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# Modelling of chloride diffusion in saturated concrete

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**Abstract.** The process of chloride ingress in saturated concrete was presented by a previous study that used a mathematical model for the same as that concrete. This model is to be studied chloride ion diffusion which is considered as a chemical phenomenon and is to be represented the chloride diffusion process to be a nonlinear partial differential equation (PDE). In this paper, this nonlinear PDE is solved by the Kirchhoff transformation to render into a linear PDE. This linear PDE associated with initial and boundary conditions is also solved by the Laplace transformation to obtain an analytical solution. To verify the serviceability and reliability of this proposed method, the practical application should be supplied. The input parameters were cited from the previous study. The free chloride concentration profiles obtained by the analytical solution of mathematical model for saturated concretes after 24 and 120 hrs of exposure were compared with the previous study. The predicted results obtained from proposed method have a tendency with experimental results obtained by the previous study and trend toward numerical results approximated by finite difference technique.

**Keywords:** chloride concentration; chloride diffusion; chloride profile; mathematical model; saturated concrete; solution

## 1. Introduction

The capability of concrete or reinforced concrete (RC) structures to carry ions through the cement matrix is a momentous process that rules their durability (Glasser, *et al*. 2008; Yang and Liang 2009; Weng *et al*. 2012; Lee *et al*. 2012; Lin *et al*. 2013; Tsai *et al*. 2014) or service life. One of deterioration of RC structures is chloride-induced corrosion of the reinforcing steel due to high concentrations of chloride ions into concrete (Darmawan 2010; Jang *et al*. 2011; Guzmán *et al*. 2011). Chloride penetration is a complicated physical and chemical phenomenon comprising numerous factors, containing both the transport of chloride ions along with the water into concrete and the diffusion of chloride ions by way of pore water in concrete. The former progress transports more large amount of chloride ions than pure diffusion. The penetration of chloride ion is

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meaningfully affected by the physical and chemical binding of ions in concrete.

