

## Modeling of Chloride Ion Ingress and Liquid Water Movement in Mortars and Concretes with Low Water-to-Cement Ratio

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### ABSTRACT

This study aims to provide possible mechanisms for chloride ions ingress in low water-to-cement ratio materials. After discussions about applicability of the existing thermodynamic analytical system to low W/C materials, two main phenomena related to chloride ion ingress in nm-size pores were considered and installed to the existing system. First, it is assumed that chloride ion is unable to pass through pores which are smaller than the threshold radius as well as pores which have inkbottle shapes. In the second phenomenon, it is considered that water movement may stop at a certain depth once the reacting friction and the acting pore water pressure is in equilibrium. To verify the proposed models, salt water immersion tests with low W/C mortars were carried out. With the comparison of analytical results with experiments, the applicability of the proposed models was verified.

**Keywords.** Chloride ion, Liquid water movement, Low W/C, Thermodynamic model, Immersion test

### INTRODUCTION

The framework to verify the durability performance on corrosion initiation due to chloride ion has been installed according to standard specifications (JSCE 2007). And it was adopted to the actual designs of concrete structures in Japan. Basic idea for predicting chloride ion ingress in the current standard is based on the Fick's diffusive law, but it is suggested that the simple diffusive law may not directly be applicable to low W/C materials. It has been reported that chloride ion distributions of a bank protection structure using fly-ash does not change with elapsed time (Oshiro *et al.* 2002) and that behavior cannot be explained only by simple diffusive law.

Meanwhile, Okazaki *et al.* (2006) discussed about the force balance between pore water pressure and reacting friction, and they suggested that water saturation can stop at a certain depth due to the equilibrium of force in the concrete which has high resistivity against mass transfer. Besides, based on this remark, Author *et al.* (2010) showed experimental results which indicates that the depth of chloride ion ingress can be strongly related to the degree of

saturation in water. The understanding and achievements which have gained from the previous research have provided that the other mechanisms than the traditional advection-diffusion law need to be considered for predicting the chloride movement in high quality concrete materials.

In this study, focusing on the phenomena in nm-size pores which are dominant in high quality concrete, new models were established and installed to the existing thermodynamic analytical system, called DuCOM, which simulates material behaviors of concrete along from its hardening stage to deterioration (Meakawa *et al.* 2008). Both chloride ion movement model and liquid water transport model were modified to achieve the high resistivity to chloride ion ingress in dense cement hydrates matrix. The proposed models were verified with the series of experimental data.

## APPLICABILITY OF EXISTING MODELS

**Existing chloride ion transport model.** First, the applicable range of existing system should be discussed. In the thermodynamic analytical system (Maekawa *et al.* 2008), each of the capillary and gel porosity distributions is represented by a simplistic Raleigh-Ritz distribution function as

$$V(r) = 1 - \exp(-Br), \quad dV(r) = Br \exp(-Br) d \ln r \quad (1)$$

where  $V(r)$  is the fractional pore volume of the distribution up to pore radius,  $r$  [m], and  $B$  is the porosity distribution parameter [1/m], which represents the peak of porosity distribution on a logarithmic scale. If we assume a cylindrical pore shape in such a distribution, the pore radius with which the equilibrated interface of liquid and vapour is created,  $r_c$  [m], can be calculated with the following equation.

$$r_c = C \cdot r_s = -\frac{2C \cdot \gamma \cdot M}{\rho \cdot RT} \frac{1}{\ln h}, \quad C = 2.15 \quad (2)$$

where  $C$  is the coefficient for considering the thickness of adsorbed water,  $\gamma$  is the surface tension of the liquid [N/m],  $M$  is the molecular mass of the liquid [kg/mol],  $\rho$  is the density of liquid water [kg/m<sup>3</sup>],  $R$  is the universal gas constant [J/mol · K],  $T$  is the absolute temperature [K], and  $h$  is the relative humidity. Assuming that all the pore of radii smaller than  $r_c$  would be filled with water, by integrating the pore volume that lies below pore radius  $r_c$  in a porosity distribution  $V(r)$ , we can obtain an expression of saturation degree  $S_c$  given by equation as

