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CO-cycle in cement and concrete : Part 7: Models for CO-absorption. Status, January 2009

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Part 7: Models for CO_2-absorption. Status, January 2009

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Background

In a previous project, funded by the Nordic Innovation Centre, CO_2-uptake during the concrete life-cycle was studied, with project participants from Denmark, Iceland, Norway and Sweden. The objective was to provide documentation of concrete carbonation during the service life and recycling and re-use. The project resulted in a number of reports.

Preliminary results indicated significant effects: "In countries with the most favourable recycling practice it is realistic to assume that 86 % of the concrete is carbonated after 100 years, taking up approximately 57 % of the CO_2 emitted during the calcining process. Examples of impact of CO_2 uptake in life cycle screenings show that 70-80 % of the potential CO_2 uptake has been absorbed within 100 years lifetime after demolition and crushing", Glavind (2006).

The project had a limited budget and the analysis was based on a number of assumptions and uncertainties. The need for further work was identified.

One weakness in the previous project was the simple square-root of time models used for carbonation and the lack of models for carbonation of crushed concrete. One part of the present project, part 7, concerns the development of new models for CO_2-uptake.

The project is funded by the Swedish Consortium for Financing Basic Research in the Concrete Field. The consortium members are: Cementa, Färdig Betong, Abetong, Swerock, Betongindustri and Strängbetong.

Model for CO2-uptake during service

Assumptions/simplifications

In a previous report current models for carbonation were described. For the choice of model(s) for predicting CO_2-uptake by carbonation, these assumptions/simplifications seem to be reasonable

1. Carbonation is modelled as a sharp carbonation front moving inwards, cf. figure 1.
2. The movement of the carbonation front is due to the combined effect of CO_2 diffusing through the already carbonated layer and CO_2 being bound by the carbonation reaction at the depth of the front.
3. The amount of CO_2 bound per volume of concrete must be quantified in the model.
4. The amount of CO_2 bound per weight of binder may not be a constant for a particular binder; possible effects of degree of hydration and moisture level should be part of a model and separately quantified.
5. The concrete is modelled as being homogenous, i.e. the higher binder content close to the exposed surface is neglected. This assumption is on the "safe" side, but could be too much on the "safe" side for crushed concrete where individual particles possibly are significantly heterogeneous, with most of the binder as a "shell" around larger aggregate grains.
6. All CaO is assumed to be fixed in position, i.e. no movement of Ca^{2+} and OH^--ions is considered.
7. The CO_2-binding capacity of carbonated concrete is set to be equal to 0, i.e. the diffusion of CO_2 could be modelled as a steady-state transport process.
8. The diffusion coefficient for CO_2 for a particular concrete should be modelled as a function of degree of hydration and moisture level.
9. The liberation of water from the carbonation reaction is neglected, i.e. does not increase the moisture content and humidity.
10. The effect of a surface treatment, paint, wall paper etc., must be considered, at least as an additional resistance to diffusion of carbon dioxide.

Theses assumptions/simplifications should be agreed upon, within the project.

The consequences of these assumptions are several:

a) The CO_2-uptake is quantified by models that include assumptions that are well known and frequently used in models for carbonation.
b) The historic moisture profiles of the concrete structure must be estimated, not only the equilibrium conditions; the effect of outdoor humidity variations and rain periods, and the early drying of excess moisture, must be considered to some extent.
c) The profiles of degree of hydration, originating from the time required for the early drying of the surface regions of the concrete structure, must be considered to some extent.
d) The significance of these effects should be smaller and smaller with time, i.e. with larger depths of carbonation.

