified model was verified again using the experiment values in the airborne chloride environment.

2. Simulations with the existing model

2.1 Overview of the existing model

Figure 1 shows the calculation scheme of the thermodynamic coupled analysis system used in the study (Maekawa et al. 2008). This analysis system consists of several subsystems including heat generation due to hydration, micropore structure development, water equilibrium and transport, and chloride transport and equilibrium models, which are used in the chloride ingress calculations. Sequential calculations applying these subsystems with shared variables make it possible to trace various time-dependent chemical and physical properties. The hydration heat model is used to calculate the hydration process of multicomponent materials composed of cement compositions and pozzolans; the pore structure development model is used to calculate the multiscale pore size distributions based on the degree of hydration obtained from the hydration heat model; and the water equilibrium and transport model is used to calculate the moisture transport and vapor/liquid equilibrium based on the pore information obtained from the pore structure development model. Based on the moisture distribution and relative humidity (RH) as well as the multiscale pore structure properties, the bound chloride equilibrium as well as the chloride transport due to diffusion and advection are calculated. This section describes the major equations used for the present study.

2.1.1 Pore structure and water equilibrium transport model

In the analytical system used in this study (Maekawa et al. 2008), the distributions of the capillary pores and gel pores are expressed by the following equation, using the Rayleigh-Ritz distribution function:

\[ V(r) = 1 - \exp(-Br), \quad dv(r) = Br \exp(-Br) \, dr \ln r \quad (1) \]

where \( V(r) \) is the pore size distribution function, \( B \) is a parameter that determines the form of the function (1/m), and \( 1/B \) represents the peak radius of the pore. Assuming a cylindrical pore shape in the distribution, the radius of the pore that has an equilibrium interface between the liquid and vapor phases, \( r_c \) (m), is expressed by:

\[ r_c = C \cdot r_m = \frac{2C \cdot \gamma \cdot M}{\rho \cdot RT} \cdot \ln h^2, \quad C = 2.15 \quad (2) \]

where \( C \) is a constant that reflects the thickness of the absorption layer (\( \gamma \)), \( r_m \) is the pore radius calculated from the Kelvin equation (m), \( \gamma \) is the surface tension of the liquid (N/m), \( M \) is the molecular mass of water (kg/mol), \( \rho \) is the density of liquid water (kg/m\(^3\)), \( R \) is the gas constant [J/(mol·K)], \( T \) is the absolute temperature (K), and \( h \) is RH (\( \gamma \)). Assuming that all pores with a radius smaller than \( r_c \) are filled with liquid water, the degree of saturation \( S \) is the summation of the volumes of pores with a radius not greater than \( r_c \), which is expressed by:

\[ S_c = \int_{0}^{r_c} 1 - \exp(-Br) \, dr \quad (3) \]

In the existing model, the volume of water entrapped in ink-bottle pores is also considered, and the degree of saturation is expressed by \( S_{ink} \) which is determined by an arbitrary temperature and the RH history. The detailed formulation of \( S_{ink} \) was investigated in the authors’ previous study (Ishida et al. 2007). The degree of saturation equivalent to the water absorbed by the pore walls, \( S_{ads} \), is expressed by:

\[ S_{ads} = \frac{r_m}{A_s} \quad (4) \]

where \( r_m \) is the thickness of the absorption layer (m), and \( A_s \) is the specific surface area of the pores with a radius greater than \( r_c \) (m\(^2\)/m\(^3\)). The formation of \( r_m \) and \( A_s \) was given as a function of the humidity and pore size distributions in the previous study (Ishida et al. 2007).

Accordingly, the total degree of saturation, \( S_{tot} \), is given by the summation of \( S_c, S_{ink} \) and \( S_{ads} \):

\[ S_{tot} = S_c + S_{ink} + S_{ads} \quad (5) \]

Hence, using the total saturation degree of the capill-
lary pores, \( S_{\text{net, cp}} \), and that of the gel pores, \( S_{\text{net, gf}} \), the total water content per unit cement paste volume, \( W \) (m\(^3\)/m\(^3\)), is expressed by:

\[
W = \phi_p S_{\text{net, cp}} + \phi_g S_{\text{net, gf}}
\]  

(6)

where \( \phi_p \) is the capillary porosity (m\(^3\)/m\(^3\)) and \( \phi_g \) is the gel porosity (m\(^3\)/m\(^3\)) in the unit cement paste volume, respectively.

For the water transport, both the liquid water and vapor are considered. The liquid water flux in the pores, \( q_l \), is obtained by integrating the liquid water flux in the pores with a radius smaller than \( r_c \) calculated from Kelvin’s law to consider the degree of partial saturation of the pores. \( q_l \) is expressed by:

\[
q_l = -\frac{\rho \phi D_v}{50 \eta} \left( \int_0^{r_c} r dV \right)^2 \nabla P = -K_l \nabla P
\]  

(7)

where \( \phi \) is the summation of the capillary porosity and gel porosity (\( \phi_p + \phi_g \)), \( \eta \) is the viscosity of liquid water (Pa·s), \( K_l \) is the liquid water permeability coefficient [kg/(Pa·m·s)], and \( P \) is the pore pressure (Pa). When the pores are under unsaturated conditions, the flux of the water vapor should be considered. The water vapor flux, \( q_v \), is expressed by:

\[
q_v = -\frac{\delta \rho \phi D_v}{\Omega_w} \int_{r_s}^{r_c} dV \left( \frac{M_h}{\rho_r RT} \right)^2 \nabla P = -K_v \nabla P
\]  

(8)

where \( \rho_v \) is the water vapor density (kg/m\(^3\)), \( D_v \) is the water vapor diffusion coefficient in a free atmosphere (m\(^2\)/s), \( \Omega_w \) is the tortuosity parameter of the pores \( = \left( \pi/2 \right)^2 \), \( N_k \) is the Knudsen number, and \( K_v \) is the water vapor permeability coefficient [kg/(Pa·m·s)]. As a result, the sum of the liquid water flux and vapor water flux, or the water flux, \( J_w \) [kg/(m\(^2\)/s)], is expressed by:

\[
J_w = -(K_l + K_v) \nabla P
\]  

(9)

### 2.1.2 Chloride transport and equilibrium model

Based on the liquid water content calculated by Eq. (6), the mass conservation law for the chloride ions in cement paste is expressed by:

\[
\frac{\partial}{\partial t} (W \cdot C_{\text{ion}}) + \nabla \cdot (J_{\text{ion}} - Q_{\text{cl}}) = 0
\]  

(10)

where \( C_{\text{ion}} \) is the free chloride ion concentration in the pore water (mol/m\(^3\)), \( J_{\text{ion}} \) is the free chloride ion flux [mol/(m\(^2\)/s)], and \( Q_{\text{cl}} \) is the bound chloride content (mol) (Ishida et al. 2007).

