Numerical tool for durability assessment of concrete Structures subjected to aggressive environment

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- Simulation of all the parameters (water, hydrates consumption, carbonation, chlorides, combination of carbonation-chlorides)
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- Perspectives
Fundamental role of water transport in the study of durability mechanism

- Carbonation
  - The saturation degree is a fundamental parameter when considering the carbonation mechanism.
  - The carbonation rate is optimum for intermediate Relative Humidity (h).
    - High enough to allow the CO₂ solubilisation.
    - Low enough to not slow down the CO₂ diffusion.

  - At low h, “free water” quantity is not enough → Limiting factor: CO₃²⁻.
  - At high h, CO₂ diffusion is 10⁴ times lower in liquid phase than in gaseous phase.

- Chlorides
  - Transport mode of chlorides according to the saturation degree of the material.

Concrete saturated in liquid water
  - Diffusion (concentration gradient)
  - Wetting/drying cycle
    - Capillary absorption
    - Convection

Tiding zone → Capillary absorption (pressure gradient)
Experimental test

Original new experimental durability test

Simulation: simulated specimen
Simulation of water and species transport in porous media

- Basic hypothesis
  - Three phases: solid phase (cement paste matrix), liquid phase (pore solution) and gaseous phase
  - Solid matrix is not deformable
  - Liquid phase is not compressible
  - Gaseous phase comprising two ideal gas:
    - Dry air (partial pressure $p_a$)
    - Vapour water (partial pressure $p_v$)
    
$$
\rho_g = p_a + p_v
$$

- Gravity is not taking into account
- Water transport are isotherm (20°C)

Governing equations

- Mass balance equation of the three constituents: liquid, solid and gas

$$\begin{align*}
\frac{\partial m_i}{\partial t} &= -\text{div}(W_i) - \dot{\mu}_i \\
\frac{\partial m_v}{\partial t} &= -\text{div}(W_v) + \dot{\mu}_v \\
\frac{\partial m_a}{\partial t} &= -\text{div}(W_a)
\end{align*}$$

$m_i$ is the total mass of the constituent $i$ per unit of material volume

$W_i$ is the mass flux of the constituent $i$

$\dot{\mu}_i$ represents the rate of mass formation per unit of volume

The “div()” operations represent the mass exchanges with the environment
Simulation of water and species transport in porous media

- Governing equations
  - Expression of the mass flux of each constituent
    \[ W_i = m_i v_i \]
    - \( m_i \) represents the total mass of the constituent \( i \) per unit of material volume
    - \( v_i \) represents the velocity of the constituent \( i \)
  - Expression of the total mass of each constituent
    \[
    \begin{align*}
    m_i &= \rho_i \phi S_r \\
    m_v &= \rho_v \phi (1 - S_r) \\
    m_o &= \rho_o \phi (1 - S_r)
    \end{align*}
    \]
    - \( \phi \) represents the total connected porosity
    - \( S_r \) represents the liquid water saturation
    - \( \rho \) represents the density of the constituent \( i \)
    - \( M_j \) represents the molar mass
      \[ j = v, o, a \]

Simulation of water and species transport in porous media

- Drying equation
  - Water in liquid and gaseous phases is taken into account
    \[
    \begin{align*}
    \frac{\partial}{\partial t} \left( m_j + \frac{m_v}{\rho_v} \right) &= - \nabla \cdot \left( \overrightarrow{w_j} - \frac{\mu_j}{\eta_j} \right) - \nabla \cdot \left( \overrightarrow{w_v} + \overrightarrow{w_o} \right) + \frac{\mu_j}{\eta_j} - \mu_j \\
    \frac{\partial}{\partial t} \left( \frac{m_v}{\rho_v} \right) &= - \nabla \cdot \left( \frac{M_j}{\rho_v} \frac{\nabla \rho_v}{\eta_j} \right) - \nabla \cdot \left( \frac{M_j}{\rho_v} \frac{\nabla \rho_v}{\eta_j} \right) + \frac{\mu_j}{\eta_j} \\
    \frac{\partial}{\partial t} \left( \frac{m_o}{\rho_o} \phi (1 - S_r) \right) &= - \nabla \cdot \left( \frac{K_i}{\eta_i} \nabla \rho_i + \frac{M_v}{\rho_v} \frac{\nabla \rho_v}{\eta_v} + \frac{M_o}{\rho_o} \frac{\nabla \rho_o}{\eta_o} \right)
    \end{align*}
    \]
    - \( m_j \) represents the amount of liquid water
    - \( m_v \) represents the diffusive flux of water vapour
    - Darcy’s flux of liquid water
    - Diffusive flux of water vapour
Simulation of water and species transport in porous media

