

Estimating Fractal Dimension of Cement Matrix for Predicting Chloride Ingress into Cement-Based Materials

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ABSTRACT

The durability performance of cement-based materials in service environments is affected by numerous factors, many of which involve attacks due to ionic transport, leading to reduced service life. The durability must be ensured in both an economically and environmentally responsible manner. Chloride-induced steel corrosion is a serious threat to the durability of reinforced concrete structures in marine environments, and the diffusion is the dominant transport mechanism of chloride ingress into concrete. Therefore, clear understanding of chloride transport mechanism, particular the diffusion path, is important for designing the durability performance of reinforced concrete structures. The purpose of this study is to determine tortuosity of cement-based materials and to predict the chloride ingress using the tortuosity values. The pore-structure model to obtain capillary pore was extended by introducing fractal dimension which represents microstructural complexity. The fractal dimension was determined by fitting experimental data to simulation results considering two types of C-S-Hs (low and high density) or two types of products (inner and outer), and it was used as tortuosity to determine effective diffusion coefficient of chlorides in the reactive transport model. The chloride ingress was simulated using the transport model and verified with experimental data for hydrated cement having water to cement (W/C) ratio of 0.5 and cured for 28 days. A good agreement between experimental data and simulated chloride profiles demonstrates that the diffusion path is influenced by presence of C-S-H types (HD-CSH and LD-CSH) and their pore structure characteristics.

Keywords: fractal dimension, tortuosity, calcium silicate hydrate (C-S-H), chloride ion, transport

1.0 INTRODUCTION

Chloride-induced corrosion is the one of the serious durability problem in reinforced concrete structures exposed to marine environment (Malhorta 2000). The chloride ions are penetrated the cover concrete via diffusion (Yu and Page 1991). Several factors influence the interaction and transport of chloride in cementitious materials (Samson and Marchand 2007; Johannesson *et al.* 2007; Hosokawa *et al.* 2011; Glasser *et al.* 2008). The chemical interaction of chloride with monosulfate forms Friedel's salt as chemical binding of chloride and physical adsorption on the surface of calcium silicate hydrate surface (C-S-H) retards further diffusion of chloride (Elakneswaran *et al.* 2010). In addition to the physical and chemical interaction of chloride with cement hydrates, pore structure parameters such as porosity, pore size distribution, and tortuosity can significantly affect the transport of chloride. The effect of porosity on the diffusion of chloride in cementitious materials is well known, and our recent

research has studied the impact of tortuosity on chloride diffusion in cementitious materials (Hatanaka *et al.* 2017). The tortuosity of hydrated cement paste was determined from the diffusivity and porosity of C-S-H. The C-S-H in the hydrated cement can be considered as low-density (LD) and high-density (HD) C-S-H (Tennis and Jennings 2000). It has been reported that pore connectivity and porosity of C-S-Hs controls the diffusion of ions in the cement matrix (Bejaoui and Bary, 2007). The density of the C-S-H may affect the pore characteristics and then ionic diffusion. Therefore, it is necessary to propose appropriate tortuosity values considering the type of C-S-H in cementitious materials for different W/C. In this study, fractal dimension, which represents the tortuosity, was estimated by extending the pore structure model proposed by Maekawa, *et al.*, 2003. The estimated fractal dimension or tortuosity was used in the reactive transport model to predict chloride ingress. The predicted chloride profiles were compared with experimental data.

2.0 MATERIALS AND METHODS

2.1 Materials and sample preparation

Hydrated cement paste (HCP) was prepared with water to cement ratio (W/C) of 0.5 and 0.7. The prepared samples were cured in water for 28 days and 91 days until to perform experiments.

2.2 Experiments

Pore size distribution of HCP was measured using Differential scanning calorimetry (DSC). Approximately 28 mg of sample was dried at 105 °C for 24 hrs and immersed in water for 3 hrs. After immersion, water adhered on the sample surface was wiped off and the samples were placed in an aluminium sample pan. Alumina powder was used as a reference specimen during measurement. The measurement range was 10 °C to -60 °C, and the scanning speed was 2 °C/min. The total moisture content was determined by the weight differences between measurements at 20 and 105 °C. Thermoporometry theory was used to determine the pore size distribution (Brun *et al.* 1977).

