A Capillarity-dependent Model for Prediction of Chloride Penetration Process into Concrete in Artificial Splash Test

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Abstract. In order to better simulate the penetration process of chloride ions in the splash zone of concrete, this paper modified existing chloride ion transport model on the basis of capillarity-dependent model under unsaturated and non-pressure conditions to make it applicable to the calculation of chloride flow flux. The artificial splash tests is firstly designed and conducted under varied conditions of water to cement ratio, splash time duration and splash period. Then the original chloride constitutive model is improved by enhancement of convection term calculation. At last, the authors simulate the chloride ions penetration process under different conditions by reasonable design of equivalent chloride and moisture boundary to verify the effectiveness of capillarity-dependent model.

1. Introduction

The deterioration of concrete due to chloride ions penetration and subsequent steel bar corrosion is a common problem and influences the durability of structures seriously. The area with a certain height above the sea level of the coastal concrete structures is called the splash zone. In this area, the boundary condition is very complicated and unsteady because moisture and chloride ion concentration are always in a rapid change and fluctuation. Chloride ions are more likely to invade the structure due to the capillary sorption and accumulation of ions in the surface with a cyclic wetting and drying state.

Many methodologies have been proposed to evaluate the durability of concrete structures exposed to marine environment including empirically and physically based models [1]. The empirical models are mainly based on the Fick’s law and the physical models are based on the mass conservation equation and nonlinear combination model of chloride ions. The physical models are most often adopted when calculating the chloride ingress in the splash zone, because it is easy to express the apparent diffusion coefficient and numbers of equations are proposed in previous researches [2-4]. Due to the cyclic drying and wetting condition, there mainly exist three methods to describe the boundary condition in the splash zone. The first one is using the normal distribution of boundary ion concentration. Another is adjusting the apparent transfer rate and the concentration coefficient. The third one is adopting the empirical model by adjusting the surface chloride concentration. However, the chloride ion intrusion in the splash zone is mainly affected by the non-stationary absorption, which is not considered in these models, making the calculation of water and ion transport difficult.

In this paper, the authors propose a capillarity-dependent model to calculate penetration process in the splash zone. The model is then verified by performing and simulating the artificial splash test.
2. Capillarity-dependent model

2.1. Constitutive model of chloride penetration

The chloride transport process can be modelled based on the initial modelling of cement hydration, multiscale pore structure and water transport model using the system of DuCOM [5]. The framework of the chloride penetration simulation is shown in figure 1.

\[ \frac{\partial}{\partial t} (\phi S C_{cl}) + \text{div} (J_{cl}) - Q_{cl} = 0 \]  

where $\phi$ is the porosity, $S$ is the liquid water saturation, $C_{cl}$ is the concentration of free chloride ions in the pore liquid, $J_{cl}$ is the chloride flux, $Q_{cl}$ is the sink term and $t$ is time. The flux term can be calculated as follows,

\[ J_{cl} = -\frac{\phi S}{\Omega} \delta D_{cl} \nabla C_{cl} + \phi SuC_{cl} \]  

where $\Omega$ is the pore tortuosity, $\delta$ is the constrictivity of the pore structure, $D_{cl}$ is the diffusivity of the chloride ions and $u$ is the flow rate of the pore liquid. The tortuosity can be calculated as,

\[ \Omega = -1.5 \tanh(8.0(\phi_p - 0.25)) + 2.5 \]  

where $\phi_p$ is the effective porosity which is the sum of capillary porosity $\phi_{cp}$ and gel porosity $\phi_{gel}$. The constrictivity represents the hinder effect due to pore radius change expressed as,

\[ \delta = 0.395 \tanh(4.0(log(r_{cp}) + 6.2)) + 0.405 \]  

where $r_{cp}$ is the peak radius of the capillary pores. $D_{cl}$ can be calculated as,

\[ D_{cl} = RT \frac{\lambda_{ion}}{Z_{cl} F^2} (1 + \frac{\partial \ln \gamma_{cl}}{\partial \ln C_{cl}}) \]  

where $Z_{cl}$ is the electric charge of the chloride ion (-1), $F$ is Faraday’s constant ($9.65 \times 10^4$ C/mol), $\gamma_{cl}$ is molar conductivity of chloride ions, $\lambda_{ion}$ is ion conductivity expressed as,

\[ \lambda_{ion} = \lambda_{25} \exp\left(-\frac{E_a}{R \left(\frac{1}{T} - \frac{1}{298}\right)}\right) \]  