$$S_c = \int_0^{r_c} dV(r) = 1 - \exp(-Br_c) \quad (3)$$

In the existing model, the volume of entrapped water in ink-bottle-shaped pores is also considered and the equivalent degree of saturation is expressed with  $S_{ink}$ , with which arbitrary temperature and relative humidity history can be considered (Ishida *et al.* 2005). Accordingly, the total degree of saturation  $S_{tot}$  is given as the summation of  $S_c$ ,  $S_{ink}$ , and  $S_{ads}$ , which represents the adsorbed water content.

$$S_{tot} = S_c + S_{ink} + S_{ads} \quad (4)$$

Hence, total water content in unit cement paste volume  $W$  [m<sup>3</sup>/m<sup>3</sup>] is expressed with the equation as

$$W = (\phi_{cp} + \phi_{gl}) \cdot S_{tot} \quad (5)$$

where  $\phi_{cp}$  is the total capillary porosity and  $\phi_{gl}$  is the total gel porosity. Based on this water volume, total chloride ion flux in cement matrix is expressed as

$$J_{ion} = -\left(\frac{W}{\Omega} \cdot \delta \cdot D_{ion}\right) \cdot \nabla C_{ion} + W \cdot \mathbf{u} \cdot C_{ion} \quad (6)$$

where  $J_{ion}$  is the flux of the chloride ions [mol/m<sup>2</sup>.s],  $\Omega$  is the tortuosity,  $\delta$  is the constrictivity,  $D_{ion}$  is the diffusion coefficient [m<sup>2</sup>/s],  $C_{ion}$  is the molar concentration of chloride ion in the liquid phase [mol/m<sup>3</sup>],  $\mathbf{u}$  is the velocity vector of a solution flow in pores [m/s]. The first term represents the flux of chloride ion due to diffusion by concentration gradient and the second term represents the advection constituent in chloride ion flux. It should be noted that, in this chloride ion transport model, two different porosities,  $\phi_{cp}$  and  $\phi_{gl}$ , are simply summed up (in Eq.5) despite each porosity has size distribution along logarithmic scales.

**Existing liquid water movement model.** Liquid water movement is strongly related to the chloride ion ingress, so model modification regarding liquid water should be discussed also. In the existing thermodynamic system, flux of liquid water in pores  $q_l$  [kg/m<sup>2</sup>.s] is expressed as Eq.7 by integrating the water flux in the pores whose sizes are smaller than radius  $r_c$  at a porosity distribution  $V(r)$ .

$$q_l = -\frac{\rho\phi^2}{50\eta} \left(\int_0^{r_c} r dV\right)^2 \nabla P = -K_l \nabla P \quad (7)$$

where  $\eta$  is the viscosity of the fluid [Pa.s],  $K_l$  is the water permeability coefficient [kg/Pa.m.s],  $P$  is the pore pressure [Pa]. Unsaturated state in porous media is considered in the model with the integration process in Eq.7.

**Analyses with existing model.** Sensitivity analyses about chloride ion ingress were conducted with the current analytical system. Concretes with different W/C in typical mix proportions were simulated to be exposed to the 3% NaCl solution. Before expositions, 1-day seal, 6-day water and 21-day atmospheric curing conditions were set in the simulations. Figure 1 shows the apparent diffusion coefficient ( $D_a$ ) calculated from the simulated chloride ion distribution at 1 year and 15 years exposition age. The equation in the JSCE standard (2007), which is formulated as an average of past measurements, is also shown in Figure 1 for referring the  $D_a$  gradient with W/C change. As a result of simulations, it was shown that