- Drying parameters

  • Resistance to the diffusion: the relative permeabilities to both liquid and gaseous phases

\[
k_{rl}(S_r) = S_r \left[ 1 - \left( 1 - S_r \right)^{\frac{1}{m^2}} \right]^2
\]

\[
k_{rg}(S_r) = (1 - S_r)^{\frac{1}{2}} \left( 1 - S_r \right)^{\frac{1}{2m}}
\]

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- Resistance of the porous media to the gas diffusion

\[ D = D_0 R_d \]

\[ D_0 = 0.127 \times 10^{-8} \frac{P_{atm}}{P_0} \left( \frac{T}{T_0} \right)^{1.88} \]

\[ R_d(\phi, S_r) = \phi^{2.74} (1 - S_r)^{4.20} \]

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Simulation of water and species transport in porous media

- Drying equation: application

$$\frac{\partial}{\partial t} \left( \rho \phi S_r + \frac{D_r M_v}{RT} \phi (1 - S_r) \right) = - \text{div} \left( \rho \frac{k_l}{\eta_l} \text{grad} p_i + \frac{M_i}{RT} R_{i,v} D_{i,v} \text{grad} p_v \right)$$

Darcy’s flux of the liquid water

Diffusive flux of the vapour water

- Main variable: relative humidity $h$

$$\left[ \rho \phi \frac{\partial f}{\partial h} + \frac{P_{sat} M_v}{RT} \phi \left( 1 - f(h) - h \frac{\partial f}{\partial h} \right) \right] \frac{\partial f}{\partial h} = \text{div} \left( \rho \frac{k_l}{\eta_l} \frac{RT}{M_i} \frac{1}{h} \text{grad} \left( 1 + \frac{M_i}{RT} R_{i,v} D_{i,v} \frac{1}{P_{sat}} \text{grad} h \right) \right)$$

Convective flux

Diffusive flux

Simulation of water and species transport in porous media

- Variation of water quantity in the carbonation mechanisms (dissolution of hydrates)

$$\begin{align*}
CH & \rightarrow 1 \\
CSH & \rightarrow 0 \\
AFt & \rightarrow 32 \\
AFm & \rightarrow 12
\end{align*}$$
Simulation of water and species transport in porous media

- Initial conditions and boundaries conditions

Hydric cycles (variation of relative humidity $h$)

$h = 50\%$

Simulation of water and species transport in porous media

- Boundaries conditions
Simulation of carbon dioxide transport

- Transport of carbon dioxide

\[
\frac{\phi(1 - S_r)}{RT} \frac{P_{CO_2}}{t} = -\text{div}(D_{CO_2} \cdot R_d \cdot \text{grad}(\frac{P_{CO_2}}{RT})) - \frac{CaCO_3}{t}
\]

\[
R_d = \phi^{2.74} (1 - S_r)^{4.2}
\]

Millington et al, Tiery et al

Simulation of carbon dioxide transport

- Initial conditions and boundaries conditions

CO\textsubscript{2} pressure (4 053 Pa)
After one day of simulation

\[ \approx 0 \text{ Pa} \]
Simulation of CH consumption

- CH consumption (expressed as equivalent Ca)

\[
\frac{Ca_{CH}}{t} = -K_1 \cdot Ca_{CH} \cdot \frac{P_{CO2}}{RT}
\]

Hypothesis: reactions are delayed. This hypothesis allows the numerical resolution.

The CH consumption depends on the CO₂ pressure

→ reaction does not occur anymore when all CH is consumed

Simulation of AFt consumption

- AFt consumption (expressed as equivalent Ca)

\[
\frac{Ca_{AFt}}{t} = -K_1 \cdot Ca_{AFt} \cdot \frac{P_{CO2}}{RT}
\]