Electron probe microanalyzer (EPMA) is used to determine the chloride profile in the sample. The cylindrical samples were cut into two halves and coated with epoxy resin all the surface except cutting face to ensure one direction of chloride penetration. The prepared samples were exposed to 0.5 mol/L chloride solution for 28 days. After exposure, the specimens were cut into two halves parallel to the path of ionic ingress; one part was used for EPMA mapping while the other was used to determine the amount of chloride by a traditional method. The chloride profile was calculated from the mapping but was expressed as X-ray counts of chloride. The counts were corrected by the determining the chloride concentration from a wet analysis as described in Japanese Industrial Standard (JIS) A 1154.

2.3 Modelling approach

Pore structure model proposed by Maekawa *et. al.*, 2003 is modified to determine fractal dimension of HCP. In the model, inner product forms within the original volume of reacting cement grains while outer product forms in the originally water-filled spaces. The capillary porosity at location, x , is proportional to pore size, r , as:

$$\varphi_c(x) = \frac{r}{D+r} = \left(\frac{\varphi_{ou}}{\delta_{max}}\right)x \quad (1)$$

where, $\varphi_c(x)$ is the capillary porosity at location x ; D is the size of CSH grains (19 nm); r is the capillary pore size; φ_{ou} is the porosity at the extreme radius of the unit cell; δ_{max} is the distance between the extreme radius of unit cell and original boundary.

Accumulated volume of capillary pore formed up to the distance x is calculated by integrating porosity with respect to location as:

$$V_x = \int_0^x \varphi_c(x)4\pi(x+x_0)^2 dx \quad (2)$$

where x_0 is the size of un-hydrated core.

In this model, porosity of inner product is assumed to be constant, and outer product is varying linearly. Both inner and outer products of C-S-H contribute to the ionic transport. Thus, the proposed model is extended by introducing fractal dimension, F , as:

$$\varphi_c(x) = \frac{r}{D+r} = \left(\frac{\varphi_{ou}}{\delta_{max}}\right)x^{3-F} \quad (3)$$

The size of un-hydrated core is determined from hydration degree as (Igarashi *et al.*, 2007):

$$x_0 = \frac{1-\alpha}{1+0.05\alpha} \quad (4)$$

Combining Eqs. (1) – (4) yield the expanded pore structure model as:

$$V_x = \int_0^x \varphi_c(x)4\pi(x+x_0)^2 dx = 4B\pi \left\{ \frac{1}{6-F} A^{\frac{6-F}{3-F}} + \frac{2x_0}{5-F} A^{\frac{5-F}{3-F}} + \frac{x_0^2}{4-F} A^{\frac{4-F}{3-F}} \right\} \quad (5)$$

$$A = \frac{1}{B} \frac{r}{D+r}, \quad B = \frac{\varphi_{ou}}{\delta_{max}}$$

An integrated thermodynamic model considering ion-ion and ion-solid interactions was used to simulate multi-ionic transport. The model was implemented in the PHREEQC geochemical code using phase-equilibrium, surface complexation, and multi-component diffusion (MCD) modules (Parkhurst and Appelo 1999). Thermodynamic properties for various phases and minerals present in the cement system were collected from CEMDATA07 (Lothenbach *et al.* 2008) and other sources (Myers *et al.* 2014) and converted into a format suitable for PHREEQC. The converted data, together with the PHREEQC default thermodynamic database (Parkhurst and Appelo 1999), were used in this study for each calculation. The details of the integrated thermodynamic model are described elsewhere (Elakneswaran *et al.* 2010).