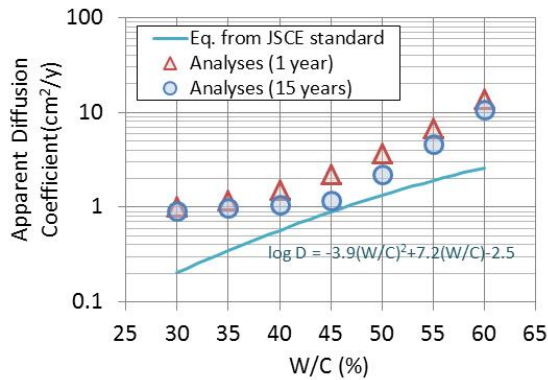


Figure 1.  $D_a$  with existing model

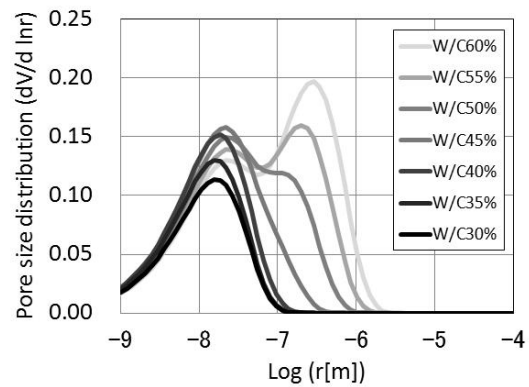


Figure 2. Pore size distributions

$D_a$  does not change significantly with W/C in low W/C range, while analyses in the range more than 40% can trace the gradients of actual measurements reasonably. Simulations for chloride ion ingress should be improved especially at the lower W/C.

Figure 2 shows the calculated pore size distribution as the summation of capillary pores and gel pores with the pore structure formation models. At higher W/C, two peaks exist significantly in pore size distributions. Generally, the larger one represents the peaks of capillary pores and the smaller one is for gel pores. Then, it can be seen that both volumes and peak radius of capillary pores decreases with W/C, hence the dominant pore sizes in distributions slides from several hundred nm to several nm. This might affect the chloride ion behaviors. But in current models, the effect of such a dominant size transition on the chloride ion ingress is not well considered based on nm-scale phenomena. For instance, in Eq. 3 and Eq. 7, the lower limits of integration range are zero, and it means that chloride ion and liquid water can move through any tiny pores. Size dependent phenomena, especially focusing on the nm-size pores, should be considered more effectively.

## MODEL MODIFICATION

**Consideration of the threshold value for chloride ion movement.** Based on the discussion in the previous section, models related to the nm size phenomena were installed to the existing system. In the previous study, Goto *et al.* (1982) suggested that ions cannot penetrate through the pores whose radii are smaller than specific size according to the electrical interaction between ions and pore walls. Yoshida *et al.* (2008) pointed out that the trends of mass transport in porous media can change with the boundary pore size, and the size is thought to be several dozens of nm.

From those idea, in this study, threshold value for chloride ion movement in pore water,  $r_{thre}$  [m], were considered. It was assumed that chloride ion is unable to pass through the pores which are smaller than  $r_{thre}$  even if the pores are saturated with water. The water in extremely small pores is thought not to be active for the chloride ion movement.

The threshold radius  $r_{thre}$  was installed to the chloride ion transport model as modified water content available for chloride movement (Figure 3). First, the water volume existing in the pores whose radii are smaller than  $r_{thre}$  (expressed as  $W_{thre}$  [m<sup>3</sup>/m<sup>3</sup>]) is formulated in the following equation.

$$W_{thre} = \phi \cdot S_{thre} = \phi \cdot \int_0^{r_{thre}} dV = \phi \cdot \{1 - \exp(-Br_{thre})\} \quad (6)$$

Where,  $S_{thre}$  is the equivalent degree of saturation for the  $W_{thre}$ . And the water volume existing in the ink-bottle pores which are connected to those pores can be formulated as follows referring the study by Ishida *et al.* (2005).