\( J_{\text{ion}} \), which is one of the focus points of the present study, is expressed by:

\[
J_{\text{ion}} = -(W_{\text{chld}} \cdot \delta \cdot D_{\text{ion}}) \nabla C_{\text{ion}} + W_{\text{chld}} \cdot u \cdot C_{\text{ion}}
\]  

(11)

where \( W_{\text{chld}} \) is the water content available for chloride transport within the pores (m\(^3\)/m\(^3\)), \( \delta \) is the constrictivity parameter, \( D_{\text{ion}} \) is the self-diffusion coefficient of the free chloride ions in the solution (m\(^2\)/s), and \( u \) is the velocity vector of the water that transports the chloride by the flow of the solution (m/s).

The first term on the right side of Eq. (11) represents the chloride ion flux owing to the diffusion due to the concentration gradient, and the second term represents the advection constituents in the chloride ion flux. The water content available for chloride transport, \( W_{\text{chld}} \), is expressed by the following equation:

\[
\begin{align*}
W_{\text{chld}} &= W - W_{\text{thre}} - W_{\text{ok}} \quad (r_c \geq r_{\text{thre}}) \\
W_{\text{chld}} &= 0 \quad (r_c < r_{\text{thre}})
\end{align*}
\]  

(12)

where \( W_{\text{thre}} \) is the amount of liquid water existing in the pores with a radius not greater than the threshold pore radius \( r_{\text{thre}} \) (Takahashi and Ishida 2016), and \( W_{\text{ok}} \) is the liquid water in the ink-bottle pores.

**Figure 2** shows each water content expressed in Eq. (12), which is placed in pore size distributions. \( W_{\text{thre}} \) is expressed as follows:

\[
W_{\text{thre}} = \phi \int_0^{r_c} dV = \phi \cdot \{1 - \exp(-B r_{\text{thre}})\}
\]  

(13)

It is supposed that chloride ions in a pore with a radius smaller than the threshold pore radius, \( r_{\text{thre}} \), cannot pass through the pore even if the pore is filled with liquid water. This \( r_{\text{thre}} \) is set as 10 nm based on the results of sensitivity analyses (Takahashi and Ishida 2016). Note, however, that this value of 10 nm reflects the pore connectivity as well as the chloride transport resistance due to the electrical properties of the pore walls.

The constrictivity, \( \delta \), is a coefficient that reflects the effect of an interaction between the pore structure’s constrictive property and the ion transport, and is expressed by:

\[
\delta = m \cdot \delta_1 \cdot \delta_2 \cdot (m = 6.38, \quad \delta_1 \geq 1.0, \quad \delta_2 = 1.0)
\]

\[
\delta_1 = 0.495 \tanh\{4.0(\log(r_{\text{peak}}) + 6.2)\} + 0.505
\]

\[
\delta_2 = 1.0 - 0.627 C_5 + 0.107 C_5^2
\]  

(14)

where \( r_{\text{peak}} \) is the peak radius of the capillary pores (m), and \( C_5 \) is the bound chloride content (%) by mass of binder). \( \delta_1 \) is a reduction parameter that corresponds to the change in pore size, and \( \delta_2 \) is a reduction parameter that corresponds to the electrical interaction between the
pore walls and the chloride ions (Ishida et al. 2007).

The relationship between chloride ion and bound chlorides modeled as a Langmuir type equation, and expressed by the following equation:

\[
C_b = \frac{\alpha \cdot C_f}{1 + 4.0C_f} \tag{15}
\]

where \( C_b \) is the concentration of bound chlorides (% by mass of binder), \( C_f \) is the concentration of chloride ions (% by mass of binder), and \( \alpha \) is the types of binders and the replacement ratio parameter effecting the binding capacity (−). \( \alpha \) is expressed by:

\[
\alpha = 11.8, \quad \text{OPC} \\
\alpha = -34.0b^2 + 23.3b + 11.8(0 \leq b \leq 0.6), \quad \text{GGBS} \tag{16} \\
\alpha = -15.5f^2 + 1.8f + 11.8(0 \leq f \leq 0.4), \quad \text{FA}
\]

where \( b \) and \( f \) are the replacement ratios by mass of ground granulated blast-furnace slag and fly ash, respectively.

### 2.2 Simulation of concrete exposure tests with the existing model

In this section, the experimental values obtained from a previous study (Limtong et al. 2019) are compared with the analytical results obtained from the existing analysis model regarding long-term chloride penetration in an airborne chloride environment. In the previous tests conducted by Limtong et al. (2019), mortar specimens of 10 × 10 × 10 cm with the mix proportions listed in Table 2 were exposed to an airborne chloride environment for 3.5 years, during which the distributions of chloride content were measured. In Table 2, N is the mix proportion with ordinary Portland cement (OPC); BB is the mix proportion with OPC of 60% and ground granulated blast-furnace slag (GGBS) of 40% by mass; and FB is the mix proportion with OPC of 85% and fly ash (FA) of 15%. The exposure site was located in a coastal area subject to severe chloride attack near the Sea of Japan, and the specimens were placed below a railway viaduct located 150 m from the coastline (Fig. 3). The previous study reported that the amount of airborne chloride at the exposure site was about 0.05 to 2.0 mdh [mg/(dm² hour)] based on the results of measurements taken every two or three months using mortar chips. The mortar specimens were collected after three months and 3.5 years of exposure, and each specimen was ground into powder by small pitch of thickness and the total chloride amounts were measured by potentiometric titration using aqueous silver nitrate. Details of the tests are described in previous literatures (Limtong et al. 2019; Wattanapornprom et al. 2018).