- Initial conditions

\[
\begin{align*}
\text{CH}_3: & \quad \text{CH}_3\text{O}-4 \text{AF}_t \quad \text{CaO} \\
\text{SiO}_2 & = \text{CSH} \\
2 \text{AF}_t & = 2 \text{Al}_2\text{O}_3
\end{align*}
\]

\[\text{avec :}\]
- CH₃: quantité moleculaire de portlandite (mol/l de pâte de ciment);
- C₃S: quantité moleculaire de C₃S-δ (δ mol/l de pâte de ciment);
- AFₜ: quantité moleculaire de monocalciumaluminate (mol/l de pâte de ciment);
- AFₙ: quantité moleculaire de tricalciumaluminate (mol/l de pâte de ciment);
- C₃AH₆: quantité moleculaire de hexahydrate (mol/l de pâte de ciment);
- CaO, SiO₂, Al₂O₃, SO₃: quantité moleculaire d’oxydes contenus dans le ciment hydraté (mol/l de pâte de ciment), pondérés par le degré d’hydratation [122].
Simulation of C-S-H consumption

- C-S-H consumption (expressed as equivalent Ca)

\[
\frac{Ca_{CSH}}{t} = -K_1 \cdot Ca_{CSH} \cdot \left(\frac{P_{CO2}}{RT}\right)^n
\]

n = 0.8

From Hyvert’s thesis work \(\Rightarrow\) At time \(t\), the rate of hydrate consumption is not the same for all hydration products.

Simulation of the calcite formation (« sink of CO\textsubscript{2} »)

- Formation of calcite

\[
\frac{CaCO_3}{t} = K_1 \cdot (Ca_{CH} \cdot \frac{P_{CO2}}{RT} + Ca_{ALF} \cdot \frac{P_{CO2}}{RT} + Ca_{AFM} \cdot \frac{P_{CO2}}{RT} + Ca_{CSH} \cdot \left(\frac{P_{CO2}}{RT}\right)^n)
\]

Hypothesis (for all reactions): The rates of convection mechanisms are lower than the rates of all the chemical reaction and all the reaction occur without any movement.
Simulation of the AFm consumption

- AFm consumption (expressed as equivalent Ca)
  \[
  \frac{AF_m}{t} = -K_1 \cdot AF_m \cdot \frac{P_{CO_2}}{RT} - K_2 \cdot AF_m \cdot (SF_{eq} - SF).Cl
  \]

- Initial conditions

\[-\text{Carbonation} \quad \text{Chemical fixation of chlorides}\]

\[\text{with}:
\begin{align*}
\text{CH} & : \text{quantity molaire de Portlandite (mol/l de pâte de ciment)} \\
\text{CSH} & : \text{quantity molaire de C-S-H (C/S=1.63) (mol/l de pâte de ciment)} \\
\text{AFm} & : \text{quantity molaire de monomylitane (mol/l de pâte de ciment)} \\
\text{AFt} & : \text{quantity molaire de trimylitane (mol/l de pâte de ciment)} \\
\text{C3ASH6} & : \text{quantity molaire de bromeite (mol/l de pâte de ciment)} \\
\text{CaO, SiO}_2, \text{Al}_2\text{O}_3, \text{SO}_3 & : \text{quantity molaire d’espèces contenues dans le ciment hydraté (mol/l de pâte de ciment), pondérée par le degré d’alcalinité (122).}
\end{align*}
\]

Simulation of the AFm consumption

- SF_{eq}
  \(SF_{eq}\) represents the total chlorides able to be chemically fixed (by formation of Friedel salts) for infinite time and for the AFm still available (that means not carbonated) \(^2\)


\[^1\] WANG X. – « Modélisation du transport multi-espèces dans les matériaux cimentaires saturés ou non saturés et éventuellement carbonatés », Thèse de doctorat soutenue le 27 Avril 2012, Université de Paris Est, IFSTTAR.
Simulation of chemical fixation of chlorides - SF

- Formation of Friedel salts

\[
\frac{\partial SF}{\partial t} = K_2 A F_m (S Feq - SF).Cl
\]

When SF = SF_{eq} the chemical fixation of chlorides and the formation of Friedel salts do not occur anymore.

Simulation of physical fixation of chlorides - YCSH

- Chlorides fixations on CSH

\[
\frac{YCSH}{t} = K_3 (YCSHeq - YCSH)
\]

When YCSH = YCSH_{eq} the chloride fixation on C-S-H does not take place anymore.

YCSH_{eq} represents the total chlorides able to be fixed after infinite time.


Simulation of chlorides transport

- Chlorides transport
  \[ \varphi \cdot S_r \cdot \frac{\text{Cl}}{t} = - \text{div}(\Phi_{\text{Cl}}) - \beta \]
  \[ = -(D_{\text{Cl}}) (S_r) \text{grad} (\text{Cl}) + \Phi_{\text{w}} \cdot \text{Cl} \]
  \[ \beta \]
  - Physical fixation of chlorides
  - Chemical fixation of chlorides
  \[ - 2 \cdot K_z \cdot (S_{\text{Feq}} - \text{SF}) \cdot \text{Cl} \]

Influence of the saturation state on the chlorides diffusion

We consider that below 60% of saturation the liquid phase is not continuous anymore and the diffusion is impossible.