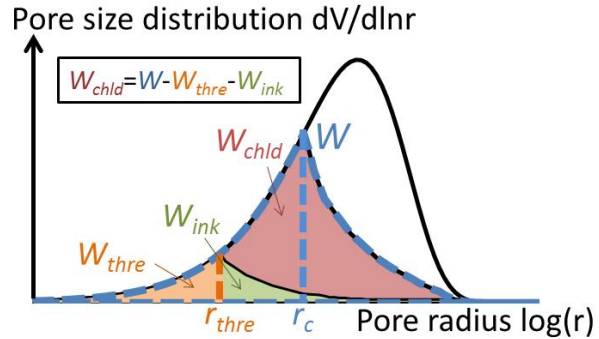


Figure 3. Water content in pore size distributions

$$W_{ink} = \phi \cdot S_{ink} = \phi \cdot (-S_{thre} \cdot \ln S_{thre}) \quad (7)$$

where  $W_{ink}$  is the water content in the ink-bottle shaped pores connected to the pores for  $W_{thre}$ . As a result, the total water content available for chloride ion movement,  $W_{chld}$ , is expressed as

$$\begin{cases} W_{chld} = W - W_{thre} - W_{ink} & (r_c \geq r_{thre}) \\ W_{chld} = 0 & (r_c < r_{thre}) \end{cases} \quad (8)$$

Using this modified water content,  $W_{chld}$ , which consider the threshold radius for chloride ion movement, chloride ion transport model was modified as

$$J_{ion} = -(W_{chld} \cdot \delta \cdot D_{ion}) \cdot \nabla C_{ion} + W_{chld} \cdot \mathbf{u} \cdot C_{ion} \quad (9)$$

Tortuosity parameter  $\Omega$ , which has been introduced for considering the great diffusion restraint in the dense cement matrix which has smaller porosity, was removed in Eq.9. This is because consideration of threshold radius  $r_{thre}$  can include the effect which had been expressed by tortuosity parameter in the direct way based on the physical and chemical phenomena in nm-size scale.

The practical value of  $r_{thre}$  for ordinary Portland cement (OPC) was decided by sensitivity analyses using an experimental result by Sugiyama *et al.* (2003). 1-year-long salt water immersion tests with W/C-30% concrete were simulated with various  $r_{thre}$  values from 1 nm to 40 nm. Figure 4 shows the simulated chloride ion distributions under those  $r_{thre}$  values and, by comparing the analytical results with experiment, 10 nm seems to be suitable for OPC.

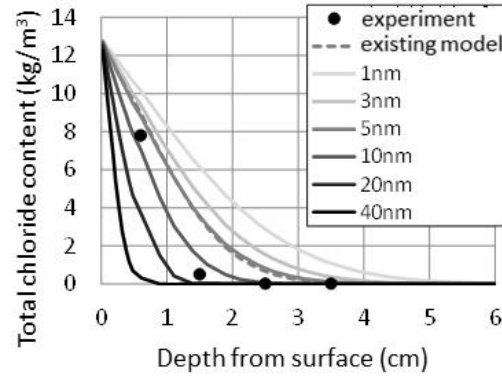


Figure 4. Results of sensitivity analyses for  $r_{thre}$

Once  $r_{thre}$  is decided, equivalent relative humidity can be calculated with Eq. 2. In the case that  $r_{thre}$  is 10 nm, corresponding relative humidity is around 80%, therefore chloride ion cannot move in the pores which relative humidity is under 80% on the analyses. This threshold RH value needs to be verified to enhance the validity of the proposed model.

**Considering the friction force between pore water and wall.** By Okazaki *et al.* (2006), it was shown that liquid water movements in high quality concrete behave as the non-Darcian flows. With non-Darcian behavior, liquid water penetration was suggested to stop at certain depth in dense materials. It is caused by force balances between friction force and water pressure and the equilibrium is expressed as Eq.8 assuming cylinder-shape pores.

$$\tau_{yield} = \frac{r_{lim}}{2} \cdot \nabla P \quad (8)$$

where  $\tau_{yield}$  is the constant for the friction at pore surface [N/m<sup>2</sup>],  $r_{lim}$  is limit pore radius [m], and  $P$  is the water pressure in pores [N/m<sup>2</sup>]. When  $\tau_{yield}$  is fixed, limit pore radius  $r_{lim}$  which is effective for water movement can be calculated under certain gradient of pore pressure. And  $r_{lim}$  was considered in water permeability coefficient ( $K_l$ ) as the lower limit of integration as Eq.9 and Figure 5.