In the analyses by the existing model, the same mix proportions of the N, BB, and FB cases used for the exposure tests were input for a one-dimensional element with a length of 10 cm. The environmental settings included the daily average temperature and humidity obtained from the observation results by the Japan Meteorological Agency and the measured airborne chloride amounts reported by Limtong et al. (2019). Figure 4 shows the results of the comparison between the measured chloride profiles (Limtong et al. 2019) and the simulated results by the existing model. The simu-

| Type | Water-binder ratio | Water | OPC | GGBS | FA | Sand | Air [%] |
|------|--------------------|-------|-----|------|----|------|---------|
| N    | 0.55               | 380   | 691 | 1000 | 2  |
| BB   | 0.55               | 375   | 409 (60%) | 273 (40%) | 1000 | 2  |
| FB   | 0.55               | 372   | 575 (85%) | 101 (15%) | 1000 | 2  |

Fig. 3 Exposure site.

Fig. 4 Comparison between the measured values of chloride in the mortar exposed to an airborne chloride environment for 3.5 years and the analytical values from the existing model.
lated values of the penetrated chloride contents, especially the depths from the surface, were smaller than the measured values in all cases (N, BB and FB). Figure 5 shows the simulated RH for the N case. Figure 5(i) shows the transition of RH at depths of 10 and 30 mm from the surface. The figure shows that RH at the depth of 10 mm was less than 80% for most of the exposure period, and RH at the depth of 30 mm was less than 80% after the material age of 400 days. Figure 5(ii) shows the RH distributions at days 70 and 400; RH at the depth of 30 mm was about 90% at 70 days and about 80% at 400 days. The figure shows that the unsaturated conditions extended for a depth of up to 50 mm. When \( r_{thre} \) [the threshold radius in Eq. (13)] was set to 10 nm, \( r_c \) in Eq. (2) became less than \( r_{thre} \) when RH decreased to below 80% and all the liquid water in the pores was included within \( W_{thre} \), the chloride transport did not occur. Figure 6 shows the distribution of the liquid water under saturated conditions and that where \( r_c \) is less than \( r_{thre} \). This figure resulted from the assumption that pores smaller than the threshold radius did not contribute to the chloride transport. However, from the experimental results in Fig. 4, it is suggested that the liquid water in pores smaller than 10 nm also contributed to the chloride transport because the chloride penetration continued in the environment of constantly unsaturated conditions and continuous chloride. As mentioned above, the \( r_{thre} \) setting of 10 nm was determined from the sensitivity analyses and might include the effect of the pore connectivity. In the present study, it was necessary to separate the effect of the pore connectivity from \( r_{thre} \). Hence, as described in the next section, we reorganized the results of previous studies on the pore structure connectivity and chloride transport, conducted chloride penetration tests under unsaturated conditions including the condition where \( r_c \) was less than 10 nm, and then attempted to clarify the pore connectivity and water connectivity, which play an important role in chloride transport.

3. Experimental investigations on the pore connectivity and water connectivity

3.1 Pore connectivity experiments

XCT and MIP are two major methods for studying the connectivity of the pore networks formed in hardened cement paste. Attempts have been made to clarify the pore connectivity based on the three-dimensional structure of pores detected with XCT. The present study referenced previous studies that addressed the three-dimensional pore structures of OPC cement paste using XCT (Zhang et al. 2012; Bossa et al. 2015; Promentilla et al. 2009; Sugiyama et al. 2010). Table 3 shows the conditions for the previous XCT tests. In those studies, the water-cement ratios were set as 0.5 and the

![Fig. 5 Analysis results for RH in the pores of the exposed mortar.](image_url)

![Fig. 6 Water content available for chloride transport in the existing model under saturated conditions and at RH of 80%.](image_url)
XCT resolution was about 0.5 to 2.0 μm. Figure 7 shows the relationship between the total porosities and the continuous porosities; the results were taken from the previous studies and reorganized here. The continuous porosity is the ratio of the volume of continuous pores to the volume of total pores detected by XCT in the cement paste. The horizontal axis in Fig. 7 shows the total porosity and the vertical axis shows the ratio of the continuous porosity to the total porosity. As a result, it was found that the smaller the total porosity, the smaller the ratio of the continuous porosity to the total porosity.

Regarding the methods using MIP, many studies have employed the re-pressurization method to examine the continuous porosity. As for MIP, although it is quite common to measure total porosities and pore distributions with pressurizing mercury, some studies have identified ink-bottle pores, dead-end pores, and continuous pores by applying repeated pressure. These studies are based on the hypothesis that by depressurizing the specimen after injecting the mercury, the mercury remains in the ink-bottle pores and dead-end pores. Then, by re-pressurizing the specimen, the mercury is injected only into the continuous pores, enabling the detection of continuous porosity (Zhuqing et al. 2018; Kamada and Kishi 2019; Kinomura and Ishida 2017; Zhuqing et al. 2017; Hyeonggil et al. 2019; Simčič et al. 2015; Qiang et al. 2016). In addition, Yoshida and Kishi (2007) and Yoshida et al. (2015) developed the step-by-step mercury intrusion porosimetry test (SMIP) where pressurizing and depressurizing are repeated. By using the SMIP method, the distribution of the ink-bottle pores as well as the change in the pore structures under high-pressure conditions can be detected. Zhou and Breugel (2010) used a similar procedure to examine the distribution of continuous porosities. Table 4 shows the conditions of the tests referred to in the present study. In the previous studies, W/C was set in the range from 0.6 to 0.3. In some studies, the mix proportions were prepared with 100% OPC as well as with OPC partially replaced with GGBS or FA. The minimum detectable pore radius with MIP is about 3 to 10 nm. Figure 8 shows the relationship between the total porosities and continuous porosities by study and by water-binder ratio (W/B) for OPC only. The results were obtained by reorganizing the experimental results of the previous studies. The horizontal axis in Figs. 8(i) and 8(ii) is the total porosity and the vertical axis is the continuous porosity/total porosity.

