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Modelling Diffusive Transport Phenomena in Carbonated Concrete Using Comsol Multiphysics®

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Abstract:

In a previous work, the time dependent carbonation process of a concrete was modelled by using the Reaction Engineering and Transport of Dilute Species interfaces of the Chemical Reaction Engineering Module of Comsol Multiphysics®. The numerical results provided the movement of the carbonation front in time and species concentration inside the carbonated concrete, the validation of our results is made by comparing them with experimental testing in an accelerated carbonation chamber was promising. In this work we update the model to better approximate the experimental results by incorporating the diffusion of O_2 and the variation of porosity in time, as the species generated by the carbonation reaction adhere to the pore walls. The decrease in pore size could affect the diffusion process to some degree, which will be modelled in this paper. The obtained results are encouraging for the next research activities.

Keywords: concrete, carbonation, reaction-diffusion process, computational modelling.

1. Introduction

Reinforced concrete is a widely used material in the civil engineering sector, mostly because of its relative low cost and good mechanical properties.

However, the chemical processes behind curing and life service of this material are very complex and numerous studies have been made to establish how they affect its properties and how they can be diminished, due to environmental factors such as the presence of CO_2 gas in the atmosphere.

In a previous work (Chinè et al., 2018), the time dependent carbonation process of a concrete was modelled by using the Chemical Reaction Engineering Module of Comsol Multiphysics®, in particular, the Reaction Engineering and Transport of Dilute Species interfaces. The numerical results provided the movement of the carbonation front in time and species concentration inside the carbonated concrete.

This model considered concrete as a porous material, the diffusion of CO_2 from the atmosphere into the structure and how it reacts with some chemical compounds of the concrete. However, other aspects where not considered, such as how the species created by the chemical reaction affect porosity and pH level of the material, as well as oxygen diffusion inside the structure, which is important as it could interact with the steel reinforcement and cause its corrosion.

The main reactions that occur during hydration of pozzolanic concrete, and the considerations that are made according to the constituents of the clinker and pozzolanic addition used to produce it, can be established by two sets of chemical reactions (Papadakis et al., 1992).

Each set corresponds to each one of the components of concrete:

Pozzolanic addition:

$C + H \Rightarrow CH$ (1)

$2S + 3CH \Rightarrow C_3S_2H_3$ (2)

$A + F + 8CH + 18H \Rightarrow C_8AFH_{26}$ (3)

$A + C\hat{S}H_2 + 3CH + 7H \Rightarrow C_4A\hat{S}H_{12}$ (4.a)

$A + 4CH + 9H \Rightarrow C_4AH_{13}$ (4.b)

Ordinary Portland cement:

$2C_3S + 6H \Rightarrow C_3S_2H_3 + 3CH$ (5)

$2C_2S + 4H \Rightarrow C_3S_2H_3 + CH$ (6)

$C_4AF + 4CH + 22H \Rightarrow C_8AFH_{26}$ (7)

$C_3A + C\hat{S}H_2 + 10H \Rightarrow C_4A\hat{S}H_{12}$ (8.a)

$C_3A + CH + 12H \Rightarrow C_4AH_{13}$ (8.b)

where: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $H = H_2O$ and $\hat{S} = SO_3$.

The theoretical composition of cured concrete can then be calculated from the composition of the mixed cement and pozzolanic addition.

With the known composition of cured concrete, several calculations can be performed, such as the effect of chemical reactions on the pH level inside the structure (changes due to carbonation), diminished porosity due to $CaCO_3$ production and deposition, among others (Papadakis et al., 1991; Radu et al., 2013; Hangx S.J., 2005).

The main objective of this work is to develop a computational model to calculate the pH and porosity changes, as well as oxygen diffusion which would participate in the corrosion reaction in the reinforcement steel bars inside the concrete structure. This first stage considered only the carbonation mechanism in the material. Another stage would include the study and prediction of the mechanical properties of steel reinforced concrete after being subject to atmospheric influence and corrosion.

2. Physical model

The concrete structure to be analysed is a cylinder of radius *R* equal to 5 cm and height *H* of 20 cm (Figure 1). The mixture consists of 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. An assumption is made that enough water is used during the hydration so that it does not become a limiting factor during the chemical reactions.

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

Specie	Content (%)
MgO (Magnesium oxide)	2.19
SO_3 (Sulphur trioxide)	2.51
C_3A (Tricalcium aluminate)	8.30
C_3S (Tricalcium silicate)	62.40
C_2S (Dicalcium silicate)	12.50
C_4AF (Tetracalcium aluminoferrite)	9.30
Impurities	2.80

Table 2. Chemical composition of the pozzolanic addition.