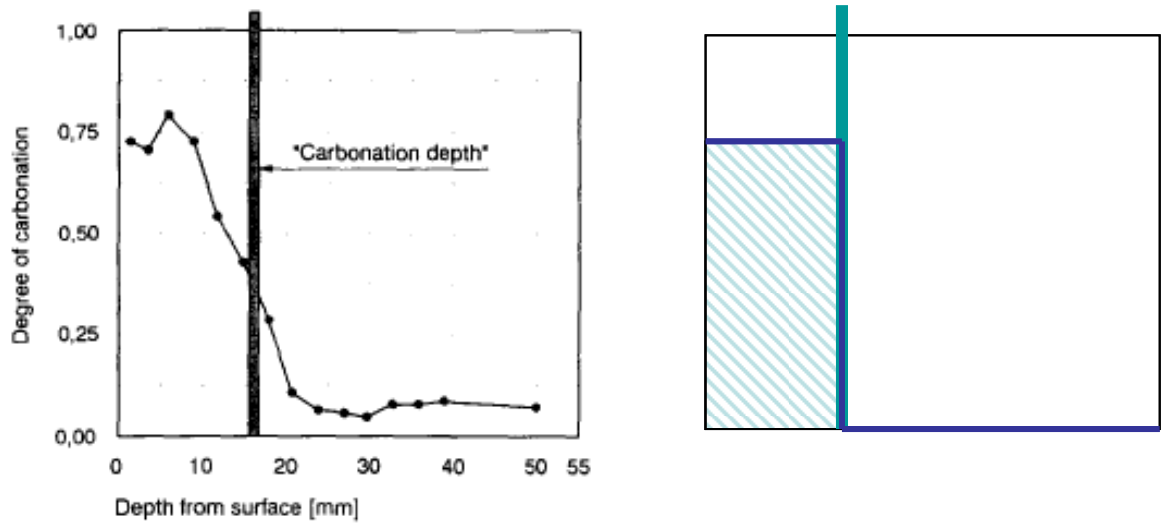


Fig. 1 The measured (left) degree of carbonation as a function of depth, Möller (1994), and corresponding CO_3-profile from a model (right)

Model for depth of carbonation

With these assumptions, a carbonation model may look like the one in figure 2.

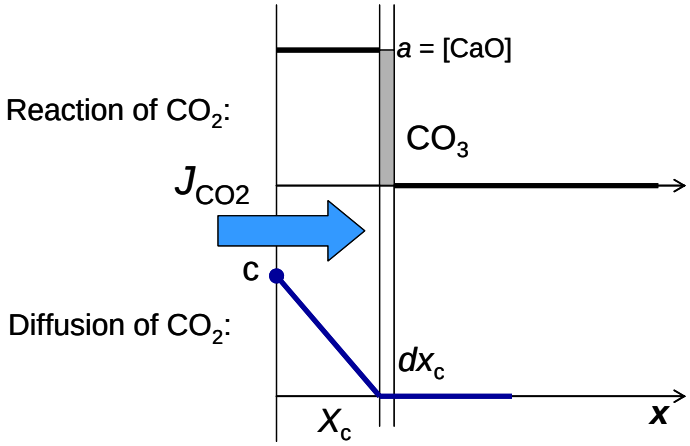


Fig. 2 A simple model for carbonation, based on the assumptions 1-8

The flux of diffusing CO_2 is based on Equation (1)

$$J_{CO_2} = -D_{CO_2}(RH,\alpha)\frac{dc}{dx} = \frac{c}{R_{CO_2}} \qquad (1)$$

where the diffusion coefficient depends on humidity and degree of hydration. The concentration difference over the carbonated layer with thickness X_{CO3} is $\Delta c = c\text{-}0 = c$. The resistance to diffusion of CO_2 of the carbonated layer is R_{CO2}, which is given by

$$R_{CO_2} = \int_{x=0}^{x=X_{CO3}} \frac{dx}{D_{CO_2}\left(RH(x), \alpha(x)\right)} \tag{2}$$

The amount of CO_2 required to carbonate a unit volume of concrete is

$$a(x) = C \cdot \frac{CaO}{C} \cdot \frac{(CaO)_{CO_3}}{CaO}(x) \cdot \frac{M_{CO_2}}{M_{CaO}} \quad [\text{kg } CO_2/m^3] \tag{3}$$

where C is the cement content, CaO/C is the amount of CaO per weight of cement, $(CaO)_{CO3}/CaO$ is the degree of carbonation and M is the molar weight. a(x) is marked as being dependent on the depth x, since the degree of carbonation may be different at different depths.

In the model in figure 2 the mass balance equation of CO_2 at the depth of carbonation X_{CO3} will be

$$J_{CO_2} \cdot dt = a(X_{CO_3}) \cdot dX_{CO_3} \text{ [kg } CO_2/m^2] \tag{4}$$

where dt is a short time step [s] during which the carbonation front advances dX_{CO3} [m]. This can also be written

$$\frac{dX_{CO_3}}{dt} = \frac{J_{CO_2}}{a(X_{CO_3})} = \frac{c}{R_{CO_2} \cdot a(X_{CO_3})} \tag{5}$$

After integration, the depth of carbonation is

$$X_{CO_3} = \int_{x=0}^{x=X_{CO3}} dX_{CO_3} = \int_{t'=0}^{t'=t} \frac{c}{a(X_{CO_3}(t)) \cdot \int_{x=0}^{x=X_{CO3}} \frac{dx}{D_{CO_2}\left(RH(x), \alpha(x)\right)}} \tag{6}$$

The "problem" with this model is that the X_{CO3} appears on both sides of the equality sign! Consequently, the equation must be solved numerically, by dividing the carbonated layer into small slices with a thickness of dx and by taking small time-steps dt. During each time-step, the moisture distribution RH(x) must be known.

