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# Numerical study of the effect of moisture on chloride and carbon dioxide transport in concrete

Mohamad Achour, Ouali Amiri, François Bignonnet and Emmanuel Rozière

*GeM Civil engineering and Mechanics Research Institute,  
École Centrale de Nantes, University of Nantes /CNRS,  
1 rue de la Noë, Nantes 44321, France*

## Abstract

In this paper a physico-chemical model is developed to study the coupled transport of chloride, carbon dioxide and moisture into concrete. To predict the chloride profile in concrete, a new approach is proposed based on the Nernst-Planck's equation, which considers multi-species transfer of aggressive ions, including diffusion, migration, chemical activity of ions, interaction between chloride ions and cement paste of concrete and convection due to the exposure conditions. Several applications of the numerical model are developed.

## 1 Introduction

Degradation of reinforced concrete structures due to aggressive agents penetration followed by reinforcement corrosion has been identified as one of the most serious problem in civil engineering. As recently known, chloride attack and carbonation are the main reasons influencing the initiation phase of the steel corrosion in concrete [1]. The initiation phase is defined as the time taken to loose the passivation state of the steel in concrete. In actual exposure conditions, concrete is rarely saturated [2], such as bridges exposed to the sea water or structures exposed to deicing salts. Therefore, the moisture transport is also integrated in this study. In order to evaluate the service-life of reinforced concrete structures exposed to these environmental actions, several numerical models based on the Fick's second law [3] are used to simulate the chloride ions penetration. But when applied to real structure in a specific environment such as tidal zone, this law with constant coefficient of diffusion cannot predict the chloride profile in concrete [4]. Carbonation process is considered using the thermodynamic equilibrium during the dissolution of carbon dioxide in the pore solution till the formation of calcite [5].

Existing literature shows that the effect of the moisture transport on the transport of chloride ions and carbon dioxide should not be neglected. The transport of moisture can accelerate 20 times the transport of ions [6]. Recently a few studies have shown carbonation influences the transport of chloride ions significantly [1] but the transport of chloride and carbon dioxide has been modeled without taking into account multi-ions transport especially  $\text{HCO}_3^-$  ions. In other work, the interaction between ions have been neglected also, as well as the effect of the porosity evolution and the changing of the hydration products [6].

The purpose of this study is to develop a numerical model which can describe the penetration profiles of chloride in concrete exposed to combined deterioration. These combined phenomena induced in a non-saturated state of concrete can be due to cyclic drying and wetting conditions. A new strategy is adopted to simulate the cyclic movement of chloride solution. Thus the humidity distribution can be related to the chloride profiles by estimating the convection depth in the concrete. This convection depth is defined as the concrete layer where the concentration of chloride ions increases with depth. However Fick's second law cannot predict this depth in these environmental conditions. In this paper, the Nernst-Planck equation is adopted in the model to take into account this depth during the numerical simulations.

The theoretical analysis and the numerical model for this combined transport is explained in section 2. The studied materials are described in section 3. A comparison between experimental results from the literature and numerical results of the model is proposed in section 4. The conclusions are listed in section 5.

## 2 Modeling of coupled transport and chemical interactions

### 2.1 Chloride penetration

The transport of chloride ions in the pore solution is described using the Nernst Planck's equation to consider the effect of multi-ions interaction, the chemical activity and the convection.

$$J_i = -D_i \left[ \text{grad}C_i + \frac{z_i F}{RT} C_i \text{grad}\Psi + C_i \text{grad}(\ln Y_i) \right] + C_i v \quad (1)$$

Where  $D_i$ ,  $C_i$ ,  $z_i$  and  $Y_i$  are respectively the effective coefficient of diffusion (m<sup>2</sup>/s), the concentration (mol.m<sup>-3</sup>), the valence and the coefficient of activity of the ion  $i$ .  $F$  the Faraday constant (96485,309 C.mol<sup>-1</sup>),  $R$  the ideal gas constant (8,3143 J.mol<sup>-1</sup>.K<sup>-1</sup>),  $T$  the temperature (K),  $\Psi$  the electrostatic potential (V) and  $v$  the velocity of water (m/s).

### 2.2 Carbon dioxide penetration

The penetration of carbon dioxide requires the presence of water because CO<sub>2</sub> dissolves in water forming H<sub>2</sub>CO<sub>3</sub>. During this process, the hydrates of the concrete specially Ca(OH)<sub>2</sub> and CSH dissolve to adjust the pH of the solution. CaCO<sub>3</sub> and silica gel are formed, which is likely to reduce the porosity of concrete. For the rate of carbonation reaction, the dissolution of hydrates and the formation of different products of carbonation, the chemical equilibrium and the kinetics of carbonation are used to calculate the amount of solid components in the concrete. The carbonation process adopted in this paper is the same as presented in Thierry's work [5].

