

# A Model of Concrete Carbonation Using Comsol Multiphysics®

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## Abstract:

In the construction sector, the concrete and the steel represent still the key components, although they are very vulnerable by the atmospheric agents, as in the case of their degradation caused by corrosion. In the same time, the carbonation controls the reinforcing bar corrosion and the durability of the whole civil structure. In this work we model the time dependent carbonation process of a concrete by using the Chemical Reaction Engineering Module of Comsol Multiphysics®. The carbonation reaction is set up in the Reaction Engineering interface, then we use the Generate Space-Dependent Model to export the properties to the Transport of Dilute Species interface. The numerical results give the carbonation front in time and species concentration of the carbonated concrete. The validation of our results is made by comparing them with experimental testing by an accelerated carbonation chamber, accomplished under controlled conditions of relative humidity, CO<sub>2</sub> concentration and temperature.

**Keywords:** concrete, carbonation, reaction-diffusion process, computational modeling.

## 1. Introduction

In the construction sector, the concrete and the steel represent still the key components, although they are very vulnerable by the atmospheric agents, as in the case of their degradation caused by corrosion. The study of the concrete carbonation, due to the CO<sub>2</sub> which permeates the porous and fractured structure of the concrete, is a fundamental issue for establishing conditions of concrete degradation. In the same time, the carbonation controls the reinforcing bar corrosion and the durability of the whole civil structure. The value of the concrete carbonation may show existence of corrosion around the reinforcing bar, denoting deterioration of the mechanical properties of the material and finally of the structure. Computational modelling and experimental testing of porous materials, are both

considered very useful methods to analyse the carbonation of concrete.

In a series of papers, Papadakis *et al.* [1, 2, 3] modeled the main mechanisms controlling the physico-chemical processes for the carbonation of an ordinary portland cement (OPC). They included the diffusion of CO<sub>2</sub> in the gas phase of the concrete pores, its dissolution in the aqueous film, the diffusion of dissolved Ca(OH)<sub>2</sub> and the fundamental chemical reactions of carbonation. The authors obtained an analytical expression able to predict the evolution of the carbonation front with time for one-dimensional geometry of an OPC and verified its validity for pozzolanic cements [4]. Saetta *et al.* [5] developed a numerical procedure based on the finite element method to solve the one-dimensional governing equations of moisture, heat and carbon dioxide flows through an OPC. Since the concentration of Ca(OH)<sub>2</sub> is usually higher than the concentration of the other hydration products, the authors modelled only the carbonation of the calcium dioxide. Later, the same authors [6] extended the carbonation model to two-dimensional domains. More recently, Radu *et al.* [7] investigated numerically a prototypical reaction-diffusion-flow problem in saturated/unsaturated porous media and applied a finite element solution for the study of concrete carbonation with convective transport and variable porosity. Other works for studying phenomena affecting the durability of concrete have been carried out using Comsol Multiphysics®, e.g the chloride transport in cracked concrete [8, 9] and the chloride-induced corrosion initiation of steel rebar [10].

In this work we model the time dependent carbonation process of a concrete by using the Chemical Reaction Engineering Module of Comsol Multiphysics®. The carbonation reaction is set up in the Reaction Engineering interface, then we use the Generate Space-Dependent Model to export the properties to the Transport of Dilute Species interface. The structure of the paper is the following. The description of the physical model is given in Section 2, while Section 3 describes the mathematical model and

the use of Comsol Multiphysics®. Finally, the computational results are presented in Section 4 and the conclusions in Section 5.

## 2. Physical model

The concrete samples are cylinders of radius  $R$  equal to 5 cm and height  $H$  of 20 cm (Fig. 1). The samples were prepared using a pozzolanic cement MP/A-28 manufactured by Lafarge-Holcim. Table 1 and 2 give the chemical composition of the cement and the pozzolanic addition, respectively. Water to binder  $w/c$  and

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

| Specie  | Content (%) |
|---|-------------|
| MgO (Magnesium oxide)                           | 2.19        |
| SO <sub>3</sub> (Sulphur trioxide)              | 2.51        |
| C <sub>3</sub> A (Tricalcium aluminate)         | 8.30        |
| C <sub>3</sub> S (Tricalcium silicate)          | 62.40       |
| C <sub>2</sub> S (Dicalcium silicate)           | 12.50       |
| C <sub>4</sub> AF (Tetracalcium aluminoferrite) | 9.30        |