The diffusive flux of a selected ion, i , considering concentration and electrical potential gradients and the chemical activity effects can be expressed by Nernst-Planck equation as follows (Elakneswaran *et al.* 2010):

$$J_i = -D_{w,i} \left[\frac{\partial \ln(\gamma_i)}{\partial \ln(c_i)} + 1 \right] \frac{\partial c_i}{\partial x} + D_{w,i} z_i c_i \frac{\sum_{j=1}^n D_{w,j} z_j \left[\frac{\partial \ln(\gamma_j)}{\partial \ln(c_j)} + 1 \right] \frac{\partial c_j}{\partial x}}{\sum_{j=1}^n D_{w,j} z_j^2 c_j} \quad (6)$$

where $D_{w,i}$ is its diffusion coefficient, γ_i is its activity coefficient, c_i is its concentration, and z_i is its valance; the subscript j is introduced to show that these species are for the potential term.

The diffusion coefficient of ions in a porous medium, D_p , is related to $D_{w,i}$, porosity, ε , and tortuosity, τ , by Archie's law (Appelo and Postma 2009):

$$D_p = D_{w,i} \varepsilon^\tau \quad (7)$$

4.0 RESULTS AND DISCUSSION

4.1 Classification of C-S-H

It has been proposed that two types of C-S-H available in the hydration products, and they can be classified based on their densities as low-density C-S-H (LD C-S-H) and high-density C-S-H (HD C-S-H) (Tennis and Jennings 2000), which is similar to inner- and outer-product proposed by Maekawa *et al.* 2003. The pore structure in these C-S-Hs is different each other. As assumed in a previous study [Jennings 2008], pores are classified as one of two types: small gel pores (< 5 nm) and large gel pores (5– 10 nm). The HD-CSH consists of small gel pores while LD-CSH has large gel pores. Jennings has proposed an equation to determine the fraction of LD-CSH to the total mass of C-S-H (Tennis and Jennings 2000), and it is shown in Fig. 1 as function of hydration degree. The degree of hydration is calculated based on our previous study (Elakneswaran *et al.* 2016), shown in Fig. 2 for hydrating HCP with W/C of 0.5 and 0.7. HCP with W/C of 0.7 cured for more than 28 days has only LD-CSH and both HD- and LD-CSH are available in the paste with W/C of 0.5. Therefore, the pore structure of the C-S-H can control the diffusion characteristics of the paste.

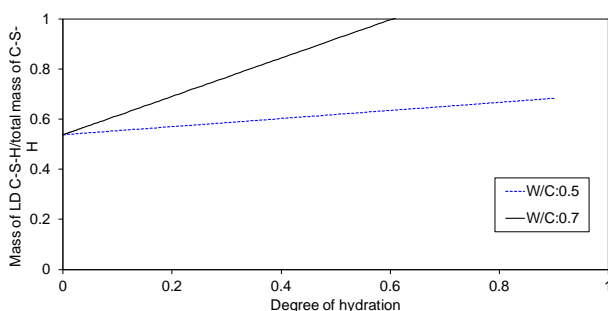


Fig. 1. Predicted fraction of LD C-S-H as a function of hydration degree

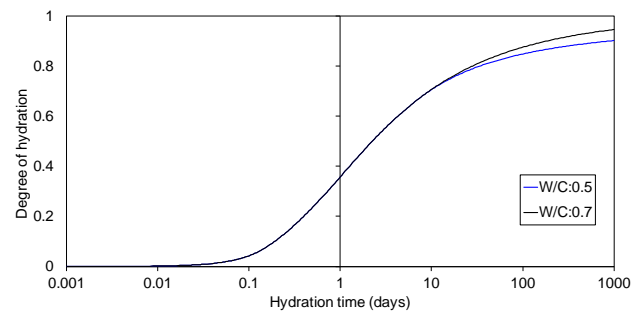


Fig. 2. Predicted hydration degree of HCP as a function of time

4.2 Pore size distribution

The pore size distribution of HCP as determined by DSC is shown in Fig. 3 for the samples cured at 28 and 91 days. As expected, the pore structure becomes finer and small in volume with the progress of the hydration and reduction of W/C. Combination with the results shown in Fig.1, the pore structure in the HCP with W/C of 0.7 corresponds to the pore of LD-CSH. However, both LD- and HD-CSH contribute to the pore size distribution in the HCP with W/C of 0.5. The dominant pore size, which is average value in the sample with W/C of 0.5 due to two types of C-S-Hs, controls the diffusion of ions in the HCP.