Specie	Content (%)
SiO_2 (Silicon dioxide)	83.6
Al_2O_3 (Aluminum oxide)	0.2
Fe_2O_3 (Iron dioxide)	1.6
CaO (Calcium oxide)	0.8
MgO (Magnesium oxide)	0.1
SO_3 (Sulphur trioxide)	0.9
K_2O (Potassium oxide)	0.0
Na_2O (Sodium oxide)	0.2
Impurities	12.6

Figure 1. A cylindrical sample of concrete with its bases covered by aluminium 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 modelled. Water saturation grade of the concrete is considered as constant and porosity will be modelled as dependant of the production of $CaCO_3$ during the chemical reactions.

The CO_2 diffusion mechanism is set in the radial direction and was modelled and compared to experimental data of a previous work (Chinè et al., 2018). Following this model, O_2 diffusion is added and is initially set as $1x10^{-8}$ m^2/s (Kobayashi, 1991).

The chemical reactions develop in the aqueous phase (solvent) and the remaining chemical species are considered diluted.

XRD measurements confirmed that no $Ca(OH)_2$ was detected and reveals the presence of calcium aluminosilicate in the pozzolanic cement and of anorthite $CaAl_2Si_2O_8$ in the finer fraction of the sands used to prepare the concrete blend. Using a theorical mixture of 75% clinker, 20% pozzolanic addition and 5% gypsum (Papadakis et al., 1992) and following the stoichiometry of the hydration reactions and the mixture used in the concrete, we confirm that no $Ca(OH)_2$ should be present.

XRD measurements also showed that anorthite is consumed completely during the carbonation process. For this reason, we assume a carbonation reaction in the liquid phase between calcium aluminosilicates and CO_2 gas. The carbonation reaction which involves anorthite and gives calcite and kaolinite as reaction products is (Oelkers et al., 2008):

$$\begin{aligned} CO_2 + CaAl_2Si_2O_8 + 2H_2O = \\ CaCO_3 + Al_2Si_2O_5(OH)_4 \end{aligned} \quad (9)$$

CO_2 gas dissolves in water and forms carbonic acid (Earle, 2015):

$$CO_2 + H_2O \Rightarrow H_2CO_3 = H^+ + HCO_3^- \quad (10)$$

$$\begin{aligned} H_2CO_3 + CaAl_2Si_2O_8 + H_2O = \\ CaCO_3 + Al_2Si_2O_5(OH)_4 \end{aligned} \quad (11)$$

Two conditions are necessary to cause steel bar corrosion: presence of oxygen and a decrease in concrete pH level. A diffusion mechanism will provide the necessary oxygen and reactions 9 and 10 (governed also by CO_2 diffusion) will change the pH level. This work will analyze if the necessary conditions are met at a specified time period inside the concrete structure and at a given depth where steel bars are placed.

For pH calculation, we assumed an initial pH level of 13, that is: $[H^+] = 1x10^{-13}$ mol/L. Following Sielemann et al (2002), an equation is derived to calculate pH from the gaseous CO_2 concentration in the system:

$$pH = -\log\left(1.209x10^{-4}\sqrt{[CO_{2(g)}]}\right) \quad (12)$$

Concerning porosity modelling, different studies relate the change of porosity to the amount of $CaCO_3$ produced during the carbonation reaction. The porosity decrease is related directly to the concentration of species, for example, in OPC (Papadakis et al., 1989):

$$\begin{aligned} \Delta\varepsilon = ([Ca(OH)_2]^0 - [Ca(OH)_2])\Delta\bar{V}_{CH} \\ +([CSH]^0 - [CSH])\Delta\bar{V}_{CSH} \end{aligned} \quad (13)$$

where $\Delta\bar{V}_{CH}$ is the volume change between $Ca(OH)_2$ and $CaCO_3$, $\Delta\bar{V}_{CSH}$ is the volume change between $C_3S_2H_3$ and $CaCO_3$.

For the anorthite reaction considered in this case, a volume increase of around 36% is expected in the diluted particles as anorthite is converted to kaolinite and $CaCO_3$ (Hangx, 2005). In rocks of similar composition, porosity will decrease in time and stabilize at around 0.18 (Hangx, 2005).

3. Equations and solution with Comsol Multiphysics®

The Chemical Reaction Engineering Module of Comsol Multiphysics® (Comsol AB, 2018) was used to model the time dependent carbonation process of concrete. Reactions are set up in the Chemistry interface and species diffusion is modelled in the Transport of Dilute Species interface.