### Table 3 Test conditions for XCT.

| Authors               | Resolution/voxel | Mixture     | Cement paste size | Material age |
|-----------------------|------------------|-------------|-------------------|--------------|
| Zhang et al. (2012)   | 500 nm           | OPC, W/C = 0.5 | ⌀250 μm  | 1, 3, 7, 28, 120 days |
| Bossa et al. (2015)   | 1800 nm          | OPC, W/C = 0.5 | ⌀20 × 10 mm | 35 days  |
| Promentilla et al. (2009) | 500 nm     | OPC, W/C = 0.5 | ⌀50 × 10 mm | 140 days  |
| Sugiyama et al. (2010) | 500 nm         | OPC, W/C = 0.5 | ⌀20 × 10 mm | 35 days  |

Fig. 7 Relationship between total porosity and continuous porosity / total porosity obtained using XCT.

Fig. 8 Relationship between total porosity and continuous porosity / total porosity obtained using MIP (100% OPC).
axis shows the ratio of the continuous porosity to the total porosity. As a result of the MIP analysis, it was found that the smaller the total porosity, the smaller the ratio of the continuous porosity to the total porosity, as in the case with XCT shown in Fig. 7. In addition, looking at Fig. 8(ii), it appears that this relationship does not change with different W/Bs. It is suggested that the continuous porosity can be estimated based on the total porosity regardless of the difference in W/B. Comparing the results of the MIP and XCT analyses, the ratios of the continuous porosity to the total porosity in the MIP results tended to be smaller than those in the XCT results. One of the reasons for this gap is likely to be the difference in the resolution of each measurement. The resolution of MIP is about 3 nm at minimum and that of XCT is around 500 nm. Compared to XCT, MIP can detect considerably smaller pores and therefore seems to be able to detect smaller pore separations. MIP does not detect ink-bottle pores as a continuous pore in the principle of measuring method, which could be another reason for the gap.

In Fig. 9, the results for the OPC+GGBS and OPC+FA cases were added to Fig. 8, which shows the test results only for OPC. For OPC and OPC+GGBS, the relationships between the total porosity and the ratio of the continuous porosity to the total porosity were similar, while the OPC+FA cases have different ratios of the continuous porosity to the total porosity. For the OPC+FA cases, the continuous porosity for the same total porosity tended to be smaller than that for the other two cases (OPC, OPC+GGBS). Zhuqing et al. (2017) confirmed the densification of the pore structures due to pozzolanic reactions even after curing for 90 days, and most of the large pores with a diameter of about 0.1 to 1 μm disappeared after curing for 3 years. The study also showed that independent micropores with a diameter of about 20 to 40 nm were formed by pozzolanic reactions at the positions where fly ash particles had existed before the reaction. As a result, the total pore amounts of the mix proportion of OPC+FA were about 10% greater than that of OPC under the same conditions. These trends suggest smaller ratios of the continuous porosity to the total porosity in the OPC+FA case, as shown in Fig. 9. In the OPC+FA case, the pore connectivity decreased during the long-term pozzolanic reactions, which had less effect on the total porosity. This difference in the pore connectivity seems to have contributed to the high chloride shielding performance of the mix proportion with FA.

Further accumulation of data in the future will enable more detailed analyses of the relationships. Within the scope of the present study, however, the relationships between the total porosity and the ratio of the continuous porosity to the total porosity for the mix proportions can be regarded as the same for both the OPC and

| Authors       | Resolution radius | Mixture                   | Cement paste or mortar | Material age          |
|---------------|-------------------|----------------------------|------------------------|-----------------------|
| Zhuqing et al. (2018) | 7 nm              | OPC, OPC+FA                | Paste                  | 28, 91, 180, 365 days |
| Kamada and Kishi (2019) | 10 nm             | OPC, OPC+GGBS, OPC+FA      | Mortar                 | 4 months              |
| Kinomura and Ishida (2017) | 3 nm              | OPC, OPC+FA                | Mortar                 | 3 months              |
| Zhuqing et al. (2017) | 7 nm              | OPC, OPC+FA                | Paste                  | 1, 7, 28, 91, 180, 365 days |
| Hyeonggil et al. (2019) | 6 nm              | OPC+GGBS                   | Paste                  | 28 days               |
| Simić et al. (2015)    | 6 nm              | OPC, OPC+FA                | Paste                  | 84 days               |
| Qiang et al. (2016)    | 3 nm              | OPC, OPC+GGBS, OPC+FA      | Mortar                 | 90 days (OPC)         |
| Yoshida and Kishi (2007) | 3 nm (SMIP)       | OPC, OPC+GGBS, OPC+FA      | Mortar                 | 28 days               |
| Zhou et al. (2010)     | 6 nm (SMIP)       | OPC                        | Mortar                 | 28 days               |

Fig. 9 Relationship between the total porosity and continuous porosity / total porosity by binder.

Table 4 Test conditions of MIP.

| Authors          | Resolution radius | Mixture                   | Cement paste or mortar | Material age          |
|------------------|-------------------|----------------------------|------------------------|-----------------------|
| Zhuqing et al.   | 7 nm              | OPC, OPC+FA                | Paste                  | 28, 91, 180, 365 days |
| Kamada and Kishi | 10 nm             | OPC, OPC+GGBS, OPC+FA      | Mortar                 | 4 months              |
| Kinomura and     | 3 nm              | OPC, OPC+FA                | Mortar                 | 3 months              |
| Ishida (2017)    | 7 nm              | OPC, OPC+FA                | Paste                  | 1, 7, 28, 91, 180, 365 days |
| Hyeonggil et al. | 6 nm              | OPC+GGBS                   | Paste                  | 28 days               |
| Simić et al.     | 6 nm              | OPC, OPC+FA                | Paste                  | 84 days               |
| Qiang et al.     | 3 nm              | OPC, OPC+GGBS, OPC+FA      | Mortar                 | 90 days (OPC)         |
| Yoshida and      | 3 nm (SMIP)       | OPC, OPC+GGBS, OPC+FA      | Mortar                 | 28 days               |
| Kishi (2007)     |                   | OPC                        | Mortar                 | 28 days               |
OPC+GGBS cases, but the ratio for the OPC+FA case tends to be smaller than that for OPC and OPC+GGBS.