### 2.3 Moisture penetration

For the humidity analysis, the adsorption and desorption isotherms are the main parameters to take into account the cyclic wetting and drying. The model equation adopted for the humidity analysis takes into account the water released by the carbonation process. This equation can be derived as follows:

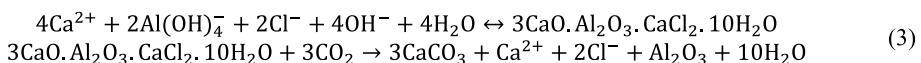
$$\frac{\partial S_e}{\partial t} = -\frac{K_e K_{re}}{\varepsilon \mu_e} \frac{\partial P_c}{\partial S_e} \text{grad}S_e + \frac{R_a D_{va}}{\rho_e} \frac{\partial \rho_v}{\partial S_e} \text{grad}S_e - \frac{M_{H_2O}}{\rho_e} \frac{\partial S_{CaOH_2}}{\partial t} \quad (2)$$

Where  $\mu_e$ ,  $\rho_e$  and  $M_{H_2O}$  are respectively the viscosity, the density and the molar mass of water.  $\rho_v$  is the density of water vapor and  $S_e$  is the saturation degree of concrete.

- $D_{va} = 2.75 \times 10^{-5} \left(\frac{T}{T_{ref}}\right)^{1.88}$  is the coefficient of diffusion of water vapor (m<sup>2</sup>/s) and  $T_{ref}$  is the reference temperature.
- $P_c = -\rho_e \frac{RT}{M_v} \ln \varphi(W)$  is the capillary pressure (atm) calculated from  $\varphi(W)$ , which describes sorption and desorption isotherms. These isotherms can be derived from experimental results depending on the type of concrete and on wetting-drying cycles
- $K_e$  (m<sup>2</sup>) =  $K_e^0 \left(\frac{\varepsilon}{\varepsilon_0}\right)^2 \left(\frac{1-\varepsilon_0}{1-\varepsilon}\right)^2$  is the intrinsic permeability which depends on the initial porosity of concrete  $\varepsilon_0$ . This permeability is obtained from Genuchten's study [7].
- $K_{re}$  (m<sup>2</sup>) =  $(S_e)^{0.5} [1 - (1 - (S_e)^{1/0.34})^{0.34}]^2$  is the relative permeability obtained from Mualem's work [8].
- $R_a = (\varepsilon)^{2.74} (1 - S_e)^{4.8}$  is the resistance to the air obtained from Thierry's work [5] based on Millington's study [9].

### 2.4 Coupled transport of chloride and carbonation into concrete

Friedel's salt (3CaO.Al<sub>2</sub>O<sub>3</sub>.CaCl<sub>2</sub>.10H<sub>2</sub>O) appears when chloride ions penetrate into concrete and react with hydration products. Then it reacts with carbon dioxide during the carbonation process. Two fractions of chloride ions exist: the first one is bound to the hydration products and the other one is free in the solution. During this combined transport, the bound chloride ions are released to the pore solution in concrete [10], which can increase the free chloride concentration as follows:



The combined transport of chloride and carbonation under wetting-drying cycles is modeled using the thermodynamical equilibrium for the dissolution of carbon dioxide in the pore solution till the formation of the calcite, the chemical equilibrium of dissolution of hydrates and Friedel's salt, the kinetics of carbonation to predict the rate of formation of carbonation products. This physico-chemical equilibrium makes the porosity changing during the process. The flow chart in figure 1 shows how different mechanisms are linked and what input data are needed to simulate the profile of chloride ions in the concrete.

The evolution of the porosity can be estimated as follows:

$$\Delta\varepsilon = \bar{V}_{\text{NaCl}}C_{\text{NaCl}} + \bar{V}_{\text{CaCO}_3}S_{\text{CaCO}_3} - \bar{V}_{\text{CaOH}_2}(S_{\text{CaOH}_2}^0 - S_{\text{CaOH}_2}) + \Delta\bar{V}_{\text{CSH}}(S_{\text{CSH}}^0 - S_{\text{CSH}}) \quad (4)$$

Where  $\bar{V}_{\text{NaCl}}$ ,  $C_{\text{NaCl}}$ ,  $S_{\text{CSH}}^0$ ,  $S_{\text{CSH}}$  and  $\Delta\bar{V}_{\text{CSH}}$  are respectively the molar volume and the concentration of NaCl, the initial and current concentrations of CSH and the volume variations due to carbonation of 1 mole of CSH.