where $\lambda_{25}$ is ion conductivity at 25 °C ($7.63 \times 10^{-3}$ Sm²/mol), $E_a$ is the activation energy for free pore fluid ($17.6 \times 10^3$ J/mol). In order to calculate $J_{cl}$, the convection term $\phi SuC_{cl}$ needs to be calculated in
which \( \phi \) and \( S \) can be obtained through microstructure model and moisture transport model, and the flow rate is calculated as,

\[
u = -K_l \nabla P / (\rho \phi S)
\]

where \( K_l \) is the liquid water permeability incorporating the effect of capillarity, expressed as [6],

\[
K_l = \psi \int_0^C r dV
\]

where \( \psi \) is a state-dependent structure parameter obtained by DuCOM system. The permeability can theoretically represent the chloride penetration process better than the conventional during drying-wetting cycles. In the process of chloride transport, the free ions may be adsorbed onto the pore wall by the charge force, therefore the \( Q_{cl} \) is determined by the adsorbed chlorides \( C_b \) which is expressed by a Langmuir form of equation as,

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

where \( C_b \) and \( C_f \) is the concentration of bounded and free chlorides respectively.

### 2.2. Modelling of chloride flux at surface

There exist two basic mechanisms in the transport of chloride ions from the outside of structures into the inside of the surface element, of which the first one is diffusion, driven by the difference between the internal and external concentration, and is expressed as,

\[
q_d = -E_{cl}(C_{cl} - C_s)
\]

where \( q_d \) is the diffusion flux of chlorides, \( E_{cl} \) is the surface conductivity (1.0\times10^{-3} \text{ m/s})], and \( C_s \) is the environmental concentration of chlorides. The second mechanism is adsorption, which refers to that the concentration of chloride ions on in the surface element is slightly higher than that in the environment due to the adsorption of ions by the cementitious material, expressed as,

\[
q_a = k_{cl}(\frac{C_{cl}}{0.51})^2 \exp(-1.15C_{cl})
\]

where \( q_a \) is the adsorption flux, \( k_{cl} \) is the adsorption coefficient which is 1.5\times10^{-3} \text{ (m/s)} for ordinary portland cement obtained by sensitivity analysis [7].

### 2.3. Boundary condition

The surface transport model of chloride ions is effective on the condition of immersed environment [8]. In this study the surface water content and chloride ion concentration in the environment changes according with the change of splash period. It is necessary to determine a reasonable way of setting boundary conditions to simulate the permeation process of chloride ions in the splash zone. Tang etc. [9] set a dynamic boundary distribution of chloride ion for the concrete zone above sea level expressed as,

\[
C_s = \bar{C}_s \exp(-3.0\tau_{cl})
\]

\[
\tau_{cl} = \frac{t - T_{s1}}{2T_m}
\]

\[
RH_s = \bar{RH}_s \exp(-3.0\tau_{RH})
\]

\[
\tau_{RH} = \frac{t - T_{m1}}{2T_m}
\]

where \( \bar{C}_s \) and \( \bar{RH}_s \) is the average concentration of environment chloride ions 1.03 mol/L and the average relative humidity 99.9% respectively, \( \tau_{cl} \) and \( \tau_{RH} \) is the chloride ion and moisture humidity
difference respectively, which are determined by actual splash period $T_{ms}$, and the curve over time of relative chloride concentration $C_s / C_s^*$ and relative humidity $RH_s / RH_s^*$ is shown in figure 2.

![Figure 2. Boundary concentration of chloride ion and humidity.](image)

3. Experient methods

The artificial splash experiment system is illustrated in figure 3. The NaCl solution is pumped through a PVC pipe by a small pump and sprayed above the concrete specimens using amounts of sprinklers to simulate the splash effect. The splash cycle, set as 2 hours and 4 hours in this study, is controlled by a timing valve. Each spray process lasts 1 minute to ensure a thin water film formed on the surface of the specimens. The parameters including water to cement ratio ($w/c$), splash period and time of experiment duration are varied as shown in table 1.

![Figure 3. Schematic of artificial splash experiment of concrete.](image)

| NO. | $w/c$ | NaCl concentration (%) | Period (hour) | Time duration (day) |
|-----|-------|-------------------------|---------------|---------------------|
| 1   | 0.50  |                         | 2             | 60                  |
| 2   | 0.57  |                         | 2             | 60                  |
| 3   | 0.57  | 6                       | 4             | 60                  |
| 4   | 0.57  |                         | 4             | 120                 |
| 5   | 0.57  |                         | 2             | 120                 |

4. Results and discussion

4.1. Analysis of experimental results

The results of chloride penetration test are shown in figure 4. Figure 4(a) shows that the chloride ion concentration increases with the increase of splash time duration. Figure 4(b) shows that the concentration near surface is larger for a larger splash period, which is caused by the severe drying-
wetting process in the splash zone. In a drying condition, the internal water tends to move towards the surface and a larger period leads to a longer drying time. Figure 4(c) show the w/c influence on the ion content and it is interesting that the chloride content is larger in the case of w/c = 0.5 than w/c = 0.57.