Here, the similarity of the pore size distributions between the total pores and the continuous pores is checked using the injection histories during the SMIP test on the OPC mortar specimens conducted by Yoshida (2009). The present study used the results for the specimens with W/C levels of 0.60, 0.45 and 0.30 after underwater curing for 14 and 28 days after demolding for 1 day to re-calculate the pore size distributions of the continuous pores and total pores. Figures 10 and 11 show the pore size distributions at the material ages of 14 and 28 days, respectively. In Figs. 10 and 11, the amounts of both the continuous pores and the total pores are normalized with the peak value of the pore amount in the distribution of the pore sizes and placed on the vertical axis as the “pore peak ratio”. These results indicate that the shapes of the distribution of the continuous pores and the total pores are comparable regardless of W/C or material age.

3.2 Water connectivity
This section examines the water connectivity in the pores. The liquid water in the continuous pores evaporates from the large pores along with the drying of the cement paste. Under unsaturated conditions, discontinuities of the liquid phase arise in the pores depending on the RH and pore size/distribution, resulting in a decrease in the chloride ion transport. Therefore, consideration of the water connectivity under unsaturated conditions is important in the present study.

Zhang et al. (2012, 2014) conducted XCT measurement, reproduced the measured pore structures as 3D analysis models and examined the water connectivity in the pores using the lattice Boltzmann method. They randomly allocated the water and the water vapor in the 3D pore structures scanned with XCT under different arbitrary RH conditions, and calculated the equilibrated distribution of the liquid and gas phases using the lattice Boltzmann method. Then, they calculated the connectivity of the liquid water by detecting the pores containing liquid water using a program for counting adjacent cells. Zhang et al. (2012, 2014) measured and analyzed three cases of cement paste with a W/C of 0.50 and different material ages (1, 7, and 28 days), and showed the relationship between the degree of saturation and the connectivity of water-filled pores for the three cases. This connectivity means the ratio of the liquid water in water-filled capillary and gel pores. The present study focused on these data and replotted the results of the study by Zhang et al. (2012, 2014), plotting the ratio of the connectivity of water-filled continuous pores on the vertical axis (Fig. 12). The connectivity of water-filled continuous pores means the ratio of the liquid water in water-filled continuous pores. As pointed out by Zhang et al. (2012, 2014), the smaller the degree of saturation and porosity, the smaller the connectivity of the liquid water. In addition, when the degree of saturation decreased to a certain level, the connectivity of the liquid water became zero even when liquid water existed in the pores; Zhang et al. (2012, 2014) defined the degree of saturation at this level as the critical saturation, $S_{cr}$. Next, as Fig. 13 shows, the results of the study by Zhang et al. (2012, 2014) were replotted, with the product of the degree of saturation and porosity on the horizontal axis and the connectivity of water-filled continuous pores on the vertical axis. The amount of pore water when the ratio of the liquid water in continuous pores becomes zero is defined as the “water content of the connection limit, $W_{crit}$. Below $W_{crit}$, chloride transport does not seem to occur because the liquid phases are

![Fig. 10 Distribution of continuous pores and total pores at the material age of 14 days.](image1)

![Fig. 11 Distribution of continuous pores and total pores at the material age of 28 days.](image2)
not connected even if there is liquid water in the pores. $W_{\text{crit}}$ seems to be an important parameter that determines the limit of the chloride transport due to the connection of the liquid phases.

### 3.3 Chloride penetration tests under unsaturated conditions

To study the relationship between RH and chloride transport in cement paste, chloride migration tests were newly conducted on mortar specimens under unsaturated conditions. The mortar specimens were soaked in salt water and the chloride was migrated to some extent, after which the specimens were thoroughly dried. The specimens were placed under controlled RH conditions and the authors experimentally examined at what degree of RH the chloride transport occurred in the mortar. It was expected that an approximate value of $\phi_{\text{thres}}$ would be obtained from the experimental trials.

The cement used in the tests was OPC with a density of 3.16 g/cm$^3$ and a specific surface area of 3420 cm$^2$/g. Crushed sand with a percentage of absorption 0.42% and ion exchanged water were used as well. Table 5 shows the series of specimens and the mortar mix proportions. To examine the chloride migration in both the ordinary strength and high strength range, $W/C$ was set to 0.5 and 0.3. The mortar prepared with these materials and mix proportions was cast in a cylindrical formwork with a diameter of 50 mm and a height of 100 mm and placed indoors at a temperature of 20°C and RH of 60%. The specimens were demolded at the material age of 3 days and soaked in tap water until the material age of 28 days. Then, to remove the effects of bleeding, the top and bottom of the specimens were cut out using a wet cutter with a thickness of about 10 mm. After drying the specimens at a temperature of 20°C and RH of 60%, epoxy resin was applied to the side and top surfaces, excluding the bottom surfaces, which would be contacted during saltwater immersion. Four days after applying the epoxy resin, the specimens were soaked in tap water for 24 h. They were then soaked in 10% salt water at a concentration of 1.71 mol/l for 28 days from the material age of 35 days.

