Simulation of chloride penetration within partially carbonated concrete

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**ABSTRACT:** A multi-species and multi-phase model was used to simulate the chloride and moisture transports through non-carbonated, carbonated and partially carbonated concrete specimens. The reduction in porosity and permeability of the carbonated material were taken into account. The input data of the model are directly obtained by means of experiments (effective chloride diffusion coefficient) or by numerical inverse analysis (binding parameters, permeability, etc.). Experiments have been carried out to assess the chloride penetration profile through partially-carbonated concretes specimens exposed to absorption. The experimental profiles are compared to the simulated ones in order to validate the reliability of the approach.

1 **INTRODUCTION**

Chloride penetration dominates the degradation of reinforcement concrete in marine and de-icing salt environment. In partially saturated conditions, advection of the liquid phase largely accelerates the penetration of chloride ions. The diffusive transport of ions contributes to the penetration, while the interactions between chloride ions and solid phases slow down the ingress (Baroghel-Bouny et al, 1995).

Carbonation-induced corrosion is another major deterioration mechanism of the reinforcement. But few data (Conciatori et al, 2008) are available about the association of carbonation and chloride penetration since the coexistence of these two mechanisms is less observed. However, carbonation occurring during the curing and the transport of prefabricated concrete elements could modify the microstructure and the binding properties of the material (Ngala, 1997) (Song, 2007). The behaviour of the concrete related to moisture transport and chloride ingress is thus modified.

In this study, absorption tests of pure water and a NaCl solution through non-carbonated and carbonated OPC concrete have been performed in order to determine the transport properties of the material. A transport model for unsaturated condition is used for numerical simulation in order to identify the transport properties (intrinsic permeability \(K_l\) for liquid) of a carbonated material. The penetration of chloride in partially carbonated concrete is illustrated.
2. MULTIPLE PHASE TRANSPORT MODEL FOR PARTIALLY SATURATED CONDITION

2.1. Mass balance equation

The IFSTTAR transport model for partially saturated condition uses a 1D finite volume platform to solve 4 mol ar balance equations for Cl, Na, K and OH−-H+, see Eq.(1). The binding of ions onto the matrix is taken into account for Cl, Na and K. Poisson’s equation is solved and two mass balances are added related to dry air as well as to moisture (liquid water and water vapour) (Eq.(1)). The main variables associated with the above equations are the concentration of the species Cl−, Na+, K+ and OH−, as well as the electrical potential, the liquid water pressure and the dry air pressure.

\[
\begin{align*}
\frac{\partial}{\partial t} \left( \phi S_l c_w + \phi (1 - S_l) \frac{\rho_v}{M_v} \right) &= -\nabla (w_w + w_r) \\
\frac{\partial}{\partial t} \left( \phi (1 - S_l) \frac{\rho_a}{M_a} \right) &= -\nabla (w_a) \\
\frac{\partial}{\partial t} (\phi S_l c_i + s_i) &= -\nabla (w_i) \\
\nabla^2 \phi &= -\frac{\rho_c}{\varepsilon_0 \varepsilon_r}
\end{align*}
\]

where \( w, c, \phi, M \) are respectively the molar flux [mol.m\(^{-2}\).s\(^{-1}\)], the concentration [mol.m\(^{-3}\) of solution], the porosity [-] and the molar mass [g.mol\(^{-1}\)]. \( \rho_v \) and \( \rho_a \) are respectively the density of water vapour and dry air [kg.m\(^{-3}\)]. \( S_l \) and \( s \) are respectively the degree of liquid-water saturation [-] and the amount of ions bound onto the cement matrix [mol.m\(^{-3}\) of material]. \( \phi, \rho_c, \varepsilon_0 \) and \( \varepsilon_r \) are respectively the electric potential [V], the charge density [C.m\(^{-1}\)], the vacuum permittivity (\( \varepsilon_0 = 8.854\times10^{-12} \text{[C/V.m]} \)) and the relative permittivity of water [C.V\(^{-1}\).m\(^{-1}\)].

The indices \( w, a, v, i \) represent respectively liquid- water, air, water vapour and ions.