If further assumptions are made, the model will of course become much more simple. If the humidity RH, the degree of hydration α and the amount a of CO_2 required to carbonate a unit volume of concrete are assumed to be constant throughout the carbonated layer, the depth of carbonation will be

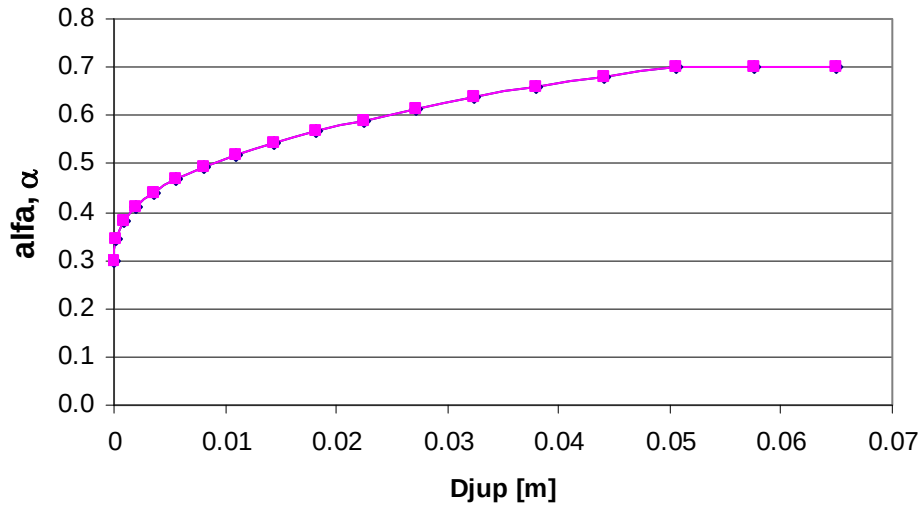
$$X_{CO_3} = \sqrt{\frac{2D_{CO_2}(RH) \cdot c}{a_{CO_2}(RH)}} \cdot \sqrt{t} \cdot \left(\frac{t_0}{t}\right)^n \tag{7}$$

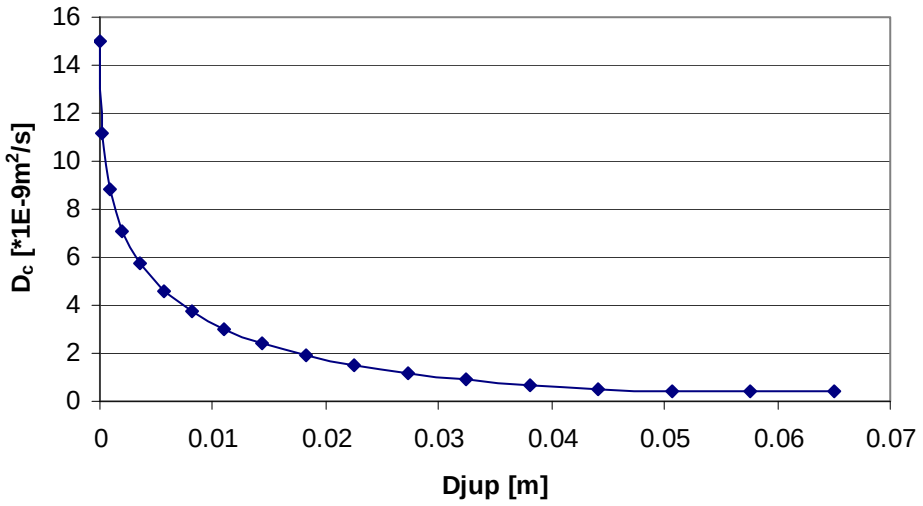
where the exponent n depends on the humidity conditions and can be quantified from exposure data.

Most of the parameters in this model are possible to quantify, theoretically and from field measurements. The a-value has already been shown to include only one uncertain parameter, the degree of carbonation, that has to be measured for a set of typical binders and humidity conditions. The diffusion coefficient could be quantified together with the a-value by equation (7) in cases where the exponent $n = 0$. Alternatively, the diffusion coefficient could be estimated from an equation, derived for old German cement, Wierig (1964)

$$D_{CO_2} = B \cdot C \cdot \varepsilon^{4.5} \cdot \left(1 - RH(x)^{10}\right)^5 \tag{8}$$

where C is the cement content, ε is the capillary porosity, B is a constant and the parenthesis gives the humidity dependency.