$$\begin{cases} K_l = \frac{\rho\phi^2}{50\eta} \left( \int_{r_{lim}}^{r_c} r dV \right)^2 & (r_c \geq r_{lim}) \\ K_l = 0 & (r_c < r_{lim}) \end{cases} \quad (9)$$

With Eq.9, it can be considered that water in tiny pores whose radii are smaller than  $r_{lim}$  does not move in spite of the pore water pressure. When liquid water permeates into unsaturated concrete materials, water pressure gradient are formed along the depth from surface and, generally, the gradient becomes smaller with the increments of the depth. This leads to the increase of  $r_{lim}$ , and, at certain depth,  $r_{lim}$  reaches to  $r_c$ , which means that the stagnation of water saturation can be achieved with the proposed model. The  $\tau_{yield}$  value for OPC was set as 4.0 [N/m<sup>2</sup>] in this study referring the study by Okazaki *et al.* (2006). Values for other cement types or admixtures should be decided experimentally in near future.

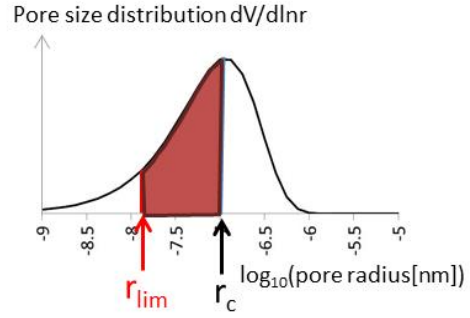


Figure 5. Water content related to the permeability coefficient

Thus, chloride ion transport model and liquid water movement model are modified and integrated into existing analytical models to realize the advanced simulations for chloride ion ingress in high quality concrete materials.

## VERIFICARTION

**Test methods and Analytical conditions.** To verify the proposed models, experiments with mortar specimens were conducted. 40mm\*40mm\*160mm specimens were made with different W/C using OPC. Mix proportions for each W/C are shown in Table.1. After 1 day sealing, specimens were sunk into water until 28 days. And after 1 day drying at 20°C-RH60% atmosphere, some faces of specimens were coated with epoxy.

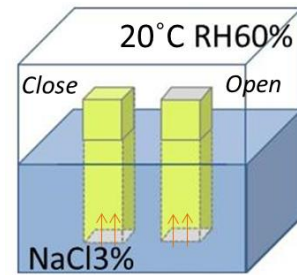


Figure 6. Test image

Coated specimens were put into the 3% NaCl solution vertically in 2 exposing conditions, i.e. *Close* condition and

Table 1. Mix proportions for experiments

|     | Unit Weight [kg/m <sup>3</sup> ] |        |      | SP/C [%] |
|-----|----------------------------------|--------|------|----------|
|     | water                            | Cement | sand |          |
| N20 | 233                              | 1165   | 1000 | 3.5      |
| N30 | 293                              | 976    | 1000 | 3.0      |
| N40 | 336                              | 840    | 1000 | 0.0      |
| N50 | 369                              | 737    | 1000 | 0.0      |

*Open* condition (Figure 6). Chloride ions can ingress upward from the bottom surface of the specimen. In *Close* condition, other 5 surfaces than penetration surface are coated with epoxy. In *Open* condition, penetration surface and the opposite surface are opened and other 4 faces are coated with epoxy, therefore at the upper surface, moisture can interact between specimens and exposed atmosphere (20°C-RH60%). It was expected that moisture distributions in the specimens might change due to the boundary conditions and behaviors of chloride ion also can be changed with the exposed conditions.