2.2. Advection and diffusion of dry air, water vapour and liquid water

2.2.1. Advection

The extend Darcy’s law is used to describe the transport of the liquid phase (l) and of the gaseous phase which is a mixture of dry air (a) and water vapour (v). \( K_l, K_v, k_d \) and \( k_g \) are respectively the “intrinsic” permeability and relative permeability for the liquid and the gaseous phase (see Eq. (3)). The relative permeability depends on the saturation of liquid-water according to the Mualem’s theory (Mualem, 1976) by integration of the capillary curve of the material (Thiery et al, 2008). The dynamic viscosity (\( \eta \)) of the liquid phase depends on the ionic concentration within the pore solution (Baroghel-Bouny et al, 2011).

2.2.2. Diffusion of water vapour and dry air

The relative diffusion of dry air and water vapour are described by Fick’s law, where the mass fractions of dry air and water vapour in the gas mixture are the main driving forces. In order to calculate the effective diffusion coefficient of dry air or water vapour, a resistance factor \( f (\phi S_l) \) is added to account for the tortuosity effects and the reduction in accessibility for gas diffusion through a partially saturated porous medium (Thiery et al, 2007).
2.2.3. Diffusion of ions

The relative diffusion of ionic species includes two mechanisms: diffusion due to concentration gradient and migration under an electrical field. The Nernst-Planck equation is used to describe this kind of transport. The effective diffusion coefficient of each ion in the pore solution can be calculated using Eq. (2)

\[
\frac{D_i (S_i = 1)}{D_i^0} = \frac{D_{Cl^-}^0 (S_i = 1)}{D_{Cl^-}^0} \quad \text{(for } i \neq Cl^-) \\
\frac{D_{Cl^-}^i (S_i)}{D_{Cl^-}^0} = S_i^i
\]

where \(D_i^0\) and \(D_i\) are respectively the self-diffusion coefficient and the effective diffusion coefficient of the considered ion \([m^2.s^{-1}]\). \(D_{Cl^-}^0\) is the effective diffusion coefficient of chloride \([m^2.s^{-1}]\). It is measured to assess the dependence on \(\phi\). A polynomial relation \(S(\lambda)\) is calibrated by using results of impedance spectroscopy measurements on various mortar specimens to represent the influence of liquid-water saturation \(S_l\) on the diffusion of ions (Francy, 1998).

The molar fluxes of the different phases are thus expressed by Eq.(3):

\[
w_g = \rho_a \frac{K_g}{\eta_g} k_{rg} (S_i) \nabla p_g - f(\phi, S_i) D_{va} p_g \frac{\rho_a}{\rho_g} \\
w_v = \rho_v \frac{K_v}{\eta_v} k_{rv} (S_i) \nabla p_v - f(\phi, S_i) D_{va} p_g \frac{\rho_v}{\rho_g} \\
w_w = \rho_w \frac{K_w}{\eta_w} k_{wl} (S_i) \nabla p_w + M_w J_w \\
w_l = \rho_l \frac{K_l}{\eta_l} k_{wl} (S_i) \nabla p_l + D_l (\nabla c_l + c_l \nabla \ln \gamma_l + \frac{c_l z F}{RT} \nabla \phi_l)
\]

Where \(K, k_{g}(S_i), k_{v}(S_i), \rho_g, \eta,\) and \(D_{va}\) are respectively the intrinsic permeability \([m^2]\), the relative permeability[-] to the gas and to the liquid-water, the pressure [Pa], the dynamic viscosity and the self-diffusion water vapour diffusion coefficient in the air \((2.47 \times 10^{-5} [m^2.s^{-1}]).\) \(D\) and \(\phi\) denote the effective diffusion coefficient of ions \([m^2.s^{-1}]\) and the local electrical potential [V]. \(F\) is the Faraday constant air (F=9.64846 \times 10^{4} [C.mol^{-1}]) and \(z\) is the valence number [-] of each ion. The chemical activity coefficient \(\gamma\) can be determined by the theory of Lin and Lee (Lin & Lee, 2003).

The indices \(g\) and \(l\) represent respectively gas and liquid.

The diffusive flux of water molecules \(J_w\) \([mol.m^{-2}.s^{-1}]\) is assessed by the molar flux balance between the water and all the other ions, see Eq.(4).

\[
M_w J_w + \sum_{i \neq w} M_i J_i = 0
\]

2.3. Liquid – water equilibrium

The equilibrium between liquid water and water vapour is described by the extended Kelvin’s law, where the chemical activity of liquid water (\(a_w\)) is included to account for the effect of the presence of salt in the pore solution (Baroghel-Bouny & Thiéry, 2010).
where $p_c$, $p_l$ and $p_g$ are respectively the capillary pressure [Pa], the liquid pressure and the gas pressure. $\rho_w$, $R$ and $T$ are the density of liquid water [g.m$^{-3}$], the ideal gas constant [J.mol$^{-1}$.K$^{-1}$] and the absolute temperature [K]. $h_r$ and $a_w$ are respectively relative humidity [-] and chemical activity of liquid water [-]. A characteristic capillary curve of the material $p_c(p(S))$ is included as input data for the model. $p_c(S)$ is inferred from the experimental determination of the sorption isotherm of the material.