After the chloride migrated into the specimens to some extent by soaking in salt water for 28 days, the epoxy resin was removed with a hand grinder. The specimens were then placed in a furnace for 24 h at a temperature of 110°C until thoroughly dried. It was confirmed that the chloride contents in the specimens rarely moved between before and after the drying process. After the drying, the side surfaces, excluding the top and bottom surfaces, of the specimens were sealed with tape. A gas exchange desiccator was prepared to provide environments with different RH settings for the specimens. Saturated salts (potassium iodide, potassium chloride and potassium nitrate) were placed in the desiccator beforehand and left to stand for about two weeks so that RH of the interior reached 70, 85 and 95%, respectively. At the time of placing the saturated salts, nitrogen was sealed in the desiccator to inhibit the carbonation of the specimens. The specimens were placed in this desiccator and each specimen was left to absorb moisture for the time shown in Table 6. Next, the chloride migration behavior in the different RH environments was observed. Figure 14 shows the desiccator and the specimens at the time of moisture absorption.

After the moisture absorption for the time periods given in Table 6, each specimen was ground into powder

| W/C | Unit weight [kg/m$^3$] | Air [%] |
|-----|------------------------|--------|
| 0.5 | 368 736 1000 2        |        |
| 0.3 | 293 977 1000 2        |        |

![Fig. 12 Relationship between the degree of saturation and the connectivity of liquid water.](image)

![Fig. 13 Water content of connection limit.](image)
using a 3 mm pitch depth and the total chloride amount at each depth of the specimen was measured by potentiometric titration using aqueous silver nitrate.

Figure 15 shows the distribution of the total chloride amounts, before and after the moisture absorption, obtained from the specimens with W/C of 0.5 and 0.3. For W/C of 0.5, the chloride profile moved slightly toward the inside of the specimen at RH of 70% after absorption for 91 days. Although the absorption period of the specimens at RH of 85% and 95% was relatively short (43 days, for operational reasons), the chloride migration was greater than in the case of RH of 70%. It was confirmed that the higher RH was, the greater the chloride transport amount was. For W/C of 0.3, it was also confirmed that the higher RH case exhibited greater chloride transport to the inside. Based on the test result that chloride transport occurred even at RH of 70%, where the Kelvin radius could be around 6.5 nm, it was confirmed again that the water content available for chloride transport \( W_{chld} \), obtained by using the threshold radius of 10 mm set in the previous model, seemingly cannot appropriately reproduce the chloride penetration amount under unsaturated conditions. These specimens might have cracks on the drying process at a temperature of 110°C. Therefore, it is necessary in the future to retest by drying process in a furnace for 7 days at a temperature of 50°C in the future. However, on the moisture term of this experiment, the vapor/liquid interface tends to be on the order of several nanometers. In addition, the widths of drying shrinkage crack may be over micrometers order. Hence, there is a low possibility that drying shrinkage cracks effect on the vapor/liquid interface, which governs the chloride movement.

4. Modified model for chloride transport focusing on the chloride migration channels in unsaturated pores in concrete

This section discusses the additional formulation for calculating the chloride migration channels using the existing model with regard to considering the pore connectivity and water connectivity. The information is based on the reorganized results of previous studies and the findings obtained from the chloride ingress tests under unsaturated conditions conducted in the present study, as described in Section 3.

4.1 Pore connectivity

The XCT and MIP results shown in Section 3.1 are useful for examining the pore connectivity in cement paste. Because the calculation of the chloride migration channels requires information on the pores in nanometer size, the measurement results from MIP, which provides a higher resolution, are referred to here. For the formulation of the pore connectivity, \( \kappa_p \) is defined as the ratio of the summation of the continuous porosity of the capillary pores and that of the gel pores to the summation of the capillary porosity and the gel porosity:

\[
\kappa_p = \frac{\phi_{cp_{conn}} + \phi_{gl_{conn}}}{\phi_{cp} + \phi_{gl}}
\]

where \( \kappa_p \) is the pore connectivity, \( \phi_{cp_{conn}} \) is the continuous porosity of the capillary pores, and \( \phi_{gl_{conn}} \) is the continuous porosity of the gel pores. Assuming that interlayer pores are too small to contribute to chloride migration, the continuous porosity is defined for the capillary pores and gel pores.

In addition, the pore connectivity, \( \kappa_p \), is defined corresponding to the type of binder, based on the results...
shown in Fig. 9:

\[ \kappa_p = 0.2 \ln(\phi_p + \phi_d) + 0.81 \quad \text{(for OPC, OPC + GGBS)} \]
\[ \kappa_p = 0.3 \ln(\phi_p + \phi_d) + 0.91 \quad \text{(for OPC + FA)} \]

As Figs. 10 and 11 show, the shapes of the pore size distribution of the continuous pores and total pores are comparable. In the present study, therefore, it was assumed that the distribution of continuous pores had the same pore-size distribution function \([\text{Eq. (1)}]\) and peak radius of pore \((1/B)\) as that of the distribution of total pores. As a result of the abovementioned modifications of the model, the amount of connected liquid water in the pores, \(W_{\text{conn}}\), is defined by:

\[ W_{\text{conn}} = \kappa_p \cdot (\phi \cdot S) \]  

Figure 16 shows the distributions of the total pores and continuous pores. By multiplying the total water amount in the total pores \((\phi \cdot S)\) by the pore connectivity \((\kappa_p)\), it is expressed that only the liquid water in the continuous pores is the amount of the connected liquid water in the pores, \(W_{\text{conn}}\).

4.2 Reconsideration of the threshold radius

In the existing model, the chloride migration limit size, \(r_{\text{thr}}\), was set to 10 nm as the value that might include the effect of the pore connectivity and the electrical properties of the pore walls. The connectivity of the pores was formulated as \(\kappa_p\) in the present, so the value of \(r_{\text{thr}}\) was reconsidered. Stuart and Berne (1996, 1999) reported that the chloride ions in liquid water do not transport alone but do so as a cluster along with 255 water molecules, and that their size ranges from 2 to 3 nm. Yang et al. (2019) studied the transport properties considering the electrical properties of the pore walls, by combining three-dimensional analysis models and the lattice Boltzmann method. The results showed that when the pore sizes decrease to below 2 nm, the diffusion coefficient of the chloride ions rapidly decreases. Furthermore, Yang et al. (2019) and Zhang et al. (2017) calculated the transport of chloride ions and water molecules when the pore diameters vary in the range from 1.0 to 3.5 nm considering their behavior on an atomic scale. The results showed that the water molecules are transported regardless of the pore size while the transport amount of chloride ions rapidly decreases along with the decrease in pore size. It was also shown that chloride ions, calcium ions and sodium ions form a cluster, accompanied by water molecules.