Both the adsorption and diffusion of gases and the absorption of liquid in unsaturated concrete are very crucial while the supreme transport process is probably to be molecular and ionic diffusion in saturated concrete at normal pressures. Sugiyama *et al*. (1996) determined chloride diffusion coefficient and gas permeability of saturated concrete by an accelerated electrical testing method. The chloride diffusion coefficient was found to be controlled by the water-to-cement ratio (w/c) with about 2.2 times higher chloride diffusion coefficient for concrete with the w/c of 0.6 as compared with that of w/c of 0.4. Gas permeability was largely affected by the degree of saturation of concrete. Climent *et al*. (2002) measured chloride diffusion coefficients through unsaturated concrete with controlled water content by an initial limit amount of $Cl^-$ to the tested concrete surface. The diffusion coefficients measured decrease about two orders of magnitude when the percentage of water saturation of concrete reduces from 80% to 30% approximately. Nevertheless, this decrease is more important for water saturation lower than 45%. Values of diffusion coefficient below $1\times10^{-13}\, m^2/s$ may be reached for concrete specimens in equilibrium with a 54% relative humidity atmosphere. Conciatori *et al*. (2008) used a numerical approach, named TransChlor which is based on finite elements and finite differences methods, to simulate transport phenomena of various substance in concrete. Water movement by capillary suction is modelled with kinematic equations. This movement is transformed into chloride ion movement caused by the chloride ion convection in water. The results indicate that the chloride ion concentration increases quickly in concrete cover when a structure is exposed to deicing salts at a mountainous location; while permeability of concrete cover is an insignificant parameter when the concrete is in direct or splash water contact. Nonetheless, fluid flow may happen at higher pressures. Song *et al*. (2008) studied factors influencing chloride transport in terms of the apparent diffusion coefficient (*D*) and the surface chloride concentration ($C_s$) in concrete structures exposed to a marine environment. They discovered that both $D$ and $C_s$ are time-dependent: $D$ and $C_s$ are remarkedably affected by concrete mix proportion, air void content in concrete, curing methods, degree of exposure to seawater and climate. Sugiyama *et al*. (2008) experimentally investigated and numerically modelled chloride penetration and calcium dissolution in saturated concrete. They established the simultaneous ion transport model (SiTraM) that permits the transport of chloride and calcium ions to be simultaneously simulated in a hydrated cement system. It was found that the SiTraM can prognosticate the profiles of chloride and calcium for self-compacting concrete. It was also revealed that the primary factor to control chloride penetration front and the dissolution front of $Ca(OH)_2$ was the pore structure characteristic of concrete. Pack *et al*. (2010) surveyed 11 concrete bridges exposed to a marine environment at 0.65-48.65 years in assessing their resistance to chloride transport through concrete in terms of diffusion. They found that the apparent diffusion coefficient (*D*) exponentially decreased with time and the surface chloride concentration ($C_s$) increased in the form of a logarithm function to time. Yuan *et al*. (2011) used numerical model to study chloride penetration into saturated concrete. The model was solved by the finite difference method by inputing parameters such as porosity, density, chemical composition of pore solution, diffusion coefficient, and chloride-binding isotherm. For a sample undergone non-steady-state migration/diffusion of chloride ion, the bound chloride will be different because chloride concentrations are different at different depths. As a result, pore structure and permeability are different. Accordingly, the chloride-migration/diffusion coefficients are depth-dependent not only because of electrochemical reasons but also because of changes in pore structure. Fraj *et al*. (2012) developed a new automatic experimental equipment to apply cyclic movement of chloride solution in controlled environmental conditions ambiance. They also used a new clever test method to control the concrete moisture content. Results revealed that blast furnace slag, used as partial substitution of cement, increases the performances of concrete. Moreover, the interaction between chloride and concrete matrix seems to increase the adsorbed water vapor. The results indicated that the decreasing of relative humidity from 90% to 50% enabled to increase by approximate 2-9 times the apparent chloride diffusion coefficient, which decreased when the number of cyclic increased. Wang *et al*. (2012) recommended a numerical procedure to prognosticate the chloride diffusion in a hydrating silica fume (SF) blended concrete. This numerical procedure includes a hydration model and a chloride diffusion model. In the hydration model, a numerical model is offered to simulate the hydration of concrete containing SF by regarding the producing of calcium hydroxide in cement hydration and the consumption of it in pozzolanic reaction. The contents of evaporable water, calcium hydroxide and porosity were acquired as assembly results of the hydration model and were adopted as input parameters for the chloride diffusion model. In the chloride diffusion model, the phsicochemical processes of diffusion of chloride ion in the aqueous phase of pores, the adsorption and binding in the solid phase of concrete, and the desorption are represented by a nonlinear partial differential equation. The estimated chloride penetration profiles in the hydrating SF blended concrete agree well with experimental results. Zhang and Zhao (2012) investigated on chloride ion diffusivity of concrete subjected to $CO_2$ environment. Results pointed out that carbonation depth is of a good linear relation with square root of carbonate time, and carbonation can make better compressive strength, but lower flexural strength. Results considering pore structure of concrete before and after carbonation have indicated that carbonation might cause a redistribution of pore sizes and increase the proportion of small pores. It also may diminish porosities. Results indicated that carbonation can accelerate chloride ion diffusion in concrete, and chloride ion diffusivity was increased due to carbonation action. This may be interpreted as the growing diffusivity of chloride ion excited by increased concentration gradient of chloride ion subjected to the release of Friedel's salt in the carbonated zone. Paul *et al*. (2014) carried out selecting concrete mixes considered different ratio of fly ash and slag to ordinary Portland cement. They input concrete parameters in virtual rapid chloride permeability test (RCPT) and obtain total charge passed through each concrete samples. They also applied Berke's law to calculate diffusion coefficients of chloride in concrete samples. Finally, they used a novel integrated approach of virtual RCPT with finite element method to predict the chloride penetration depth profiles of each concrete samples. Such an approach can actually provide a clear idea of the serviceability of a concrete structure laden in chloride environment. Nagesh and Bhattacharjee (1998) established a mathematical model that brightly distinguishes between the chloride diffusion process in saturated and unsaturated concrete. The chloride diffusion in saturated concrete belongs to Fickian diffusion process while the chloride diffusion in unsaturated concrete (Climent *et al*. 2002) is ascribed to the combination of capillary flow of solution with ionic diffusion. This model is a nonlinear partial differential equation (PDE). In order to obtain the approximate solution, Nagesh and Bhattacharjee (1998) first used Boltzmann’s transformation and then applied finite difference method. An experimental work is also suggested by them to determine the corresponding diffusion coefficients. The values of chloride diffusion coefficient obtained from the experimental method proposed by them are approached to those obtained from the Nagesh and Bhattacharjee's model.