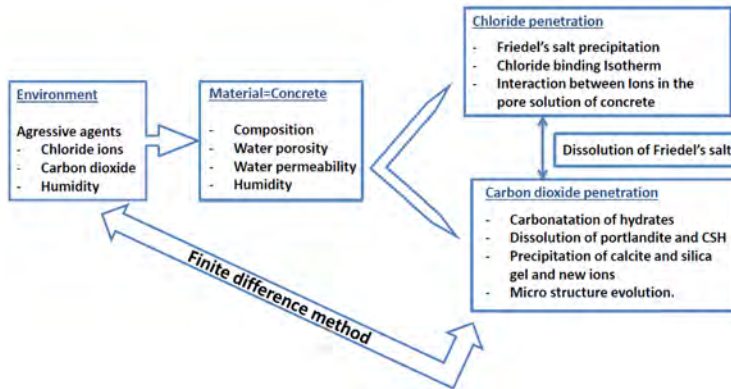


Fig 1 Flowchart of the numerical model.

### 3 Materials and experimental procedures

The studied concrete mixture L75 was chosen from the literature because all the input data needed for this complex model were available. The input data were assessed experimentally: initial composition, the sorption desorption and the chloride binding isotherms, the coefficient of diffusion of chloride ions. All the input data and the boundary and initial conditions are shown in tables 1, 2 and 3 [2].

Table 1 Composition of the concrete specimen.

Materials	L75
Gravels 6/14 mm	1037 kg/m <sup>3</sup>
Sand 0/4 mm	816 kg/m <sup>3</sup>
Blast furnace slag	310 kg/m <sup>3</sup>
Cement CEM I 52.5N	103 kg/m <sup>3</sup>
Water	170 kg/m <sup>3</sup>
W/(C+BFS)	0.41

The input data were assessed experimentally and are shown in table 2. The effective coefficient of diffusion was measured by steady-state migration test.

Table 2 Input data needed for the model.

	L75
Density of concrete	2340 Kg/m <sup>3</sup>
Water porosity	0.145
Chloride binding isotherms	$C_{cl,bound} \text{ (mol/m}^3\text{)} = \frac{0.00013C_{cl,free}}{1 + 0.0004C_{cl,free}}$
Sorption desorption isotherms	Sorption: $W = \frac{94.64\phi - 1 - 0.121\phi}{1 + 5915\phi - 0.935\phi}$
	Desorption: $W = \frac{26.706\phi - 1 - 0.637\phi}{1 + 445.1\phi - 0.902\phi}$
Coefficient of diffusion of chloride ions	$0,54 \times 10^{-12} \text{ m}^2/\text{s}$

The boundary conditions correspond to a concrete specimen covered with aluminum on all sides except the surface exposed to chloride solution only during one year of time exposure. Table 3 shows the boundary and initial conditions.

Table 3 Initial and boundary conditions.

Initial conditions	Boundary conditions
$[Cl^-] (x, t=0) = 0$	$[Cl^-] (x=0, t>0) = 500 \text{ mol/m}^3$
$S_e(x, t = 0) = 70\%$	6h/6h of wetting and drying cycle $S_e(x = 0, t > 0) = 60\%$ drying $S_e(x = 0, t > 0) = 92\%$ wetting

## 4 Results and discussion

The discretization approach for 1D domain to model the ionic transport and carbonation process is adapted to the present model by using the finite difference method.

### 4.1 Chloride and moisture transport

The presented numerical results have been carried out by dividing a 50 mm concrete specimen into 75 nodes and using a time step of 1 hour.

In order to assess the validity of the proposed numerical model, the experimental results were obtained from the concrete described in section 3 [2]. Figure 2 shows the comparison of the free chloride concentration predicted by the present numerical model and those experimentally observed.

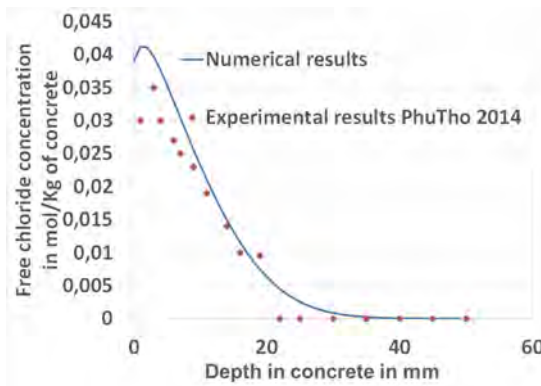


Fig 2 Comparison between numerical results and experimental observations for the penetration of chloride ions.

It can be seen that the results predicted agree well with the experimental results. In the first millimetres depth in the concrete, a lack between the experimental results and the numerical prediction can be observed. It can be explained by the porosity on the surface of the concrete which are considered constant in the beginning in the model. In addition the convection depth which is defined as the distance from the surface of concrete till the depth where the concentration of chloride ions is maximum can be predicted with our model. It can be observed the same convection depth in the two results (5 mm).