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

| Specie  | Content (%) |
|---|-------------|
| SiO <sub>2</sub> (Silicon dioxide)              | 83.6        |
| Al <sub>2</sub> O <sub>3</sub> (Aluminum oxide) | 0.2         |
| Fe <sub>2</sub> O <sub>3</sub> (Iron dioxide)   | 1.6         |
| CaO (Calcium oxide)                             | 0.8         |
| MgO (Magnesium oxide)                           | 0.1         |
| SO <sub>3</sub> (Sulphur trioxide)              | 0.9         |
| K <sub>2</sub> O (Potassium oxide)              | 0.0         |
| Na <sub>2</sub> O (Sodium oxide)                | 0.2         |

aggregate to binder  $a/c$  ratios were 0.52 and 4.17, respectively. Next, the samples were cured for 90 days in a wet chamber at  $23 \pm 2$  °C and at a relative humidity greater than 95%.

To develop the carbonation of the concrete of the experimental work, the cylindrical specimens were placed in the accelerated carbonation chamber shown in Fig. 2. In the chamber, two separated streams, respectively of wet air and CO<sub>2</sub> gas, were fed and automatically controlled. To settle up a radial diffusion process in the concrete, the two base surfaces of each concrete samples were recovered with aluminum foils. Therefore, by applying axisymmetric conditions we can model the transport of the species in the concrete sample by using a system of cylindrical coordinates  $r, z$ .



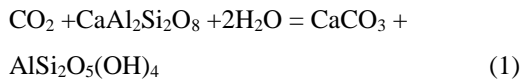
**Figure 1.** A cylindrical sample of concrete with its bases recovered by aluminum foils.

The physical phenomena occur in a dilute solution of the porous media. We consider a transient, isothermal, bi-dimensional diffusion mechanism for the species transport in the water, which is the solvent, neglecting convective processes. We assume that the species are already in the liquid phase liquid, i.e. the gas-liquid and liquid-solid equilibrium are not modeled. Porosity and water saturation grade of the concrete are considered as constants. The CO<sub>2</sub> diffusion mechanism is set in the radial direction, therefore the carbonation front is moving forward from the



**Figure 2.** Accelerated carbonation chamber used in the experimental work.

the external vertical surface of the sample to the centre of it. The velocity of this front depends on the CO<sub>2</sub> effective diffusivity inside the pores of the carbonated concrete, in particular the diffusion coefficient is a function of the water/cement (w/c) ratio and the degree of saturation of the pores with water [1,4]. The chemical reaction develops in the aqueous phase (solvent) and the remaining chemical species are considered diluted. The XRD analysis confirmed the presence of calcium aluminosilicate in the pozzolanic cement and of anorthite CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> in the finer fraction of the sands used to prepare the concrete blend. No Ca(OH)<sub>2</sub> was detected by the XRD measurements. For the pozzolanic cement we assume a carbonation reaction in the liquid phase between calcium aluminosilicates and CO<sub>2</sub> gas. According to Oelkers *et al.* [11], a carbonation reaction which involves anorthite and gives calcite and kaolinite as reaction products is:



### 3. Equations and solution with Comsol Multiphysics®

We model the time dependent carbonation process of the concrete by using the Chemical Reaction Engineering Module of Comsol Multiphysics® [12]. The carbonation reaction is set up in the Reaction Engineering interface, then we use the Generate Space-Dependent Model to export the properties to the Transport of Dilute Species interface. 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:

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

For the reacting specie *i* of Eq. 2, *c<sub>i</sub>* is its concentration, *D* is the diffusion coefficient and *R<sub>i</sub>* is the reaction rate expression. The above equation is obtained by writing the conservation of the mass flux vector *N<sub>i</sub>* of the specie *i*, starting with the first Fick's law for the diffusion of the specie in a diluted solution and in absence of convective mechanisms:

$$\mathbf{N}_i = -D\nabla c_i \quad (3)$$

Then the conservation equations is written in term of concentrations per water volume of the porous media, feature that in Comsol Multiphysics® can be set up by using the Partially Saturated Porous Media definition. The porosity  $\varepsilon_p$  is 0.25, the water saturation grade *s* is 0.27 (relative humidity RH in the accelerated carbonation chamber is 65%), therefore the liquid volume fraction  $\theta$  is  $\varepsilon_p s$  equal to 0.0675.

Additionally, we assume an effective CO<sub>2</sub> diffusion coefficient of  $1 \times 10^{-8}$  m<sup>2</sup>/s and define the experimental value of the CO<sub>2</sub> concentration in the accelerated carbonation chamber as 25% in volume. To model the reaction rate and the rate constants of the chemical reaction we use the standard values of the Comsol Multiphysics® data base. In the computational model, the temperature is 25 °C and the pressure is 1 atm. Table 3 gives molar mass, density and diffusion coefficient for each reacting species of the carbonation reaction described by Eq.1.