In this paper, the mathematical model (Nagesh and Bhattacharjee 1998) related to the nonlinear PDE associated with initial and boundary conditions of chloride diffusion in saturated concrete was solved by the Kirchhoff transformation in conjunction with the Laplace transformation for obtaining an analytical solution. The values of chloride diffusion coefficient predicted by the proposed method will also compare with those results obtained by Nagesh and Bhattacharjee (1998). The present results will help for predicting the diffusion coefficients of chloride penetration into concrete in saturated state.

## 2. Theoretical model

### 2.1 Chloride ingress process

Nagesh and Bhattacharjee (1998) pointed out that the process of chloride ingress in unsaturated concrete obviously needs to be made different from that in saturated concrete. The driving force bringing about the ingress in the former contains: (a) capillary flow of solution, which is caused by capillary suction. (b) ionic diffusion owing to electrostatic field in combination with the concentration gradient.

Except these driving forces, the degree of solution saturation in unsaturated concrete is probably to increase with time at any point within a certain place. In addition, chloride is probably to attain physically and chemically bound to the cement hydrate. The driving force of capillary suction in saturated concrete is not existed and the degree of solution saturation is moreover probably to be uniform. A generally theoretical model for chloride ingress in unsaturated concrete is introduced following which the peculiar case of ingress in saturated concrete is also derived in the following passage.

### 2.2 Capillary flow

Neglected the effect of gravity and based on the extended Darcy's law for one-dimensional capillary flow in unsaturated porous media, volume rate of flow of solution per unit area of concrete $\left(q_s\left(m^3/m^2\sec\right)\right)$ can be expressed as

$$q_s = -D\left(C_s,\theta_s\right)\frac{d\theta_s}{dx} \tag{1}$$

where $D\left(C_s,\theta_s\right)$ is the solution diffusivity in $m^2/\sec$, $C_s$ is the free chloride concentration in $kg/m^3$ of the solution, $\theta_s$ is the solution saturation in $m^3$ of solution/$m^3$ of concrete, and $x$ is the relevant space coordinate in concrete continuum (m).

The flux of mass of chloride at any point in the concrete ($J_c$ in $kg/m^2\sec$) resulted from capillary suction accordingly can be stated as

$$J_c = C_s q_s = -C_s D\left(C_s,\theta_s\right)\frac{d\theta_s}{dx} \tag{2}$$

### 2.3 Chloride diffusion

Free chloride concentration in unsaturated concrete is probably to vary from point to point caused by differential spatial binding of chloride in concrete and moreover caused by different solution content of concrete. Therefore, the resulting concentration gradient generates diffusion from higher concentration to lower concentration. Neglected the effect of electrostatic interaction of cation on chloride diffusion process and based on Fick's first law, the equivalent ionic diffusion flux of chloride $J_d$, in $kg/m^2$ of concrete in unit time (*sec*), can be expressed in terms of

$$J_d = -D_d(C_v)\frac{dC_v}{dx} \tag{3}$$

where $D_d$ is the diffusion coefficient in $m^2/\sec$ and $C_v$ is the free chloride concentration in $kg/m^3$ of concrete.

### *2.4 Total flux*

The total flux of chloride in unsaturated concrete can be obtained from Eqs. (2) and (3) and expressed as

$$J = J_c + J_d = -\left[C_s D(C_s, \theta_s)\frac{d\theta_s}{dx} + D_d(C_v)\frac{dC_v}{dx}\right] \tag{4}$$

Both $C_s$ and $C_v$ in Eq. (4) are referred to free chloride concentrations and are not probably to migrate either in solution phase or owing to ionic migration. Nonetheless, measurement of free chloride concentration in concrete is generally performed on mass basis expressed in terms of *kg* of free chloride/*kg* of concrete. Indicating the mass basis free chloride concentration as $C_m$, where subscript *m* supports mass basis, the $C_s$ and $C_v$ in Eq. (4) can be put in the place of $C_m$.