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:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D\nabla c_i) = R_i \quad (14)$$

c_i is its concentration, D is the diffusion coefficient and R_i is the source term for species produced by chemical reactions.

The source term, R_i, is obtained from the stoichiometric coefficient v_i and the reaction rate:

$$R_i = v_i * r \quad (15)$$

Conservation equations are written in term of concentrations per water volume of the porous media, which are set up in the Partially Saturated Porous Media definition.

Several parameters are kept from previous model: porosity ε_p is 0.25, the water saturation grade s is 0.27, liquid volume fraction θ is equal to $s\,\varepsilon_p = 0.0675$. The CO_2 diffusion coefficient is 1×10^{-8} m^2/s, temperature is 25°C and pressure is 1 atm. As mentioned earlier, O_2 diffusion is added and set as 1×10^{-8} m^2/s (Kobayashi, 1991).

Chemical reaction rates have not been calculated and are modelled using the Comsol Multiphysics® database.

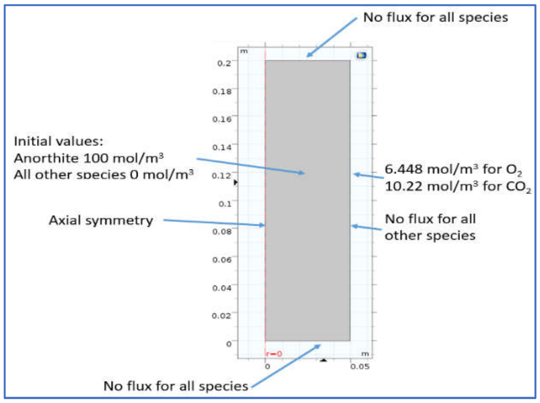

Figure 2. Boundary and initial conditions used for the study.

Boundary and initial conditions shown in Figure 2 are kept for all reacting species. CO_2 concentration on the vertical wall of the concrete sample ($r = R$) as 10.22 mol/m^3, O_2 concentration on the same wall as 4.465 mol/m^3 and mass flux equal to zero for the other dilutes species. We use no mass flux for all the chemical species on the two base surfaces and 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 100 mol/m^3 for $CaAl_2Si2O_8$ and zero concentration for the rest of reacting species.

The resulting system of partial differential equations is numerically solved in Comsol Multiphysics® version 5.4, by dividing the 2D region of the concrete sample with 10^4 quad elements of a mapped mesh.

4. Computational results and discussion

The first addition to the model is the O_2 diffusion. As expected from the assumption that oxygen does not react with other species, it diffuses into the concrete at a faster rate than all other species. As shown in Figure 3, at the end of 44 days it is almost in equilibrium with the O_2 concentration outside the sample. We consider that oxygen does not react with any other species in the model, so this contributes to the speed at which it permeates inside the structure.

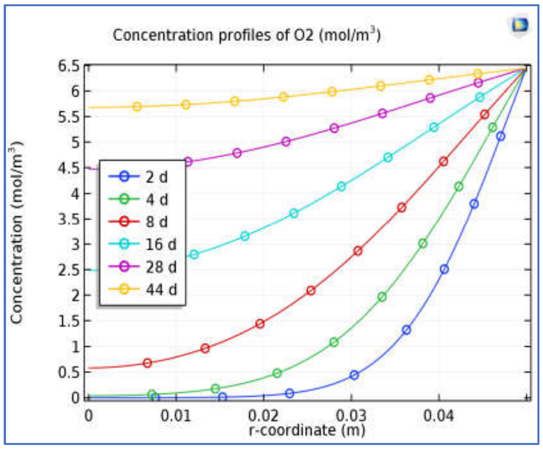

Figure 3. O_2 concentration at t = 0 and t = 1 day.

The pH level is plotted in Figure 4 using the derived formula based on CO_2 concentration. Since experimental data was obtained with phenolphthalein to indicate the pH change caused by the carbonation reactions, a line at pH = 8 is added for visual comparison to the experimental results.