**Table 3.** Molar mass, density and diffusion coefficient of the reacting chemical species of Eq. 1.

| Specie   | Molar mass (g/mol) | Density (kg/m <sup>3</sup> )     | Diffusion coeffic. (m <sup>2</sup> /s) |
|--|--------------------|----------------------------------|--|
| CO <sub>2</sub> (*) (gas)                                  | 44.01              | $p^*0.044 / (8.31 \cdot 451^*T)$ | $1 \times 10^{-8}$                     |
| CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (solid)   | 278.20             | 2740                             | $1 \times 10^{-9}$                     |
| H <sub>2</sub> O (liquid)                                  | 18.02              | 1000                             | solvent                                |
| CaCO <sub>3</sub> (solid)                                  | 100.09             | 2710                             | $1 \times 10^{-9}$                     |
| AlSi <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> (solid) | 258.16             | 2600                             | $1 \times 10^{-9}$                     |

(\*) CO<sub>2</sub> is assumed to be an ideal gas at pressure *p* (Pa) and temperature *T* (K).

Then, boundary and initial conditions are specified for all the reacting species. Known the % CO<sub>2</sub> concentration in the carbonation chamber, we can compute the boundary value of this gas on the vertical wall of the concrete sample (*r* = *R*) as 10.22 mol/m<sup>3</sup>. For the same value of the *r* coordinate, the boundary condition for the other dilutes species is mass flux equal to zero. Furthermore, we set no mass flux for all the chemical species on the two base surfaces and use a condition of axial symmetry on the *z* axis of the concrete sample. Finally, the initial condition for the specie concentrations in the liquid fraction is

280 mol/m<sup>3</sup> for CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> and zero concentration for the rest of reacting species.

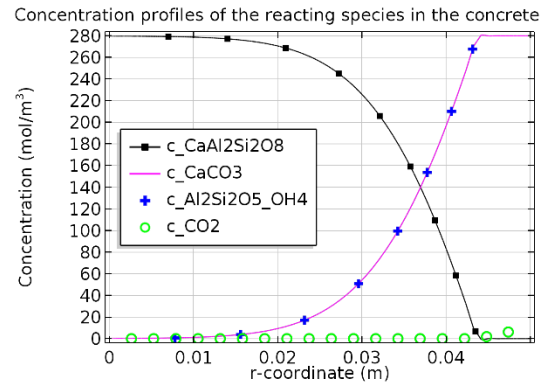
The resulting system of partial differential equations is numerically solved in Comsol Multiphysics® version 5.3a, by dividing the 2D region of the concrete sample with 10<sup>4</sup> quadrilaterals of a mapped mesh.

#### 4. Results and discussion

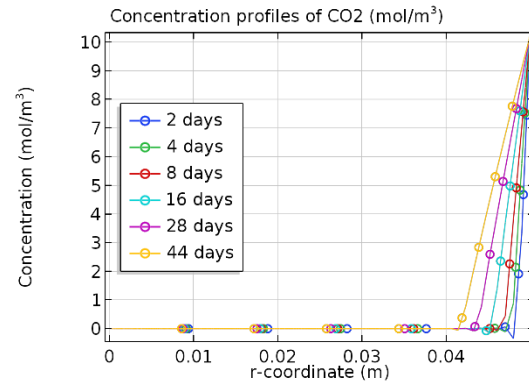
For the experimental values of RH=65%, CO<sub>2</sub>=25% and isothermal condition of 25°C, Fig. 3 gives the computational results of the chemical species concentrations in the concrete, corresponding to a carbonation time of 28 days. The results are consistent with the formation of a carbonation front which is indicated by the spatial change of the species concentration. In proximity of the external wall, we observe that CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> has completely reacted with the CO<sub>2</sub> gas diffusing into the concrete from outside, producing CaCO<sub>3</sub> and AlSi<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. In the inner region, the concentration of CaCO<sub>3</sub> diminishes according to a diffuse pattern and reaches half of its maximum value at r = 37 mm, i.e. at a distance of 13 mm from the external wall. We can assume this half value as an estimate of the carbonation depth. On the other hand, the concentration of CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> must show a similar but opposite behaviour, confirmed by the same values of Fig. 3.

The spatial concentration profiles of CO<sub>2</sub> are shown in Fig. 4 for six different times of accelerated carbonation. The gas diffuses from the exterior and reacts simultaneously with CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> and H<sub>2</sub>O to form calcite and kaolinite, according to Eq. 1. The penetration of the carbonation front may be observed in Fig. 5 which plots the spatial concentration of CaCO<sub>3</sub>, corresponding to the same carbonation times of Fig. 4.