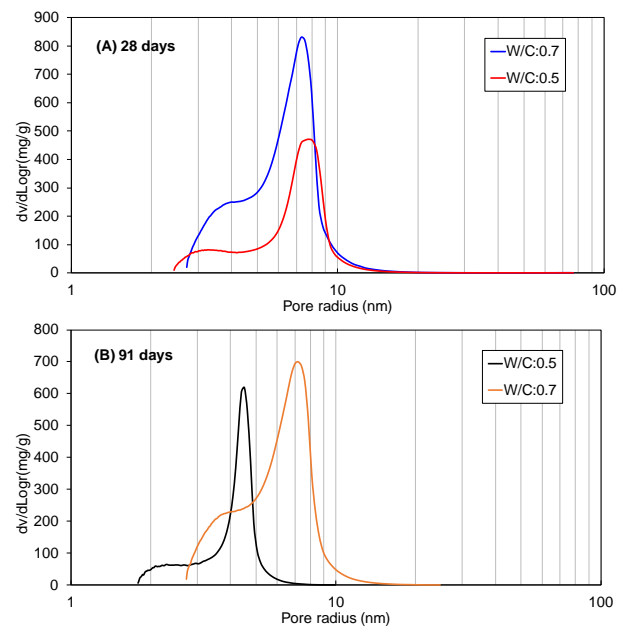


Fig. 3. Pore size distribution of HCP cured for, (A) 28 days; (B) 91 days

4.3 Fractal dimension of hydrated cement paste

Based on the results shown in Figs. 1 and 3, it is assumed that the pore structure distribution in the HCP with W/C of 0.7 is due to the pore structure of LD-CSH, and both HD- and LD-CSH pore structure attribute the pore size distribution of HCP with W/C of 0.5. Further, the size of pore in HD-CSH is less than 8 nm in diameter whereas pores of LD-CSH is

greater than 8 nm. The enhanced model (Eq. (5)) is used to predict the pore size distribution and the simulation results are fitted to experimental data to determine fractal dimension. The fitting results are shown in Fig. 4. The model fits the experimental data well except the HCP with W/C of 0.5 cured for 91 days. The determined fractal dimension for HD- and LD-CSH are tabulated in Table 1 together with porosity and dominant pore size. Fractal dimension of HD-CSH is higher than that of LD-CSH. As discussed previously, the fractal dimension is the indirect representation of tortuosity. The fractal dimension increases with the reduction of W/C and the increase of curing period, indicating the pore structure become tortuous as the HCP becomes dense. The estimated fractal dimension is used in Eq. (7) instead of tortuosity to predict the chloride diffusion in the HCP.

