A Model of Concrete Carbonation Using Comsol Multiphysics®

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Overview

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Concrete carbonation

- CO₂ permeates the porous and fractured structure of concrete.
- Establishes conditions of concrete degradation.
- Controls reinforcing bar corrosion and durability of the whole civil structure.
- May cause corrosion around reinforcing bars, causing deterioration of material and structure mechanical properties.

Figure 1. Carbonation of an OPC, validated also for pozzolanic cements [Papadakis et al, 1992]
Physical model

- 10 cm diameter and 20 cm height cylinders.
- Two base surfaces covered with aluminum foil to set up a radial diffusion process.
- Pozzolanic cement MP/A-28 manufactured by Lafarge-Holcim.
Water to binder w/c and aggregate to binder a/c ratios were 0.52 and 4.17, respectively.

Samples were cured for 90 days in a wet chamber at 23±2 °C and at relative humidity higher than 95%.

**Table 1.** Chemical composition of Lafarge-Holcim MP/A-28 cement.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (Magnesium oxide)</td>
<td>2.19</td>
</tr>
<tr>
<td>SO$_3$ (Sulphur trioxide)</td>
<td>2.51</td>
</tr>
<tr>
<td>C$_3$A (Tricalcium aluminate)</td>
<td>8.30</td>
</tr>
<tr>
<td>C$_3$S (Tricalcium silicate)</td>
<td>62.40</td>
</tr>
<tr>
<td>C$_2$S (Dicalcium silicate)</td>
<td>12.50</td>
</tr>
<tr>
<td>C$_4$AF (Tetracalcium aluminoferrite)</td>
<td>9.30</td>
</tr>
</tbody>
</table>

**Table 2.** Chemical composition of the Pozzolanic addition.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (Silicon dioxide)</td>
<td>83.6</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (Aluminum oxide)</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (Iron dioxide)</td>
<td>1.6</td>
</tr>
<tr>
<td>CaO (Calcium oxide)</td>
<td>0.8</td>
</tr>
<tr>
<td>MgO (Magnesium oxide)</td>
<td>0.1</td>
</tr>
<tr>
<td>SO$_3$ (Sulphur trioxide)</td>
<td>0.9</td>
</tr>
<tr>
<td>K$_2$O (Potassium oxide)</td>
<td>0.0</td>
</tr>
<tr>
<td>Na$_2$O (Sodium oxide)</td>
<td>0.2</td>
</tr>
</tbody>
</table>
• Samples placed in accelerated carbonation chamber.
• Water is the solvent for the chemical reactions.
• CO₂ diffusion mechanism is set in the radial direction.
• Velocity of carbonation front depends on CO₂ effective diffusivity.
• Diffusion coefficient is a function of water/cement (w/c) ratio and degree of saturation of pores with water [Papadakis et al., 1989; Papadakis et al., 1992].
• XRD confirms calcium aluminosilicate presence in the pozzolanic cement and of anorthite CaAl₂Si₂O₈ in sands used to prepare the concrete blend. No Ca(OH)₂ was detected.
Mathematical model

- Transient, bi-dimensional diffusion mechanism for species transport.
- Convective processes are neglected, isothermal conditions are assumed.
- Chemical species are considered to be diluted.
- Porosity and water saturation in concrete are considered constant.
- Results are validated by comparing with experimental testing.
- We assume a carbonation reaction in the liquid phase between calcium aluminosilicates and CO$_2$ gas:
  \[
  \text{CO}_2 + \text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}_2\text{O} = \text{CaCO}_3 + \text{AlSi}_2\text{O}_5(\text{OH})_4
  \]
  \[\text{(1)}\]
The partial differential equation for the mass conservation of a chemical specie $i$ in a time dependent, diffusion transport process in a liquid of a partially filled saturated porous media is:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D\nabla c_i) = R_i$$  \hspace{1cm} (2)

For the reacting specie $i$ of Eq. 2, $c_i$ is its concentration, $D$ is the diffusion coefficient and $R_i$ is the reaction rate expression.