Propose the density of concrete $\rho_c$ is constant (This means that the physical unit of $\rho_c$ is ignored.) , then

$$\theta_s = \rho_c \theta_{sm} \tag{5}$$

and

$$C_v = \rho_c C_m \tag{6}$$

It is needed to point out that the volume solution content of concrete ($\theta_s$) can be replaced by the easily measurable mass basis solution content ($\theta_{sm}$ in *kg* of solution/*kg* of concrete). The substitution of Eqs. (5) and (6) into Eq.(4) yields

$$J = -\left[\left\{D(C_s, \theta_{sm})\rho_c \frac{C_m}{\theta_{sm}}\frac{d\theta_{sm}}{dx}\right\} + \left\{\rho_c D_d(C_m)\frac{dC_m}{dx}\right\}\right] \tag{7}$$

Soliciting the mass balance condition, we know

$$\frac{dJ}{dx} = -\frac{dC_T}{dt} \tag{8}$$

where $C_T$ is the total chloride concentration (i.e., the sum of both bound and free chloride concentrations in $kg/m^3$ of concrete) and *t* is the time.

Assume the bound chloride concentration to be included in $\theta_s$. The total chloride concentration can be stated as

$$C_T = \alpha C_v = \alpha \rho_c C_m \tag{9}$$

where $\alpha$ is a factor relying on the concrete porosity and solution saturation. This factor can be divided into two components: one component depicts the free chloride exhibit in the solution phase depending on the solution saturation and another component describes the free chloride perform in the solid phase depending on the concrete porosity and the binding capacity of concrete. Therefore, $\alpha$ in unsaturated concrete can be represented as

$$\alpha = \theta_s + (1-\theta_{sa})\gamma \tag{10}$$

where $\gamma$ is the coefficient that measures the binding capacity of chloride in concrete. The value of $\gamma$ representatively may range from 1.25 to 1.8 for $NaCl$ ingress. $\theta_{sat}$ ($m^3$ of solution/$m^3$ of concrete) is the saturated solution content of concrete. The value of $\theta_s$ ($m^3$ of solution/$m^3$ of concrete) usually may vary from 0 to $\theta_{sat}$. In the case of a saturated concrete, $\theta_s$ equals $\theta_{sat}$ and accordingly $\alpha$ is constant.

Substituting Eqs. (7) and (9) into Eq.(8), we obtain a nonlinear PDE equation as follows

$$\alpha \frac{dC_m}{dt} = \frac{d}{dx}\left[\frac{C_m}{\theta_{sm}} D(C_m, \theta_{sm}) \frac{d\theta_{sm}}{dx} + D_d(C_m)\frac{dC_m}{dx}\right] \tag{11}$$

### 2.5 Saturated condition

For the special case of saturated concrete, the flux resulted from capillary flow is zero, so Eq. (11) can be change as

$$\alpha \frac{dC_m}{dt} = \frac{d}{dx}[D_d(C_m)\frac{dC_m}{dx}] \tag{12a}$$

The corresponding initial and boundary conditions are

$$IC \;\; C_m(x,0) = C_i = C_1 \tag{12b}$$

$$BC \;\; C_m(0,t) = C_s \tag{12c}$$

$$C_m(x \to \infty, t) = C_f \tag{12d}$$

where $C_i = C_1$ , $C_s$ and $C_f$ are the initial, surface, and final chloride concentrations, respectively.

Eq. (12a) is a non-linear PDE. To solve this equation, the Kirchhoff transformation is employed to render the non-linear problem into a linear one (Sun *et al.*, 2008, 2010, 2012). A new variable $\psi$ is defined such that

$$\frac{d\psi(x,t)}{dC_m} = D_d(C_m) \tag{13}$$

Eq. (13) can also be written in integral form as in the following,

$$\psi(x,t) = \int_{C_R}^{C} D_d(C_m)dC_m = K(C) = K_C \tag{14}$$

where $C_R$ is an arbitrary reference value of concentration, $C$ is a nominal chloride surface concentration at t, and Eq. (14) is called the Kirchhoff transformation. By using the concepts of chain rule and Leibniz's rule to Eqs. (13) and (14). The following three equations can be obtained, respectively.

$$\frac{\partial\psi}{\partial t} = \frac{\partial\psi}{\partial C_m}\frac{\partial C_m}{\partial t} = D_d\frac{\partial C_m}{\partial t} \tag{15}$$

$$\frac{\partial\psi}{\partial x} = \frac{\partial\psi}{\partial C_m}\frac{\partial C_m}{\partial x} = D_d\frac{\partial C_m}{\partial x} \tag{16}$$

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left(D_d\frac{\partial C_m}{\partial x}\right) \tag{17}$$