By using this law on Francy's data, Nguyen demonstrated that \( \lambda = 6 \).
### Simulation parameters

- **All the parameters input in the model**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>0.154</td>
<td>Experimental</td>
</tr>
<tr>
<td>$T$ [K]</td>
<td>293</td>
<td>Environmental conditions of the test</td>
</tr>
<tr>
<td>$\rho_l$ [kg/m$^3$]</td>
<td>$10^3$</td>
<td>Water density</td>
</tr>
<tr>
<td>$R$ [J/mol/K]</td>
<td>8.32</td>
<td>Constant of ideal gas</td>
</tr>
<tr>
<td>$M_v$ [kg/mol]</td>
<td>$18 \times 10^{-3}$</td>
<td>Molecular mass of the water vapour</td>
</tr>
<tr>
<td>$p_{sat}$ [Pa]</td>
<td>2325.5</td>
<td>Saturated vapour pressure</td>
</tr>
<tr>
<td>$f(h)$</td>
<td>-</td>
<td>Sorption/desorption</td>
</tr>
<tr>
<td>$K_l$ [m$^2$]</td>
<td>$4 \times 10^{-10}$</td>
<td>Experimental</td>
</tr>
<tr>
<td>$\eta_l$ [Pa.s]</td>
<td>$1.002 \times 10^{-3}$</td>
<td>Dynamic viscosity</td>
</tr>
<tr>
<td>$k_{rl}$</td>
<td>-</td>
<td>Ranaivomanana’s thesis</td>
</tr>
<tr>
<td>$D_0$ [m$^2$/s]</td>
<td>$2.48 \times 10^{-5}$</td>
<td>Diffusion coefficient out of porous media</td>
</tr>
</tbody>
</table>

### Simulation results (CPU time of simulation: 20 minutes)
Simulation

- Results – mass gain of water in samples

Perspectives

- Decalcification

\[
\frac{\partial \phi [Ca^{2+}]}{\partial t} = - \text{div} \left( D_e \text{grad}[Ca^{2+}] \right) - \frac{\partial [Ca_s]}{\partial t}
\]
Simulation of the oxygen consumption at the steel/concrete interface

$$\varphi(1-Sr) \frac{\partial \rho}{\partial t} = -\text{div}(D_{O_2} R_d \text{grad}(O_2))$$

0.25 mol/m³ (hypothesis: the maximal concentration in the environment at the atmospheric pressure)

$$\Phi = f(CI, \rho) \cdot O_2$$

= 0.25 mol/m³

The oxidation rate of iron is very fast compared to the rate of oxygen reduction. The corrosion rate is governed by the rate of reduction mechanisms and the oxygen diffusion.

Drying mechanisms are taken into account.

The oxygen diffusion is much faster in the air than in water.
The oxygen flux gives 4/3 of the iron flux according to the corrosion equation.

The ratio $M(\text{Fe})/\rho(\text{Fe})$ represents the quantity of corrosion products which is produced (for one mol of iron) to express the iron flux into corrosion rate.

$2Fe + \frac{3}{4}M(\text{Fe}) + 3H_2O \rightarrow 2Fe(OH)_3$

$V_{\text{corr}} = \frac{2}{3} \frac{M(\text{Fe})}{\rho(\text{Fe})} \cdot K_4 \cdot \varphi \cdot Sr \cdot C_{O_2}$ in m.s$^{-1}$

$H : \text{function which takes into account the depassivation conditions of the reinforcement}$

Carbontation $\rightarrow$ Decrease of pH $\rightarrow$ Destruction of the passive layer $\rightarrow$ Chlorides

$H(\text{pHeq}) \Rightarrow \text{pHeq} < 9$

$H(\text{Cl}_{\text{tot}}) \Rightarrow \text{Masse}_{\text{Cl}} / \text{Masse}_{\text{ciment}} \geq 0.006$

$H = \max(H(\text{Cl}_{\text{tot}}), H(\text{pHeq}))$

$V_{\text{red}} = H \cdot K_4 \cdot \varphi \cdot Sr \cdot C_{O_2}$
Thank you for your attention