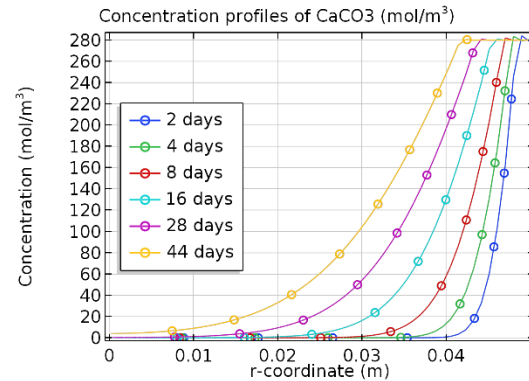
Fig. 6 shows a slice obtained from a sample of carbonated concrete which has been carbonated for 28 days in the accelerated carbonation chamber. The phenolphthalein indicator, which changes colour at pH 9.3 [2] highlights the internal region (r ≤ 35 mm, approximately) where the concentration of CaCO<sub>3</sub> has practically vanished. By processing with the phenolphthalein indicator all the set of carbonated concrete samples, we obtain the experimental carbonation depth of Table 4 (also displayed in Fig. 7), which are listed together with the computational values of Fig. 5. By comparing the computational results



**Figure 3.** Concentration profiles of the reacting species after 28 days of carbonation (25% CO<sub>2</sub>, 65% RH, 25°C).



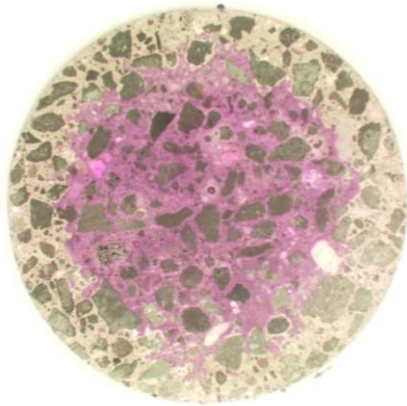
**Figure 4.** Concentration profiles of CO<sub>2</sub> in the concrete, for the carbonation times of Table 4 (25% CO<sub>2</sub>, 65% RH, 25°C).



**Figure 5.** Concentration profiles of CaCO<sub>3</sub> in the concrete, for the carbonation times of Table 4 (25% CO<sub>2</sub>, 65% RH, 25°C).

with the experimental data, we can observe a quite good matching between them. In this case we have to take also into account that, by the pH indicator, it is not possible to make an accurate

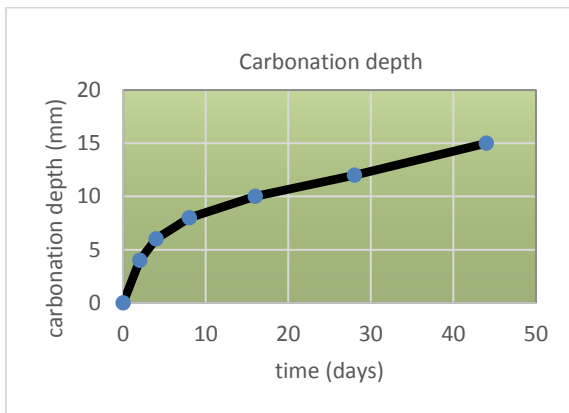
measurement of the position with a colour change.



**Figure 6.** Slice of a concrete sample, after 28 days of carbonation in the accelerated carbonation chamber (25% CO<sub>2</sub>, 65% RH, 25°C). The carbonation depth is revealed by the phenolphthalein indicator.

**Table 4.** Carbonation depth in the concrete with time (25% CO<sub>2</sub>, 65% RH, 25°C).

| Carbonation (days) | Experimental values of carbonation depth (mm) | Computational values of carbonation depth (mm) |
|--------------------|---|--|
| 2                  | 4   | 3.5  |
| 4                  | 6   | 4.5  |
| 8                  | 8   | 6.5  |
| 16                 | 10  | 9.5  |
| 28                 | 12  | 12.5   |
| 44                 | 15  | 17.0   |



**Figure 7.** Plot of the carbonation depth with time in the concrete (25% CO<sub>2</sub>, 65% RH, 25°C).

## 5. 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 of the carbonated concrete. The validation of the results has been made by comparing them with experimental testing in an accelerated carbonation chamber, accomplished under controlled conditions of relative humidity, CO<sub>2</sub> concentration and temperature.

The computational results obtained with Comsol Multiphysics® are encouraging for future studies including the steel bar corrosion.

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