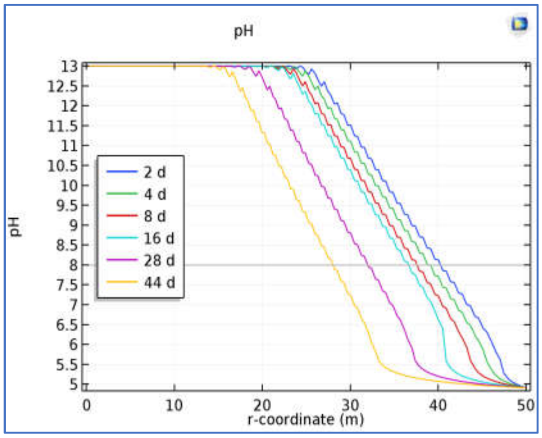

Figure 4. pH level based on CO_2 concentration.

The calculated pH level according to computational results is shown in Figure 4. These results, although promising, are slightly different than the data collected experimentally, resumed in Table 4.

Table 4. Carbonation depth variation in time inside the concrete at specified conditions ($r^2 = 0.98$).

Time (days)	Carbonation depth (mm)		
	Experimental value	Derived formula	Corrected formula
2	4	9	3.5
4	6	11	5.5
8	8	12.5	7
16	10	13	9
28	12	18	13
44	15	22	16

However, it was found that applying a correction factor of 10^{-2} to the formula the expected results were obtained. The correction factor is in the order of 10^{-2}. The results are also shown in Table 4 and Figure 5.

Given the complex mechanisms that occur inside concrete, the difference might depend on other reactions that have not been modelled and might act as sinks for CO_2 concentration.

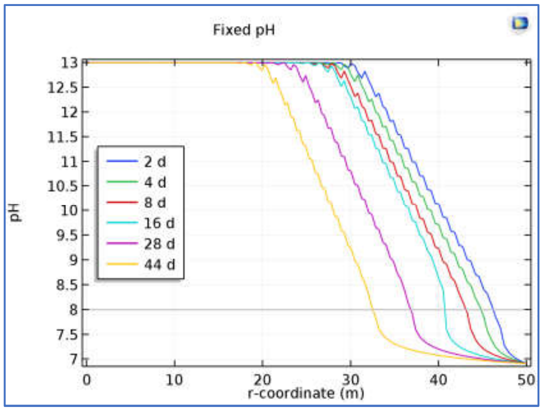

Figure 5. pH level calculated from the computational results applying a 10^{-2} correction factor to the derived formula.

Since the exact composition of the concrete is not known at this point, it is difficult to evaluate the relationship between the results of chemical reactions and the initial values considered for the model.

Another consideration is that the model is susceptible to the magnitudes of the different variables. This limits the ranges in which the model can be compared to experimental results or modified to analyze how the different variables affect the results (i.e: the effect of adding more anorthite or limiting the available CO_2, etc.).

The numerical instability of the model also affected modelling of the porosity change. Attempts were made to model a transient change of porosity, but this caused convergence problems. Then, the porosity change was graphed after results were obtained, we use a suitable factor to produce the expected change of porosity, which is from 0.25 to 0.18, shown in figure 6.

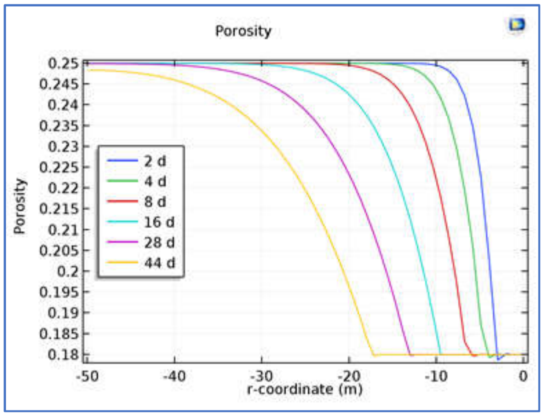

Figure 6. Porosity variation in time according to $CaCO_3$ concentration.

In this way the resulting porosity change varies as expected, however, the approximation could be improved if dilution/precipitation rates of species are considered.

As a final remark, the present work provided insight on the importance of the complex relations between concrete composition, pH levels and gaseous/diluted species equilibrium. These mechanisms, which were initially neglected, prove to have a significant effect on the behavior of the computational model and its capacity to describe the experimental behavior of the concrete. Additionally, an effort must be made to improve the numerical stability for future calculations.

5. Conclusions

- A finite element analysis of a concrete sample subject to carbonation was performed.
- Results indicate oxygen should not be a limiting factor if corrosion takes place inside the structure.
- Other chemical reactions must be considered in order to analyze how they affect pH levels.
- The anorthite - CO_2 reaction does not consider how much of both species dissolve into water.
- A thorough experimental composition analysis is necessary to continue improving the model.

- The numerical stability of the model should be improved for future, more complex analysis.

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