Similar results have been given by previous researcher Sandberg etc. [10] that a smaller w/c may result in a higher content of chloride ions which is cause by tiny cracks. Another possible reason is the material with a smaller w/c has a larger ratio of capillary porosity and thus leads to more sorption of chlorides according to the capillarity-dependent model.

![Figure 4. Mass percent of experimental chloride distribution.](image)

**4.2. Verification of penetration model**

The capillarity-dependent model is model is verified by numerical simulation and the results are shown in figure 5. The results indicate that the model can simulate the characteristic of chloride ion transport and distribution, especially in the long-time duration of splash that the ion migration to the surface with water and the concrete with a smaller w/c absorbs more ions.

![Figure 5. Mass percent of simulated chloride distribution.](image)

To further verify the capillarity-dependent model, the comparison with the traditional model [7] ignoring the capillarity is given in figure 6. The case of w/c = 0.57 and 0.5 are simulated respectively. For the case of w/c = 0.57, the new model can better simulate the distribution of chloride ion with the depth under the condition of splash while the comparison model gives a larger results than the experimental ones. For the case of w/c = 0.5, the new model has a better overall performance form the surface to the inner part of the specimen. The material with a larger w/c has a larger porosity and moisture gradient with a smaller saturation. The comparison model is controlled by saturation and cannot represent the high diffusivity of chloride ions. However, a larger moisture gradient makes a larger \( K_f \) which can lead to a larger chloride flux. When the w/c decreases, the material has a smaller porosity and moisture gradient and the convection term is very small making the simulated results have little differences relatively. In practical engineering project, the internal chloride ion is more likely to corrode.
the steel reinforcement therefore the capillarity-dependent model can better suit the engineering calculation.

Figure 6. Comparison of chloride distribution simulated by new and old models.

5. Conclusions
In this research, a new capillarity-dependent model is adopted to simulate the chloride ion penetration into unsaturated concrete in splash test. For the alternate wetting and drying condition in splash zone, the water sorption force has a strong effect on the transport and migration of chloride ions between surface and inner part of the concrete. The flow flux is calculated by the enhancement of permeability equation to effectively simulate the alternate saturated and unsaturated condition. This kind of approach is advantageous for splash zones of concrete in real environment.

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References
[1] Kim J., McCarter W.J., Suryanto B., Nanukuttan S., Basheer P.A.M., Chrisp T.M. (2016) Chloride ingress into marine exposed concrete: A comparison of empirical- and physically- based models. Cement and Concrete Composites, 72:133-145.
[2] Maheswaran T., Sanjayan J.G. (2004) A semi-closed-form solution for chloride diffusion in concrete with time-varying parameters. Magazine of Concrete Research, 56(6):359-366.
[3] Petcherdchoo A. (2013) Time dependent models of apparent diffusion coefficient and surface chloride for chloride transport in fly ash concrete. Construction and Building Materials, 38:497-507.
[4] Pack S., Jung M., Song H. (2010) Prediction of time dependent chloride transport in concrete structures exposed to a marine environment. Cement and Concrete Research, 40(2):302-312.
[5] Maekawa K., Chaube R., Kishi T. (1999) Modelling of Concrete Performance. Taylor &Francis Group, London.
[6] Han X., An X.H., Maekawa K. (2017) Hygro-Gradient Model for Permeability of Unsaturated Cementitious Composites. Journal of Advanced Concrete Technology, 15(8):407-425.
[7] Maekawa K., Ishida T., Kishi T. (2008) Multi-scale modeling of structural concrete. CRC Press, Boca Raton.
[8] Takahashi Y., Ishida T. (2016) Modeling of Chloride Transport Resistance in Cement Hydrates by Focusing on Nanopores. Journal of Advanced Concrete Technology, 14(11):728-738.
[9] Tang L. (2002) ClinConc model for prediction of chloride penetration into concrete—From the original to the latest modifications. International Conference on Durability of Building Materials and Components. In: International Conference on Durability of Building Materials & Components. Goteborg. pp:1-14.
[10] Sandberg P., Tang L., Andersen A. (1998) Recurrent studies of chloride ingress in uncracked marine concrete at various exposure times and elevations. Cement and Concrete Research, 28(10):1489-1503.