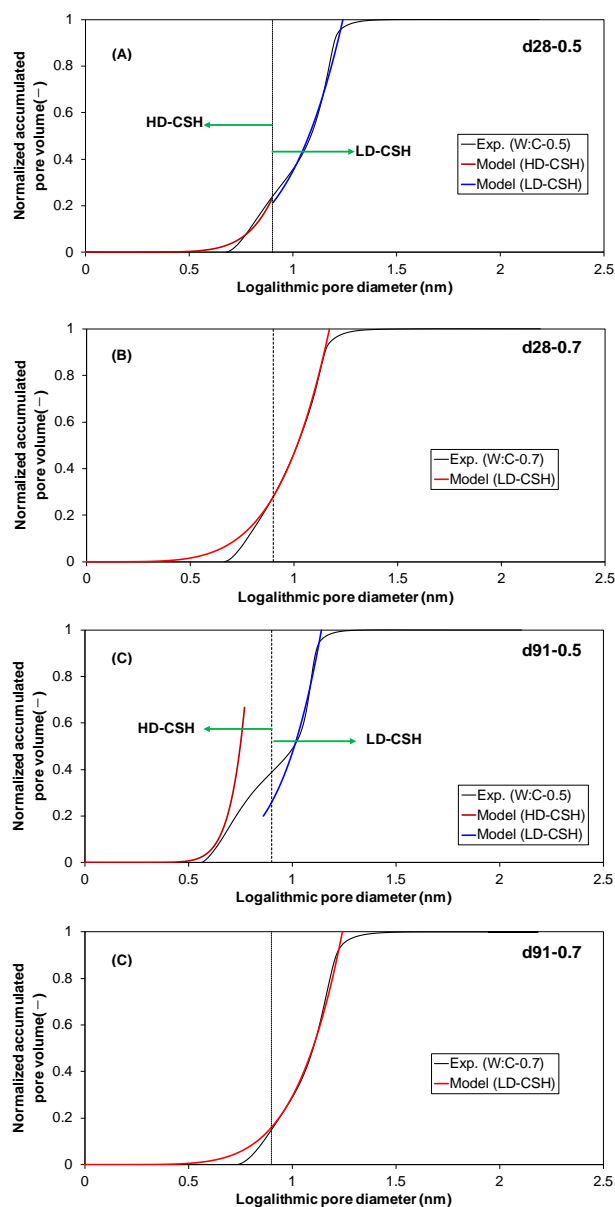


Fig. 4. Fitted pore size distribution of HCP, (A) W/C of 0.5 cured for 28 days, (B) W/C of 0.7 cured for 28 days, (C) W/C of 0.5 cured for 91 days, and (D) W/C of 0.7 cured for 91 days

Table 1. Estimated pore structure parameters

	28 days		91 days	
	W/C:0.5	W/C:0.7	W/C:0.5	W/C:0.7
Porosity	0.245	0.332	0.2	0.311
Dominant pore diameter (nm)	15	15	9	14
Fractal dimension, Ave.	2.80	2.75	2.85	2.80
-HD-CSH	2.85	-	2.90	-
-LD-CSH	2.75	2.75	2.80	2.80

4.4 Prediction of chloride ingress

One-dimensional multi-species reactive transport simulation was carried to predict the chloride ingress into HCP. The experimental conditions for chloride ingress, HCP samples exposed to 1 L of 0.5 mol/L NaCl for 28 days, were adopted for the simulation as well. The concentration of NaCl solution and zero flux were set respectively as initial and final boundary conditions. The pore solution concentration and the amount of hydrates required for the simulations were calculated based on a hydration model reported previously (Elakneswaran *et al.* 2016). The other pore structure parameters such as porosity, pore size, and tortuosity, necessary for the simulation are tabulated in Table 1. It is considered that chloride diffusion is controlled by C-S-H because the amount of C-S-H is more than 70% in volume. The chloride ions diffuse through a series of pores having various diameter. A cylindrical pore shape having a single size (given in Table 1) was assumed for the diffusion, which influences on the ionic diffusion. The simulated total chloride is compared with experimental data in Fig. 5. The chloride in free water of the pore solution, diffuse double layer, chemically bound as Friedel’s salt, and adsorbed on C-S-H surface contribute to the simulated total chlorides. The simulation result agrees well with experimental data indicates that the integrated model could reproduce the experimental data. Based on the experimental and simulation results, it can be inferred that diffusion path for chloride ions in both HD- and LD-CSH.

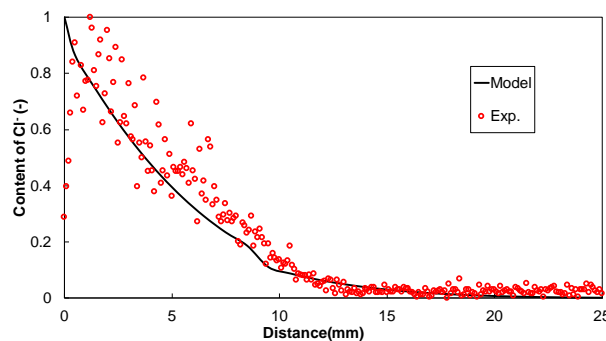


Fig. 5. Comparison of simulated chloride profiles with experimental data for HCP with W/C of 0.5 cured for 28 days

5.0 CONCLUSIONS

The fractal dimension, which is the indirect representation of tortuosity of cementitious materials, is determined by extending the pore structure model proposed in a previous study (Maekawa, 2003). The HCP with W/C of 0.7 has only LD-CSH and both HD- and LD-CSH are present in HCP with W/C of 0.5. The simulation results for the pore size distribution from the extended pore structure model were fitted to experimental data to determine the fractal dimension of HCP. Longer the curing period and lower the W/C increase the fractal dimension, indicates the pore structure become tortuous. The estimated fractal dimension together with porosity and dominant pore size were used to predict the chloride profiles in HCP. The simulation results are consistent with experimental data, suggesting that the path of chloride is in both HD- and LD-CSH in HCP of W/C of 0.5.