The abovementioned previous findings suggest that a radius of at least 1.0 to 1.5 nm is necessary for chloride transport. The authors judged it reasonable to consider the minimum radius for chloride penetration as 1.5 nm, as the value evaluated on the safe side. Therefore, for the OPC mix proportion, we set the threshold radius, \(r_{\text{thr}}\), where the transport of chloride ions ceases due to physical and electrical actions, to 1.5 nm. With this modification of the threshold radius, the water content available for chloride transport expressed by Eq. (12) is modified as \(W_{\text{chld}}\) in Eq. (20) below. Figure 17 shows the concept of Eq. (20).

\[ \begin{align*}
W_{\text{chld}} &= \kappa_p \cdot (W - W_{\text{thr}} - W_{\text{ink}}) \quad (r_i > r_{\text{thr}}) \\
W_{\text{chld}} &= 0 \quad (r_i < r_{\text{thr}}), \quad r_{\text{thr}} = 1.5 \text{ nm (20)}
\end{align*} \]

Regarding the threshold radius for the OPC+GGBS and OPC+FA cases, although the radius seems to in-
crease due to the changes in the electrical properties of the pore walls (Takahashi et al. 2014), relevant data is still being accumulated, including the data on the connectivity of liquid water under unsaturated conditions, which is discussed later. Therefore, instead of suggesting the threshold radius as a fixed value, only the results of sensitivity analyses in the case where the threshold radius is changed are shown in Section 5.

4.3 Water connectivity

This section introduces the formulation of the water connectivity under unsaturated conditions. The findings on water connectivity reported by Zhang et al. (2012, 2014) and discussed in Section 3.2 were based on the analysis of XCT having a resolution of about 500 nm. Therefore, the water connectivity in pores smaller than 500 nm under unsaturated conditions is unknown at present. In addition, because the water in dead-end pores is also detected as connected liquid water, the amount of water as an ion migration channel may be different from the actual state. Therefore, it is not appropriate to formulate the water connectivity by only approximating the results from the water connectivity measured by XCT as shown in Fig. 12. However, it was assumed in the present study that the qualitative trend shown by Zhang et al. (2012, 2014), “the smaller the degree of saturation and porosity, the smaller the connectivity of liquid water” would also be applicable to micropores, and the water connectivity was defined as \( \kappa_i \).

\[
\kappa_i = 1.0 - \frac{(1.0 - S) \cdot S_{\text{crit}}}{(1.0 - S_{\text{crit}})} \cdot (0.1 < \phi_{p+g} \leq 0.4)
\]  

(21)

where \( S_{\text{crit}} \) is the critical saturation and is determined by the water content of the connection limit, \( W_{\text{crit}} \), and the connectivity, \( \phi_{p+g} \).

\[
S_{\text{crit}} = \frac{W_{\text{crit}}}{\phi_{p+g}}
\]  

(22)

To find the water content of the connection limit, \( W_{\text{crit}} \), which determines the limit of the water connectivity in continuous pores, the authors conducted sensitivity analyses using the results of the chloride transport tests in different RH environments discussed in Section 3.3 (Fig. 15). The analyses considered the moisture and water content distribution during the moisture absorption process. Figure 18 shows the results of the sensitivity analyses on chloride transport with different values of \( W_{\text{crit}} \). As Fig. 18 shows, the reproducibility was highest when \( W_{\text{crit}} = 0.10 \), and therefore, this value was adopted in the present study. This value also meets the range of the water content connection limits found in previous studies (Fig. 13).

Figure 19 shows the relationship between the degree of saturation and the water connectivity, \( \kappa_i \), for different porosities. The figure indicates that the water connectivity is 1.0 when the degree of saturation is 1.0, for all the liquid water in continuous pores is connected, and then it decreases as the degree of saturation decreases. In addition, because \( S_{\text{crit}} \) is determined by \( W_{\text{crit}} \) and the porosity, the water connectivity \( \kappa_i \) reaches zero and chloride penetration ceases at different degrees of saturation depending on the porosity.

Considering the water connectivity under unsaturated conditions described above, the water content available for chloride transport, \( W_{\text{chld}} \), is expressed as follows by modifying Eq. (20):

\[
W_{\text{chld}} = \kappa_i \cdot (W - W_{\text{crit}} - W_{\text{pad}}) \cdot \phi \cdot (r_i > r_{\text{thr}})
\]

\[
W_{\text{chld}} = 0 \quad (r_i < r_{\text{thr}}), \quad r_{\text{thr}} = 1.5 \text{ nm}
\]  

(23)

Figure 20 shows a conceptual diagram of the modified model in the present study. Regarding the water content available for chloride transport as chloride ion migration channels, the model shows that only the liquid water in continuous pores contributes to chloride transport, by multiplying the amount of water in total pores by the pore connectivity, \( \kappa_i \), and that only the connected water in continuous pores contributes to chloride transport, by multiplying the amount of liquid water in continuous pores under unsaturated conditions by the water connectivity, \( \kappa_i \).
5. Simulations with modified models

This section examines the validity of the modified chloride transport model based on the results of exposure tests and sensitivity analyses of long-term chloride penetration in an airborne chloride environment described in Section 2.