During the exposure, the transport of chloride ions due to water ingress under drying-wetting cycles cannot be ignored. When concrete is subjected to drying-wetting environment, the convection depth can be observed after an exposure period of 1 and 5 months, 1, 3 and 10 years. Figure 3 shows the increase of the convection depth and the free chloride concentration during the exposure. This coupling effect can relate the convection depth to the saturation degree of the concrete. The moisture transport actually accelerates the penetration of chloride ions.

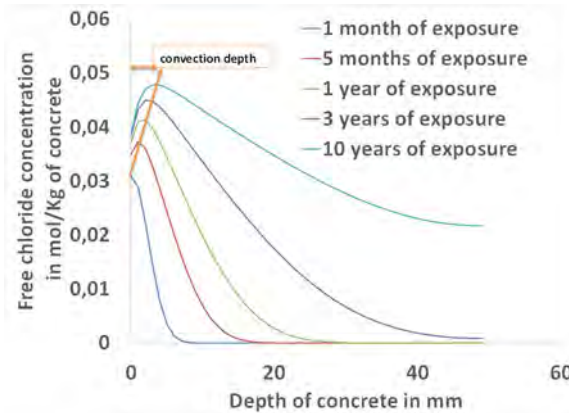


Fig 3 Profiles of free chloride concentration.

#### 4.2 Influence of carbonation on the transport of chloride ions in the concrete

In this paragraph, a combined deterioration analysis is performed on the same concrete. Table 4 shows the new initial and boundary conditions of the problem. All the input data as the thermodynamical equilibrium, the kinetics of dissolution of hydration products and the formation of calcite and silica gel are presented in details in Thiery's research work [5].

Table 4 Initial and boundary conditions.

Initial conditions	Boundary conditions
$[\text{CO}_2](x, t=0) = 0$	$[\text{CO}_2](x=0, t>0) = 0.02 \text{ mol/L}$
$S_e(x, t = 0) = 70\%$	6h/6h of wetting and drying cycle
	$S_e(x = 0, t > 0) = 60\%$ drying
	$S_e(x = 0, t > 0) = 92\%$ wetting

It can be observed in figure 4 (left) that for a fixed depth of the concrete cover, the chloride content increases with the time of exposure. In this study, the critical free chloride content that induces corrosion of steel reinforcement is assumed to be  $0.02 \text{ kg/m}^3$ . In order to ensure the initiation time of corrosion beyond 50 years under combined transport, the thickness of concrete cover should be higher than 40 mm as shown in figure 4 (left). It can be observed also that for a fixed concentration of chloride (concentration of sea water) the minimum concrete cover is higher when taking into account all the phenomena: 40 mm (figure 4 left) > 36 mm for chloride transport only (figure 4 right). During carbonation the Friedel's salt dissolves to release free chloride ions. Although when neglecting the effect of convection and carbonation, the service life of concrete structures is overestimated. Finally the corresponding study confirms that carbonation and moisture reduce the service life and the initiation time of corrosion.

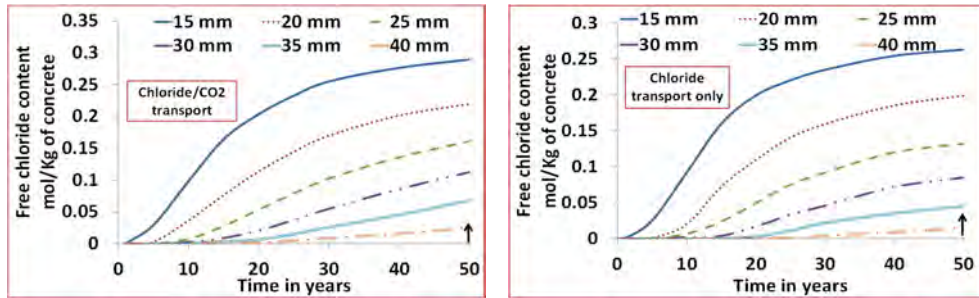


Fig 4 Comparisons between concrete cover prediction for coupled transport (left) and chloride transport only (right) under wetting drying cycles.

## 5 Conclusions

An integrated numerical model has been developed. It can reasonably predict the service life of reinforced concrete structures exposed to combined deterioration i.e. chloride attack and carbonation under cyclic wetting-drying cycles. The interactions between moisture and chloride penetration are considered. The increase of the penetration depth of free chloride ions due to carbonation can be attributed to the dissolution of Friedel's salt and exposure conditions. When drying-wetting cycles are simulated in the model, a convection depth appears experimentally. Numerical model based on the Nernst Planck's equation allows to predict the chloride profile in such case. From the presented analysis, it can be concluded that the model can predict the chloride content in unsaturated concrete.

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