Eq. (12a) is multiplied by $D_d$ and changed as

$$\alpha D_d\frac{dC_m}{dt} = D_d\frac{d}{dx}\left(D_d(C_m)\frac{dC_m}{dx}\right) \tag{18}$$

Inserting Eqs. (15), (16), and (17) into Eq. (18), we gain the following linear PDE.

$$\alpha\frac{\partial\psi}{\partial t} = D_d\frac{\partial^2\psi}{\partial x^2} \tag{19a}$$

The initial condition (*IC*) and boundary condition (*BC*) stated above were also transferred as

$$IC\ \ \psi(x,0) = \int_{C_R}^{C=C_1} D_d(C_m)dC_m = K(C = C_i = C_1) = K_1 \tag{19b}$$

$$BC\ \ \psi(0,t) = \int_{C_R}^{C_S} D_d(C_m)dC_m = K(C = C_S) = K_S \tag{19c}$$

$$\psi(x \to \infty, t) = \int_{C_R}^{C_f = 0} D_d(C_m) dC_m = K(C = C_f) = K_0 \tag{19d}$$

The method of Laplace transformation is used to solve Eq. (19). The definition of Laplace transformation of $\psi(x,t)$ (O'Neil, 2011) is given as

$$\Omega(x,s) = L[\psi(x,t)] = \int_0^{\infty} \psi(x,t) e^{-st} dt \tag{20}$$

Thus, the Laplace transformation of Eq. (19a) after using Eq. (19b) is given as follows,

$$\Omega'' - \frac{\alpha s}{D_d}\Omega = -\frac{\alpha K_1}{D_d} \tag{21}$$

Eq. (21) is a non-homogeneous ODE. The general solution of Eq. (21) is

$$\Omega(x, s) = C_1 e^{\sqrt{\frac{\alpha s}{D_d}}x} + C_2 e^{-\sqrt{\frac{\alpha s}{D_d}}x} + \frac{K_1}{s} \tag{22}$$

where $C_1$ and $C_2$ are arbitrary constants.

Taking Laplace transformation to Eqs. (19c) and (19d), we have

$$\Omega(0,s) = \frac{K_s}{s} \tag{23}$$

$$\Omega(x \to \infty, s) = \frac{K_0}{s} \tag{24}$$

Putting Eqs. (23) and (24) into Eq.(22), we respectively obtain

$$\Omega(0,s) = C_1 + C_2 + \frac{K_1}{s} = \frac{K_s}{s} \tag{25}$$

$$\Omega(x \to \infty, s) = C_1 \lim_{x\to\infty} e^{\sqrt{\frac{\alpha s}{D_d}}x} + C_2 \lim_{x\to\infty} e^{-\sqrt{\frac{\alpha s}{D_d}}x} + \frac{K_1}{s} = \frac{K_0}{s} \tag{26}$$

Since $\lim\limits_{x\to\infty} e^{\sqrt{\frac{\alpha s}{D_d}}x} = \infty$ and $\lim\limits_{x\to\infty} e^{-\sqrt{\frac{\alpha s}{D_d}}x} = 0$, in order to do the value of $\Omega(x \to \infty, s)$ in Eq. (26) having convergence, the value of $C_1$ should be chosen as $C_1 = 0$. Thus $K_1 = K_0$ (i.e., $C_1 = C_i = C_f = 0$).

Substituting $K_1 = K_0$ into Eq. (25) and using $C_1 = 0$, we know $C_2 = \dfrac{K_s - K_1}{s} = \dfrac{K_s - K_0}{s}$.

Inserting the values of $C_1$ and $C_2$ into Eq. (22), we have

$$\Omega(x,t)=\frac{K_1}{s}+\frac{K_s-K_0}{s}e^{-\sqrt{\frac{\alpha s}{D_d}}x} \tag{27}$$

Using the formula (O'Neil 2011) of inverse Laplace transformation

$$L^{-1}\left[\frac{e^{-\sqrt{\frac{\alpha s}{D_d}}x}}{s}\right]=1-erf\left(\frac{x}{\sqrt{4\alpha D_d t}}\right)=erfc\left(\frac{x}{\sqrt{4\alpha D_d t}}\right) \tag{28}$$

where $erf(\cdot)$ and $erfc(\cdot)$ are respectively the error and complementary error functions, and taking the inverse Laplace transformation to Eq. (27), we have

$$\Psi(x,t)=K_1+\left[\left(K_s-K_0\right)erfc\left(\frac{x}{\sqrt{4\alpha D_d t}}\right)\right] \tag{29}$$