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References

- Appelo, C. A. J., & Postma, D., (2009). *Geochemistry, groundwater and pollution*: CRC Press Taylor & Francis Group.
- Bejaoui, B. S & Bary, B., Modeling of the link between microstructure and effective diffusivity of cement pastes using a simplified composite model, *Cement and Concrete Research* 37, pp.469–480 (2007).
- Brun, M., Lallemand, A., Quinson, J. F., and Eyraud, C., (1977). "A New Method for the Simultaneous Determination of the Size and Shape of Pores: The Thermoporometry." *Thermochimica Acta* 21(1), 59–88.
- Elakneswaran, Y. *et al.* (2010). "Ion-cement hydrates interactions govern multi-ionic transport model for cementitious materials." *Cement and Concrete Research* 40, 1756–1765.
- Elakneswaran, Y. *et al.* (2016). "Hydration Study of Slag-Blended Cement Based on Thermodynamic Considerations." *Construction and Building Materials* 124, 615–25.
- Glasser, F. P., Marchand, J., and Samson, E., (2008). "Durability of Concrete - Degradation Phenomena Involving Detrimental Chemical Reactions." *Cement and Concrete Research* 38(2), 226–46.
- Hatanaka, A., Y. Elakneswaran, K. Kurumisawa, T. Nawa, The Impact of Tortuosity on Chloride Ion Diffusion in Slag-Blended Cementitious Materials, *Journal of Advanced Concrete Technology* 15, 426 (2017)
- Hosokawa, Y. *et al.* (2011). "Development of a multi-species mass transport model for concrete with account to thermodynamic phase equilibrium." *Materials and Structures* 44, 1577–1592. characterisation of magnesium silicate hydrate gels. *Cement and Concrete Research*, 35(1):85-98.
- Igarashi *et al.*, Quantitative evaluation of spatial structure of constituent phases in cement pastes by second-order stereology, *Doboku Gakkai Ronbunshuu* Vol.63 No.3, pp.444-458 (2007).
- Jennings, H. M., (2008). "Refinements to Colloid Model of C-S-H in Cement: CM-II." *Cement and Concrete Research* 38, 275–89.
- Johannesson, B., Yamada, K., Nilsson, L. O., and Hosokawa, Y., (2007). "Multi-Species Ionic Diffusion in Concrete with Account into Interaction between Ions in the Pore Solution and the Cement Hydrates." *Materials and Structures* 40 (7), 651–65.
- Lothenbach, B. *et al.* (2008). "Thermodynamic Modelling of the Effect of Temperature on the Hydration and Porosity of Portland Cement." *Cement and Concrete Research* 38 (1), 1–18.
- Maekawa, K., Ishida, T., and Kishi, T., (2003). "Multi-Scale Modeling of Concrete Performance." *Journal of Advanced Concrete Technology* 1(2), 91–126.
- Malhorta, V., (2000) "Durability of Concrete". *Corrosion*. R. W. Revie Ed., Wiley.
- Myers, R. J., Bernal, S. A., and Provis, J. L., (2014). "A Thermodynamic Model for C-(N-)A-S-H Gel: CNASH_{ss}. Derivation and Validation." *Cement and Concrete Research* 66, 27–47.
- Parkhurst, D. L., Appelo, C. A. J (1999). "A computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations." USGS report.
- Samson, E., Marchand, J. (2007). Modelling the transport of ions in unsaturated cement-based materials, *Computer & Structures*, 85, 1740-1756
- Tennis, P. D., and Jennings, H. M., (2000). "Model for Two Types of Calcium Silicate Hydrate in the Microstructure of Portland Cement Pastes." *Cement and Concrete Research* 30(6), 855–63.