Model for CO_2-uptake

The CO_2-uptake of a unit area of concrete will be

$$m_{CO_2} = X_{CO_3} \cdot \int_{x=0}^{x=X_{CO3}} a(x) \cdot dx \quad [\text{kg } CO_2/m^2] \tag{9}$$

or, if a is assumed to constant throughout the carbonated layer, simply

$$m_{CO_2} = X_{CO_3} \cdot a \quad [\text{kg } CO_2/m^2] \tag{10}$$

This model should be possible to set up in an Excel sheet and include all the parameter variations mentioned above.

Model for CO_2-uptake of crushed concrete

With the same assumptions as for carbonation during service, carbonation of crushed concrete could be modelled in a simple way. The difference is mainly the diffusion or convection of CO_2 in the hollow space between the grains. Depending on the movement of air and the depth from the surface of the lump of grains, the consumption of CO_2 by the grain surfaces may decrease the concentration of CO_2 in the air in the hollow space. Consequently, that concentration must be included in the model as a variable.

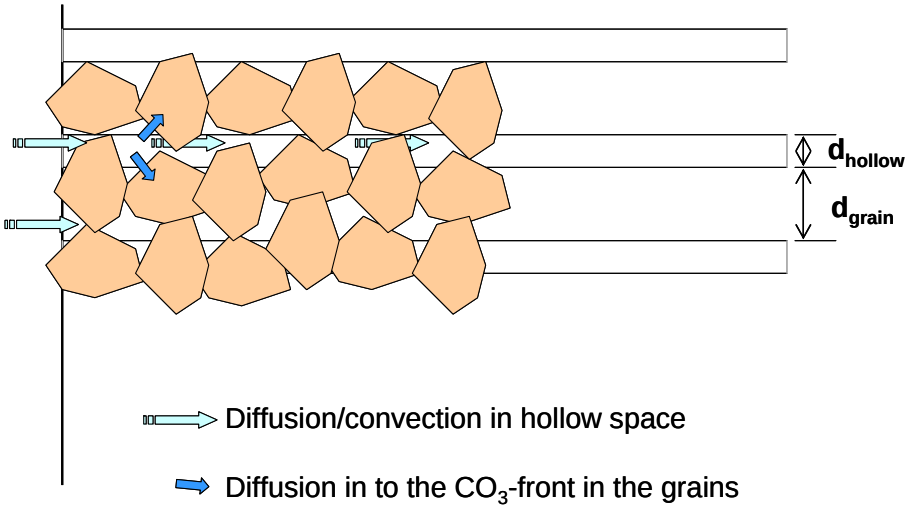


Fig. 3 The carbonation process, in principle, for crushed concrete

This process could be simplified into the simple model in figure 4.

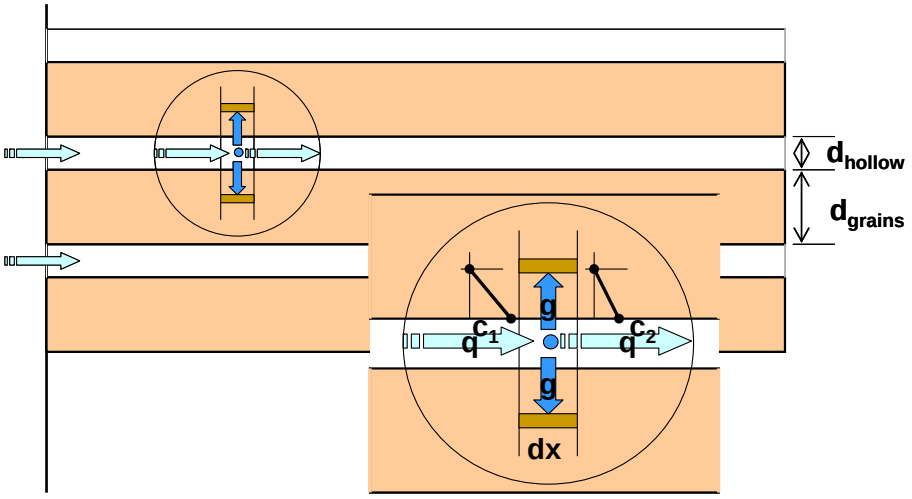


Fig. 4 A possible, simple model for the rapid carbonation process for crushed concrete

The model consists of these parts

1. A constant air flow Q [$m^3/(m^2\ s)$] between the grains.
2. Convection of CO_2 with that air flow.
3. A concentration $c(x)$ of CO_2 as a function of depth from the surface of the lump of concrete grains.
4. Diffusion of CO_2 in that air, from a concentration gradient in the air.
5. A concentration $c(x_i)$ of CO_2 at the surface of a concrete grain at a depth of x_i.
6. Carbonation of the concrete grain *i*, in the same way as described above.
7. The humidity *RH* at different depths *x* from the outer surface must be modelled. If the carbonation is very rapid, the liberation of water from the carbonation reaction may have to be included.

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