The substitution of Eqs. (14), (19b), (19c), and (19d) into Eq.(29) yields

$$\frac{\int_{C_R}^{C_s}D_d(C_m)dC_m-\int_{C_R}^{C_i=0}D_d(C_m)dC_m}{\int_0^{C_s}D_d(C_m)dC_m-\int_{C_R}^{C_f=0}D_d(C_m)dC_m}=\frac{\int_0^{C}D_d(C_m)dC_m}{\int_0^{C_s}D_d(C_m)dC_m}=erfc\left(\frac{x}{\sqrt{4\alpha D_d t}}\right) \tag{30}$$

Eq. (30) supplies the relationship among diffusion coefficient $D_d$, chloride concentration $C_m$, penetration depth *x*, and time *t*. The left side of Eq. (30) is clearly the area ratio between areas under the $D_d-C_m$ curve from $C$ to 0 and $C_s$ to 0, as shown in Fig. 1, respectively (Sun *et al.* 2008, 2012).

## 3. Results and analyses

To verify the theoretical model mentioned above with feasibility and reliability, the commercial software programme "Mathematica" (Wolfram Research, 2013) is used as an algorithmic tool of calculation process.

According to the previously experimental data and results and using Eq. (30), the free chloride concentration profiles of saturated concrete for 24 and 120 hrs of exposure are shown in Figs. 2 and 3, respectively. From Figs. 2 and 3, the average values of two free chloride concentrations at depths 0.025, 0.075, 0.125 and 0.175 m after 24 and 120 hrs of exposure of experimental results are 0.0887, 0.0688, 0.0750 and 0.0710 and 0.1528, 0.1787, 0.1065, 0.1000% by mass of concrete, respectively. The error estimate of free chloride concentration predicted by finite difference method to experimental results are 1.24, 0, -11.2, -6.20 and 26.05, -1.57, 14.74, 0% (percentage) at depths of 0.025,0.075, 0.125 and 0.175 m after 24 and 120 hrs of exposure, respectively. However, the error estimate of free chloride concentration predicted by the proposed method to experimental results are 5.01, 15.98, -8.27, -18.59 and 24.80, -9.85, 30.33, 11.1%, at depths 0.025, 0.075, 0.125

and 0.175 m after 24 and 120 hrs of exposure, respectively. Using Figs. 2 and 3 or using Eq. (30) in combination with experimental data, the values of the chloride diffusion coefficient are summarized in Table 1. Based on Eq. (30), the more the values of the chloride diffusion coefficient, the more the free chloride ingress increases (Sun *et al*. 2008). In the case of Table 1, the values of the chloride diffusion coefficient obtained by the proposed method are really better than those calculated by the finite difference method.

In so far as Eq. (30), the value of the chloride diffusion coefficient is inversely proportional to time while the radical value of the chloride diffusion coefficient is proportional to the depths of chloride ingress. Nevertheless, Nagesh and Bhattacharjee (1998) obtained the values of the chloride diffusion coefficient were not proportional to the depths of chloride ingress (see Table 1). Moreover, the values of the chloride diffusion coefficient at time 24 hrs were the same as those at 120 hrs. This is completely not correct.

Table 1 Chloride diffusion coefficients in saturated concrete

| Distance from the exposed end x(m) | Chloride diffusion coefficients $D_d(C_m)(m^2/\sec)$ | | |
|---|---|---|---|
| | Finite difference method | Analytical solution | |
| | | $t$=24 hrs | $t$=120 hrs |
| 0.025 | $2.70\times10^{-9}$ | $4.00\times10^{-10}$ | $6.89\times10^{-11}$ |
| 0.075 | $1.03\times10^{-9}$ | $3.60\times10^{-9}$ | $6.20\times10^{-10}$ |
| 0.125 | $1.89\times10^{-9}$ | $1.00\times10^{-8}$ | $1.72\times10^{-9}$ |
| 0.175 | $7.90\times10^{-9}$ | $1.96\times10^{-8}$ | $3.37\times10^{-9}$ |