In this study, the chloride ion distributions were measured at 1 year test age. Specimens in the low W/C were thought to have extremely high resistance against chloride ion ingress, so, finer measurements of chloride ion distribution seemed to be needed. Grinder was used for this purpose to collect sample powders. Specimens were fixed and grinded at 1-3 mm interval with vacuuming the powder (Figure 7). With this method, quick sampling in such a fine pitch was realized. Then the chloride ion amounts in collected powders were measured by potentiometric titration tests using  $\text{AgNO}_3$  solutions.

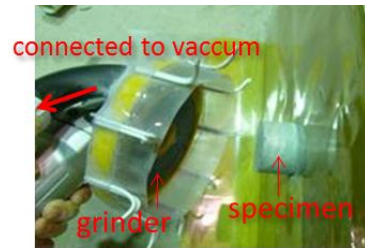


Figure 7. Grinder method for powder sampling

After grinding the specimens for the chloride measurement, 5-mm-size samples were picked from the middle of the specimen using hammers for pore structure measurements by mercury intrusion porosimetry (MIP) tests. The samples are soaked into acetone for 24 hours and drying at D-dry condition for 24 hours before measurements.

To simulate above experiments, one-dimensional analyses about chloride ion ingress were carried out. The same size of the specimens, mix proportions, curing conditions, and exposing conditions are set as input parameters and simulated with both existing model and proposed model.

**Test results.** Measured chloride ion distributions in all 8 specimens at 1 year age are shown in Figure 8, and simulated results with existing model and proposed model are shown in Figure 9 and Figure 10, respectively.

Detailed measurements were achieved successfully with the grinding method for sample collection and, from the results of the experiments, the depth of chloride ion ingress is

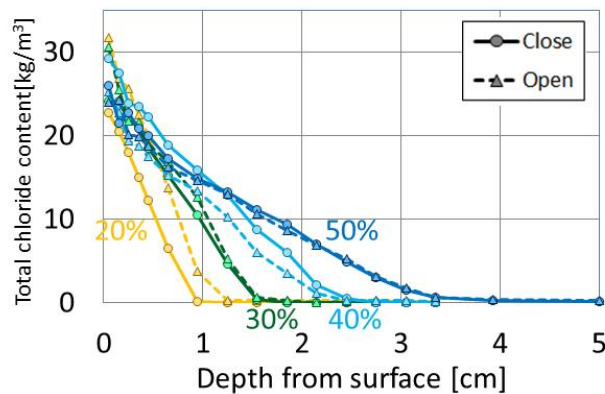


Figure 8. Measured chloride ion distribution

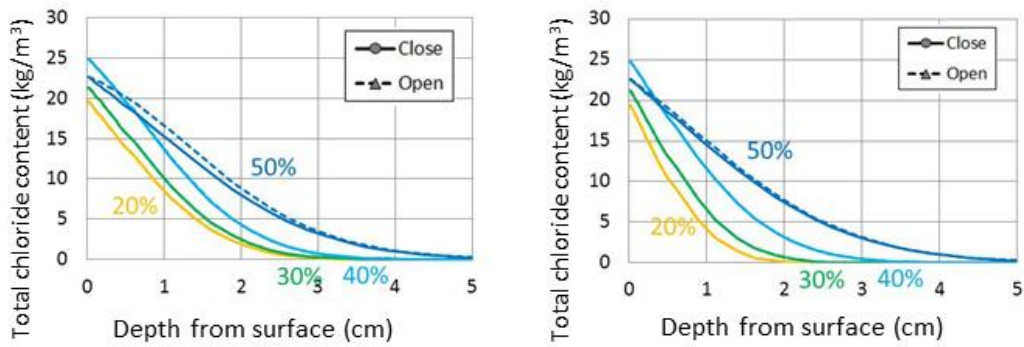


Figure 9. Results with existing model Figure 10. Results with proposed model

drastically reduced with W/C decrement. In the analyses with existing model, the results for W/C 40% and 50%, which has been often verified in previous study (e.g. Ishida *et al.* 2009), can follow the experimental trends, but for W/C 20% and 30%, which are the main focus in this study, the simulated depths of chloride ion ingress overestimate the actual ones. With the proposed model, simulated results for low W/C are improved clearly, while the applicability of the proposed models for high W/C is kept well as shown in Figure 10.