2.4. Binding of chloride and alkalis onto the solid matrix

The interaction between ions in pore solution and the solid is taken into account for chloride ions and alkalis.

A Langmuir formula is used to describe the physicochemical binding of chloride onto the solid (Baroghel-Bouny et al, 2010), while the binding of alkalis ions is described by linear relations proposed by Chen (2010). If we simulate absorption when transport of chloride ions is governed by liquid advection, the chemical reactions are very fast and a kinetics equation should be added to account for a delayed binding (Baroghel-Bouny et al, 2011).

3 INFLUENCE OF CARBONATION ON MICROSTRUCTURE AND MOISTURE TRANSPORT PROPERTIES

It is well known that in materials made of OPC the porosity will decrease due to carbonation since the carbonation products (CaCO$_3$, silica gel) have higher molar volumes than the parent hydration products (Ca(OH)$_2$ and C-S-H).

A recent research (Thiéry et al, 2011) confirmed the impact of carbonation on the capillary porosity. Actually, carbonation leads to the clogging of mesopores in the range of 10-100nm (attributed to the voids among outer CSH clusters) as well as to the appearance of larger coarse capillary pore in the range of 100-200nm if w/c>0.45. However, it seems that carbonation has a weak influence on the water vapour adsorption/desorption isotherm of the material $S(h)$, while an increase in permeability (both for gas and liquid) due to carbonation may be observed (Thiéry et al, 2011).

The chemical composition of the interstitial solution in the pores of concrete (the pores solution pH will drop from 13 to 9) and the chloride bound capacity will be modified as well since carbonated C-S-H are not able to fixe Cl$^-$. 

4 ABSORPTION TESTS ON NON-CARBONATED, CARBONATED AND PARTIALLY CARBONATED CONCRETE SPECIMEN

4.1 Description of the material and the test

A 2-year-old concrete M25 made of OPC (w/c = 0.84, s/(s+agg) = 0.47) was used. Three cylindrical specimens of 100mm (H) x 110mm (D) were prepared.

The specimens were laterally sealed by an adhesive aluminium sheet. Non carbonated specimen (NC) was kept in water as reference. The others were exposed to 10% CO$_2$ in a box where the humidity was fixed at RH=53.5% using a salt solution. One of them (Partially Carbonated, PC) was exposed to CO$_2$ during 15 days while the other (Totally Carbonated, TC) were carbonated for 2 months until the mass of specimen is stabilized, meaning a full carbonation state.

After being exposed to CO$_2$, the specimens were saturated with pure water in vacuum during 72 hours. Then the specimens have been dried at 45°C in a sealed oven where a humidity of
RH=53.5% was fixed during 56 days in order to homogenize the moisture state inside of the specimens.

Before absorption, the bottoms of the specimens were sealed with an adhesive aluminium sheet to avoid evaporation from the other side of specimens during the test. Then the specimens NC, TC and PC have been exposed to a NaCl solution of 30g/L for absorption.

The displacement of liquid driven by capillary force was monitored by gamma-ray attenuation (Villlain, 2006) during the test (about 6 hours). After the test, the total chloride content (tcc) and free chloride content (fcc) profiles were determined by grinding, extraction and potentiometric titration.

4.2. Experimental results

The absorption results in a variation of volume occupied by liquid phase in the specimens, which could be identified and measured by gamma-ray attenuation.

The Boltzmann profiles (volume variation in function of the ratio of depth by the square of the time) of the three absorption tests on NC, TC and PC specimens are illustrated in Fig 1. Comparing the NC profile and TC profile, we can deduce that the test on TC needs more time to get the same liquid water content at a giving depth, which means that absorption in TC specimen is “slower” than that in NC specimen. As a result, the permeability of TC is certainly weaker as expected. The TC profile shows a lower final water content than NC at the end of the test, due to the fact that TC specimen has a lower porosity because of carbonation. The Boltzmann profile for PC is reasonably between the NC and the PC profiles.

