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CO-cycle in cement and concrete : Part 1: Examination of a previous NIC-project - Part 2: Further literature study on mechanisms/models

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CO$_2$-cycle in cement and concrete

Part 1: Examination of a previous NIC-project
Part 2: Further literature study on mechanisms/models

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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, see the reference list.

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.

In the current project, the first step is to examine the previous project and identify weaknesses, where improvements should be made. This report gives a summary of that examination. The second step is to further study literature on carbonation models and mechanisms. That is also included in this report, in Part 2.

The project is funded by the Consortium for Funding A-research at CBI, the Swedish Cement and Concrete Research Institute. The consortium members are: Cementa, Färdig Betong, Abetong, Swerock, Betongindustri and Strängbetong.

Part 1: Examination of a previous NIC-project

The six reports from the previous NIC-project have been thoroughly examined. In general, most parts of the project seem to be performed excellently, limited with those assumptions and uncertainties that are mentioned. A summary of the examination is

Mechanisms/models
Chemical/phenomenological: *excellent*
Physical/mathematics: *doubtful*

Surveys
Amount & type of concrete
Exposed surfaces/volume of concrete
Difficult. Different between countries

CO_2-uptake of crushed concrete
Certain experimental data
Relevance linked to real use
Carbonated volume portion of concrete: *sometimes exaggerated*

Exceptions are mainly three:

1) Unexpectedly small, typical concrete products
2) Misuse of the 1D-carbonation model
3) Over-simplified and erroneous physical parts of carbonation models.

These three parts are described in more detail.

1) Unexpectedly small, typical concrete products

In the report by Jónsson (2005) a series of inventories are made to estimate the amount of concrete in each of the countries, their cement type and quantity, w/c, concrete strength class, the distribution of the use of the concrete in different parts of the building structure (walls, facades, slabs, columns, shallow core slabs, pavement, pipes etc.) and the area of surfaces being coated. Most of this information is based on estimations and it is not quite clear how these estimations have been done. A number of tables are given but the relationships between the tables are not always clear. The reader more or less has to accept the results without being able to trace the origin of the estimates. This is a severe drawback of this report.

Most remarkable are the numbers from Denmark and Sweden on the typical thicknesses of Precast Concrete Products. Some "paving, blocks, elements and pipes, etc." are said to have an average thickness of 60-80 mm. The exposure of these products are said to be "outdoor, underground, outdoor", where it is not quite clear what is meant with "underground".

This could be roughly OK, but when these numbers are later used for CO_2-uptake calculations, see the report by Kjellsen et al (2005), "all six sides" are assumed to carbonate! Concrete blocks from Denmark, having a typical thickness of 0.08 m, are used in the example. The total volume of concrete used for that purpose is divided by the typical thickness and multiplied by a factor of 6 to obtain a surface area that is carbonated. This means that the

concrete volume is assumed to be used to make 8 cm concrete cubes, where all six surfaces are carbonated.
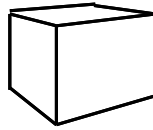
This could not be correct and this example of estimation gives the impression that the numbers are "pushed" to create as much CO_2-uptake as possible. This is a serious drawback of the report.

2) Misuse of the 1D-carbonation model

In the report by Kjellsen et al (2005) one example is given where the CO_2-uptake is calculated. That example concerns the concrete blocks produced in Denmark 2003, see above. The example shows that some 50 % of the concrete is carbonated during a 70 year service-life.

> An example for calculating concrete carbonation during a 70 year service life period is provided in Table 7.1. The example regards 'concrete blocks' produced in Denmark in 2003. The example shows that approximately 50% (76.264 m³) of the volume of concrete used for blocks in Denmark will be carbonated in the service life period of 70 years.

The carbonation model used in the calculation is a pure 1D-model, i.e. the volume of carbonated concrete is calculated from the depth of carbonation d and the thickness L of the concrete element

1D-model

The volume ratio being carbonated is given by

$$\frac{V_{CO_3}}{V} = \frac{d}{L/2} = \frac{2d}{L}$$

For a cube with an edge of L, where all surfaces are assumed to be carbonated, the 1D-model gives a volume ratio of carbonated concrete of

$$\frac{V_{CO_3}}{V} = \frac{6 \cdot L^2 \cdot d}{L^3} = \frac{6 \cdot d}{L}$$

e.g. three times the carbonation of a 1D slab. The 1D-model, however, does not exclude the edges and corners of the cube that are carbonated three times of times!
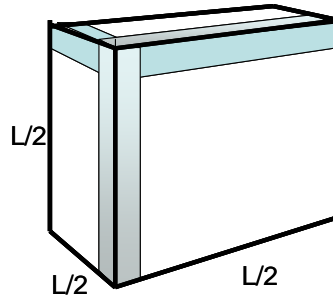
The correct volume ratio is instead

$$\frac{V_{CO_3}}{V} = \frac{L^3 - (L-2d)^3}{L^3} = \frac{L^3 - (L-2d)^2 \cdot (L-2d)}{L^3}$$