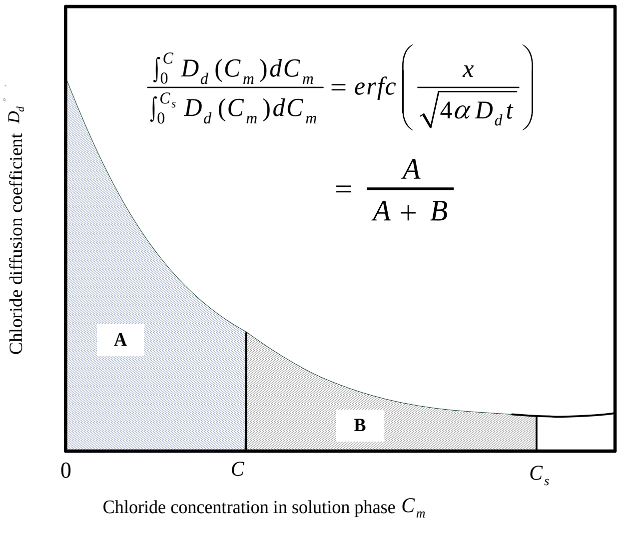

Fig. 1 Area ratio under the $D_d$-$C_m$ curve for interpreting the geometric meaning of Eq. (30)