In the experimental results, slight gaps between different experimental conditions were observed. In low W/C specimens (20% and 30%), *Open* case have higher amounts of penetrated chloride ion than *Close* case, while high W/C specimens (40% and 50%) show reverse trends. One possibility for explaining these behaviors can be the balance between the internal relative humidity as the results of self-drying in the specimens and outer exposed relative humidity (60%). However, analytical results do not show such differences. The possibility of the effect of boundary condition will be validated with the measurements at different experimental ages.

Figure 11 shows the measured pore size distributions by mercury intrusion porosimetry (MIP). Clear densification in the cement rich materials were observed in the experimental results. The peak radius decreases with W/C and the total pore volume also decreases from 50% to 30% significantly. For the case of 20%, total volume of pores is relatively larger than other W/C cases. Figure 12 shows the simulated pore size distributions as a summation of capillary pores and gel pores with the proposed model. The peak radii and total pore volumes are almost same as measured results for 30-50% cases; thus, the analytical system can simulate the actual pore size distributions properly. There is a gap between experiment and

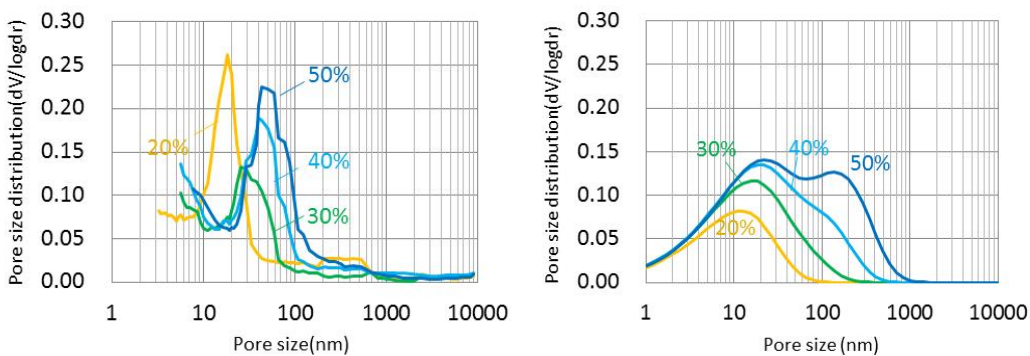


Figure 11. Measured pore size distributions Figure 12. Simulated pore size distributions



analysis in the total pore volume for the case of W/C 20%. However, taking into account the fact that the analyses of chloride ion ingress fit to the experimental results, the validity of simulated pore size distribution cannot be ignored. Some more experimental works and analyses are needed on this aspect. It will be done in the future works.

## CONCLUSION

In this study, phenomena which strongly affect the transport of chloride ion in nm-size pores of cement-based materials are studied, and the associated theories were installed into the current analytical system (DuCOM). At the beginning of this study, the evaluating the applicability of existing models (chloride ingress and moisture transport) in the system makes it clear that the models need to be improved especially for low W/C range, where the dominant size of pores is in the nm range. Then two phenomena were considered for the modification. Threshold pore radius for the chloride ion movement was considered as the first phenomenon. Water content for the chloride ion transport was modified and the necessary parameter value was decided by comparing the results of sensitivity analyses with experimental data. In the second phenomenon, a model for friction force between pore wall and pore water was formulated and installed to the equation for the water permeability coefficient based on the previous study. An accurate simulation on the transport of chloride ions into high quality concrete was targeted by incorporating the proposed models into the system.

The salt water immersion test and micro-structure measurement were carried out to verify the proposed models. The chloride profile was measured by powder sampling method with grinder and vacuum as a function of depth. The experimental results show that the chloride ion distributions close to the boundary are significantly influenced by W/C. By comparing simulated results to experimental data, it can be inferred that the proposed analytical system can potentially be applied at low W/C cement-based materials for chloride ingress and pore structure formation.

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