The free and total chloride contents profiles after the absorption test of all the three cases are illustrated in Fig 2. For non carbonated condition (NC), the binding of chloride occurs even though the movement of chloride ions is very fast during the absorption. In the case of total carbonated condition (TC), the tcc and fcc profiles are very close indicating that the binding of Cl ions onto the matrix is largely reduced. It confirms that most of the C-S-H phases in the specimens were carbonated thus no fixation reactions can occur. Due to the reduction in porosity and increase in density, the total and free chloride contents (tcc and fcc profiles) for TC specimens are much lower than that obtained for NC specimens. Concerning the partially carbonated condition, the profiles show the characteristics of both NC and TC. In the carbonated region (0-0.015m), the tcc and fcc profiles are thus very close and the chloride content are close to those obtained for TC specimen. In the non carbonated zone, the tcc and fcc profiles both increase to the NC level, and a notable fixation of Cl ions appears.
5 NUMERICAL SIMULATIONS AND VALIDATION

The IFSTTAR multispecies transport model for non-saturated condition is used to perform the numerical simulation. General and transport properties of the material are obtained by measurement provided by earlier researches (Baroghel-Bouny, 2007) (Thiéry et al, 2011) (Wang et al, 2009), while the contents of C-S-H, C₃A and alkalis are accessed by analytical calculation using a hydration model (Thiéry, 2005). Inverse analysis was used to identify the Kᵢ of carbonated specimen from the experimental profiles for TC. The value is used later to predict the profiles for PC conditions.

5.1. Fitting from Boltzmann and tcc profiles of NC and PC specimens

General properties, transport properties and other parameters for both NC and TC specimens are listed in Table 1.

Table 1: Material properties and transport parameters

<table>
<thead>
<tr>
<th>Input data</th>
<th>M25-non carbonated</th>
<th>M25 carbonated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Key parameters of transport</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity (-)</td>
<td>0.16</td>
<td>0.12</td>
</tr>
<tr>
<td>Gas Permeability (m²)</td>
<td>3.7E-16</td>
<td>8.0E-16</td>
</tr>
<tr>
<td>Liquid Permeability(m²)</td>
<td>1.3 E-17(fit)</td>
<td>6.0 E-18(fit)</td>
</tr>
<tr>
<td>Effective diffusion coefficient of chloride (m².s⁻¹)</td>
<td>8.4E-12</td>
<td>6.3E-12</td>
</tr>
<tr>
<td>Hydrate content</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CSH content (mol.m⁻³ solid)</td>
<td>370</td>
<td>0</td>
</tr>
<tr>
<td>C3A content (mol.m⁻³ solid)</td>
<td>3.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The numerical Boltzmann profiles of liquid water saturation Sᵢ and chloride content profiles which fit best with the experimental data are illustrated in Fig. 3 and Fig. 4.
5.2. Prediction of Boltzmann and chloride content profiles for PC specimens

Parameters identified from 5.1 were employed to simulate the absorption into PC specimens. In the carbonated zone (0-1.5 cm) parameters corresponding to a TC material are used while in the non carbonated zone (3-10 cm) parameters of NC material are implemented. A transition zone is defined between the two zones mentioned above (1.5 cm - 3 cm), where the parameters change linearly from the TC values to the NC ones. The predicted Boltzmann profile and the predicted chloride content profiles are obtained and compared to experimental profiles for PC specimens, as illustrated in Fig 5 and Fig 6.

![Fig.5: Boltzmann profiles (predicted)](image)

![Fig.6: Chloride content profiles (6h absorption) (predicted)](image)

A good agreement is observed between the predicted and the experimental profiles.

6 CONCLUSION AND PERSPECTIVES

A group of absorption tests has been performed on non carbonated, carbonated and partially carbonated OPC concrete. The notable influence of carbonation on moisture transport and on chloride penetration was confirmed by experiments.

A 1-D numerical model was used to simulate the moisture transport and chloride penetration. The changes on transport proprieties caused by carbonation have been taken into account including the modification of porosity, of the composition of pore solution and of the permeability. The numerical results were compared to experimental data and a good agreement was point out. The relevance of the model was therefore proved.

In future study, other wetting-drying tests will be performed on OPC concrete with lower water/binding ratio (w/c=0.5) and on concretes with SCM like fly ash or slag. The influence of carbonation on chloride binding would be investigated in order to enhance the IFSTTAR transport model.

Reference