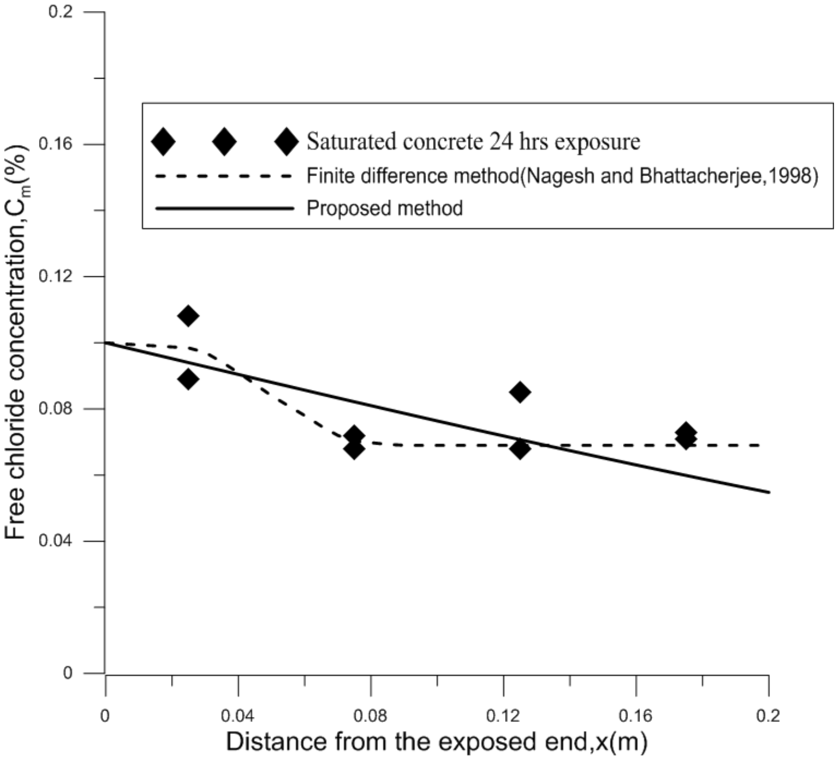

Fig. 2 Free chloride concentration profiles after 24 hrs of exposure

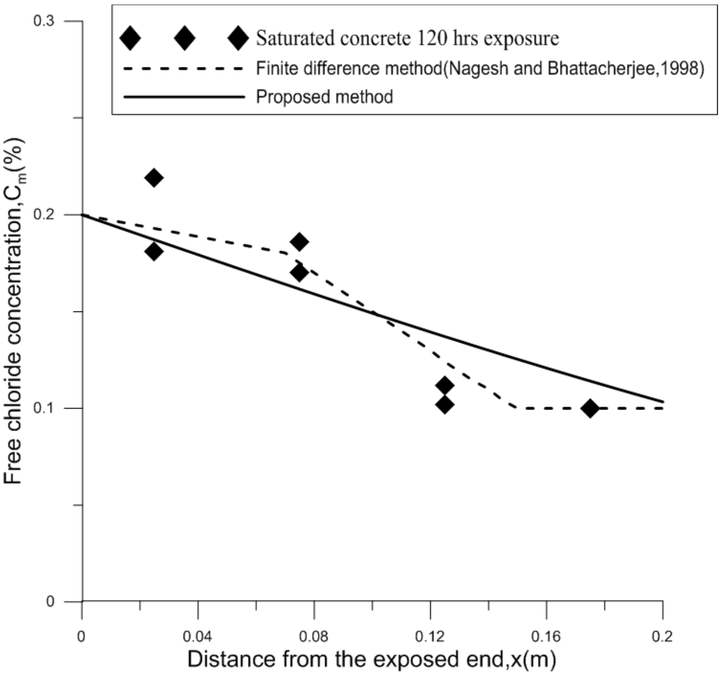

Fig. 3 Free chloride concentration profiles after 120 hrs of exposure

## 4. Discussion

Eq. (11) is a nonlinear PDE. Nagesh and Bhattacherjee (1998) applied Boltzmann's transformation, i.e., a new variable $\phi = xt^{-(1/2)}$, to Eq. (11) for rendering into an ordinary differential equation (ODE) as given below :

$$\frac{d}{d\phi}\left[\frac{C_m}{\theta_{sm}}D(C_m,\theta_{sm})\frac{d\theta_{sm}}{d\phi}+D_d(C_m)\frac{dC_m}{d\phi}\right]+\left[\frac{\alpha}{2}\phi\frac{dC_m}{d\phi}\right]=0 \tag{31}$$

with relevant boundary condition

$$\phi(x \to \infty, t=0)=\infty, C_m = C_1 \tag{32}$$

where $C_1$ is the initial free chloride concentration in concrete.

In the particular case of saturated condition, the flux due to capillary flow is zero, i.e., $D(C_m,\theta_{sm})\frac{d\theta_{sm}}{d\phi}=0$, and so, Eq. (31) reduces to

$$\frac{d}{d\phi}\left[D_d(C_m)\frac{dC_m}{d\phi}\right]+\frac{\alpha}{2}\phi\frac{dC_m}{d\phi}=0 \tag{33}$$

Nagesh and Bhattacherjee (1998) used finite difference method to Eqs. (32) and (33) for obtaining the approximate value of diffusion coefficient $D_d(C_m)$.

In the case of unsaturated condition, Nagesh and Bhattacherjee (1998) again employed finite difference method to Eqs. (31) and (32) for getting the approximate value of diffusion coefficient $D_d(C_m)$. However, they applied the mass balance equation due to

$$\frac{dJ_c}{dx}=-\frac{d\theta_{sm}}{dt} \tag{34}$$

or

$$\frac{d}{dx}\left[D(C_m,\theta_{sm})\frac{d\theta_{sm}}{dx}\right]=\frac{d\theta_{sm}}{dt} \tag{35}$$

They applied Boltzmann's transformation and used finite difference method to obtain the approximate value of diffusion coefficient. Finally, they found the approximate value of diffusion coefficient of chloride diffusion in unsaturated concrete through the principle of linear superposition. Although Eq. (31) is ODE, it is still nonlinear. The principle of linear superposition can not to be adopted. In a few words, Eq. (11) is a nonlinear PDE and render into a nonlinear ODE (see Eq. (31)) through Boltzmann's transformation. If we want to find the analytical or approximate solution of Eq. (11) in combination with relevant boundary condition, then we may use the principle of superposition to find the solution of Eq. (31) associated with boundary condition under that Eq. (31) should be of linearity.

## 5. Conclusions

Based on both the theoretical analysis and the previously experimental results, the following conclusions can be drawn.

- The analytical solution of mathematical model of chloride diffusion process in saturated concrete has been solved and applied to predicting the chloride penetration profiles.
- The free chloride concentration profiles predicted by the proposed method have a particular tendency with experimental results and trend toward numerical results approximated by finite difference method obtained by previous study.
- The analytical solution (see Eq. (30)) can be shown that the value of the chloride diffusion coefficient is inversely proportional to time whereas the radical value of the chloride diffusion coefficient is proportional to the depth of chloride penetration. However, the radical values of the chloride diffusion coefficient predicted by finite difference method were not proportional to the depths of chloride ingress.
- The analytical solution or other numerical solutions of the nonlinear PDE, modelling of chloride diffusion in unsaturated concrete (see Eq. (11)), associated with initial and boundary conditions is to be suggested to study in-depth for future work.

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