5.1 Verification using the results of exposure tests

The authors conducted analyses of the exposure tests described in Section 2.2 using the modified model. Figure 21 shows the results of analyses on the distribution of the total chloride amounts in the N series at 3 months and 3.5 years using the modified model, along with the results of analyses using the previous model. The analysis values from the modified model show a high reproducibility when compared with the test values at the exposure periods of 3 months and 3.5 years. In the analyses using the previous model, the pore size in the vapor/liquid interface, \( r_c \), was lower than the threshold pore radius, \( r_{thre} (= 10 \text{ nm}) \) for a wide range of depth from the surface, along with the decrease in the degree of saturation. As a result, the chloride rarely penetrated to the inside at 3 months and 3.5 years, and the analysis values differed greatly from the measured values (Fig. 4). On the other hand, in the analyses using the modified model, the excessive stagnation of chloride penetration under unsaturated conditions was eliminated by modifying the value of \( r_{thre} \) from 10 nm to 1.5 nm, as well as limiting the chloride migration channels to continuous liquid water in continuous pores instead of total pores. As a result, the gradual progression of chloride penetration under unsaturated conditions seemed to be more closely related to the real phenomenon. Thus, the modified model has made it possible to accurately predict measured values for both short (3 months) and long (3.5 years) terms. This confirms that an analysis model can consider the chloride attack progression caused by the gradual penetration of chloride ions via a small amount of continuous liquid water, while the liquid water in the pores is limited to the nanometer level due to the effect of drying and its connectivity decreases in an airborne chloride environment.

On the other hand, for the mix proportions of BB and FB, the electrical properties of the pore walls change along with the decrease in the Ca/Si ratio, leading to an increase in the transport resistance of the chloride. This paper presents the results of a parametric study using different values of \( r_{thre} \). Figure 22 shows the results of reproduction analyses using the modified model setting values of \( r_{thre} \) as 1.5, 3.0 and 5.0 nm for comparison with the test results reported by Limtong et al. (2019). Figures 22(i) and 22(ii) show the results for the cases of BB and FA, respectively, at 3.5 years. Figure 22(i) shows that in the case of BB, the analysis values corresponded best with the measured values when \( r_{thre} \) was 5 nm. In the case of BB, the analysis values were smaller than the measured values when \( r_{thre} \) was 5 nm. Because the water connectivity, \( \kappa_l \), in the modified model is based on the tests conducted only on the OPC mix proportion, the applicability of the GGBS or FA mix proportion to the water connectivity is uncertain. Therefore, it is not certain whether the value of \( r_{thre} \) for reproducing the measured values with sensitivity analyses using the modified model of the GGBS and FA mix proportions is quantitatively reasonable or not. It may be necessary to re-examine the threshold radius through further studies on the water connectivity when admixtures are used and confirmation of the validity of the water connectivity. The increase in \( r_{thre} \) in the admixture replacement mixings seemingly varies depending on the composition of the admixture and the amount of re-
placement. Therefore, it is necessary in the future to improve the versatility of analysis models through additional formulation corresponding to the materials used.

5.2 Long-term chloride penetration analysis in airborne chloride environment

Finally, the authors show the results of analyses on long-term chloride penetration under different RH conditions using the existing model and the modified model, assuming an airborne chloride environment. The analyses were conducted on the concrete with the mix proportion and W/C shown in Table 7, setting the same temperature and airborne chloride environment as that shown in Fig. 21. Setting the daily average value of the temperature as that observed by the Japan Meteorological Agency and the environment with actually measured airborne chloride amounts on the coast of the Sea of Japan, chloride penetration analyses for 10 years were conducted for different constant RHs ranging from 95 to 50%. Figures 23(i) and 23(ii) show the results of the long-term chloride penetration analyses using the existing model and the modified model, respectively. In the analysis results from the existing model shown in Fig. 23(i), the case at 70% RH showed extremely lower chloride penetration than that in the cases at greater than 80% RH. On the other hand, in the analysis results from the modified model shown in Fig. 23(ii), only the case at 50% RH showed extremely lower chloride penetration than that in the cases at greater than 60% RH. As the relative humidity in an ordinary airborne chloride environment is often 70 to 80%, and severe chloride attacks are frequently observed in such environments, the analysis results from the modified model appear to be more realistic. It is also necessary to further study the pores that are smaller than the detection limit of MIP and XCT as well as the water connectivity in those pores. Regarding the modified model in the present study, the modeling was conducted assuming that the connectivity of the smaller pores exhibited the same tendency as that of the larger pores, considering the detection limit of MIP and XCT for the pores and water connectivity. The extreme decrease in chloride transport observed in the case at 50% RH, as shown in Fig. 23(ii), was possibly caused by micropore structures of nanometer size and the connectivity of the liquid water in them. By clarifying the behavior of chloride transport due to more microscopic pore structures and liquid water, the accuracy of the prediction of long-term chloride penetration would be further improved, and the applicability of the modified model would be enhanced.

6. Conclusions

In the present study, the chloride transport model in the existing multiscale thermodynamic analytical system

![Fig. 22 Comparison between the test values and analysis values of the total chloride amount in the mix proportions of GGBS and FA as well as sensitivity analyses of the threshold pore radii, in coastal exposure.](image)

![Fig. 23 Sensitivity analysis results for 10 years of exposure in an airborne chloride environment (W/C = 0.5).](image)
was improved by considering the connectivity of the pore networks and water paths. The limitations of the existing chloride transport model were pointed out by comparing the experimental and analytical results of the chloride penetration in concrete in an airborne chloride environment. Focusing on the connectivity of the pores and the liquid water in hardened cement paste as the migration channels of chloride ions, the pore connectivity as the ratio of the continuous porosity to the total porosity was formulated by reorganizing the results of MIP tests. Furthermore, referring to the results of previous studies that examined the water connectivity in pores under unsaturated conditions by applying XCT, the qualitative tendency of the connectivity of liquid water in continuous pores to decrease as the degree of saturation decreased, was formulated as the water connectivity. Accordingly, considering the cluster sizes of the chloride ions and the effects of the pore walls, the threshold pore radius for chloride transport was revised from 10 nm to 1.5 nm. As a result of these revisions, the amounts of chloride penetration into concrete with ordinary Portland cement in an airborne chloride environment could be reproduced more realistically than before by calculating the chloride transport amounts based on the pore connectivity and the water connectivity. On the other hand, micropore structures of nanometer size and the connectivity of the liquid water in them may be in the range not fully detectable by MIP or XCT. A future issue is to clarify the behavior of chloride transport in micropores of nanometer size and the liquid water in them.

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