The above equation is obtained by writing the conservation of the mass flux vector $N_i$ of the specie $i$, starting with Fick’s 1st law for diffusion of species in a diluted solution, and in absence of convective mechanisms:

$$-D\nabla c_i = N_i$$  \hspace{1cm} (3)
• Conservation equation is written in term of concentration per water volume of the porous media (Comsol Multiphysics® - Partially Saturated Porous Media definition).

• The porosity \( p \) is 0.25, water saturation grade \( s \) is 0.27 (relative humidity in the accelerated carbonation chamber is 65%).

• Therefore liquid volume fraction is \( s \Theta = 0.0675 \).

• \( \text{CO}_2 \) diffusion coefficient is assumed as \( 1 \times 10^{-8} \text{ m}^2/\text{s} \)
  and the \( \text{CO}_2 \) concentration in the accelerated carbonation chamber as 25% in volume.

• Reaction rate and the rate constants of chemical reactions are set with the standard values of Comsol Multiphysics® database.

• Temperature is 25 °C and the pressure is 1 atm.

### Table 3. Molar masses, densities and diffusion coefficient of the reacting chemical species of Eq. 1.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Molar mass (g/mol)</th>
<th>Density (kg/m³)</th>
<th>Diffusion coeffic. (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 ) (*) (gas)</td>
<td>44.01</td>
<td></td>
<td>1x10⁻⁸</td>
</tr>
<tr>
<td>( \text{CaAl}_2\text{Si}_2\text{O}_8 ) (solid)</td>
<td>278.20</td>
<td>2740</td>
<td>1x10⁻⁹</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) (liquid)</td>
<td>18.02</td>
<td>1000</td>
<td>solvent</td>
</tr>
<tr>
<td>( \text{CaCO}_3 ) (solid)</td>
<td>100.09</td>
<td>2710</td>
<td>1x10⁻⁶</td>
</tr>
<tr>
<td>( \text{AlSi}_3\text{O}_5\text{(OH)}_4 ) (solid)</td>
<td>258.16</td>
<td>2600</td>
<td>1x10⁻⁹</td>
</tr>
</tbody>
</table>

(*) \( \text{CO}_2 \) is assumed to be an ideal gas at pressure \( p \) (Pa) and temperature \( T \) (K).
Boundary conditions

• Set CO$_2$ concentration in vertical wall of sample ($r = R$) as 10.22 mol/m$^3$, obtained from %CO$_2$ concentration in the carbonation chamber.

• For the same wall, boundary conditions for the other dilutes species is mass flux equal to zero.

• Base surfaces are set as no mass flux for all chemical species.

• Axial symmetry is used on z axis of the concrete sample.

• Initial conditions for the species concentrations in the liquid fraction are 280 mol/m$^3$ for CaAl$_2$Si$_2$O$_8$ and zero for other reacting species.
Figure 3. Concentration profiles of reacting species after 28 days of carbonation (25% CO$_2$, 65% RH, 25°C).

Figure 4. Concentration profiles of CO$_2$ in the concrete, for the carbonation times of Table 4 (25% CO$_2$, 65% RH, 25°C).

Figure 5. Concentration profiles of CaCO$_3$ for the carbonation times of Table 4 (25% CO$_2$, 65% RH, 25°C).
Table 4. Carbonation depth in the concrete.

<table>
<thead>
<tr>
<th>Carbonation (days)</th>
<th>Experimental values of carbonation depth (mm)</th>
<th>Computational values of carbonation depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>4.5</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>6.5</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>9.5</td>
</tr>
<tr>
<td>28</td>
<td>12</td>
<td>12.5</td>
</tr>
<tr>
<td>44</td>
<td>15</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Figure 6. Carbonation depth in a sample of concrete, after 28 days of accelerated carbonation.

Figure 7. Carbonation depth with time in the concrete sample.
Conclusions

• A time dependent carbonation process of a concrete manufactured with pozzolanic cement has been modeled by using the Chemical Reaction Engineering Module of Comsol Multiphysics®.

• The numerical results give the carbonation front in time and species concentration in the carbonated concrete.

• Validation of results is made by comparing them with experimental testing in an accelerated carbonation chamber, under controlled conditions of relative humidity, CO₂ concentration and temperature.

• Computational results obtained with Comsol Multiphysics® are encouraging for a next study which will also include steel bar corrosion.
References


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