which is shown in figure 1.
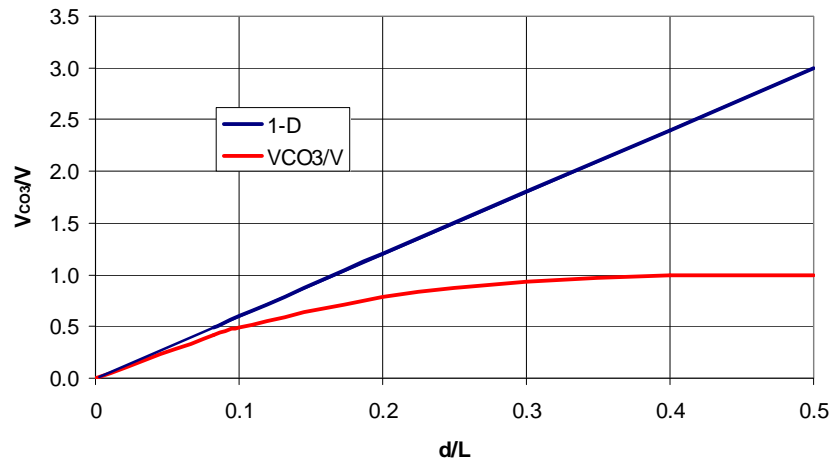
Fig. 1   *The volume ratio of carbonated concrete for a cube when using the 1D-model (straight line) or a correct model (lower curve)*

For a small cube with size L and significant depths of carbonation d the error in the calculated volume ratio of carbonated concrete is significant. For $d/L = 0.3$ the error is almost a factor of 2! This effect should be considered when carbonation that is not purely one-dimensional is considered.

3) Over-simplified and erroneous physical parts of carbonation models.

The chemical part of the carbonation mechanism is thoroughly described in detail by Lagerblad (2005) in an excellent way. The physical part of the carbonation model description, however, is not mathematically correct; it ends up in a crude and simple model that is not the solution to the given mathematics. That simple model sometimes over-estimates the depth of carbonation and, consequently, the CO_2-uptake. Decisive parameters are not identified and it needs to be developed for new applications.

The flux equation that is given, called "Fick's 1st law", with c as the concentration of carbon dioxide and D as the diffusion coefficient for CO_2, is

$$J = D\frac{dc}{dx}$$ (1)

Here a minus (-) sign is missing; with a positive gradient in the x-direction, the flux will be opposite to that direction.

The mass balance equation, called "Fick's 2nd law, is given as

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$ (2)

This means that the mass balance equation only includes the gaseous carbon dioxide, with a concentration c, but not the carbon dioxide that is "bound", in the carbonate. A binding term is missing. This equation is said to be "difficult to solve" and all sorts of complication are listed.

In spite of this, the depth of carbonation d_c is then given by a simple formula

$$d_c = k\sqrt{t}$$ (3)

This is the traditional carbonation model which, in fact, is not the solution to Fick's 2nd law, at least not where more or less a carbonation "front" is expected. The parameter k is not further explained, just taken as a parameter to be identified.

The correct flux equation should be

$$J = -D\frac{dc}{dx}$$ (1')

And the mass balance equation should have a binding term that includes the drop in carbon dioxide concentration due to carbonation binding it in carbonates

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}D\frac{\partial c}{\partial x} - \frac{\partial c_{CO_3}}{\partial t}$$ (2')

The diffusion coefficient is here place inside the first derivation, which means that it may be non-constant with depth x, e.g. due to moisture profiles.

The mass balance equation must be solved numerically, if all aspects are to be considered. A simple solution with certain assumptions, see next section, is

$$d_c = \sqrt{\frac{2D_{CO_2}(RH,\alpha) \cdot c}{a_{CO_2}(RH,\alpha)}} \cdot t^n \qquad (3')$$

which could be made equal to equation (3) if the exponent n is set to ½. The parameter k in equation (3) can then be identified to include both material parameters and environmental parameters: the diffusion coefficient D for carbon dioxide, being dependent on moisture RH (relative humidity) and degree of hydration α, concentration c of carbon dioxide and amount of carbon dioxide a required for carbonating a unit volume of concrete. The parameter a is directly linked to the cement content.

The amount of carbon dioxide a that is absorbed in a unit volume of concrete is described in the text on page 24 and later, on page 28, with an equation

$$a = 0.75 \cdot C \cdot \frac{CaO}{C} \cdot \frac{M_{CO_2}}{M_{CaO}} \quad [\text{kg } CO_2/\text{m}^3] \qquad (4)$$

where C is the cement content, CaO/C the amount of CaO per weight of cement and M the molar weights; all well known for a particular concrete. The number 0.75 is in fact the "degree of carbonation", i.e. the portion of the CaO that has been carbonated. Sometimes this number is replaced by the degree of hydration α, Möller (1994), implying that all of the CaO in the reaction products can be carbonated but none in the unhydrated cement. This assumption can be questioned. For the time being, the degree of carbonation must be regarded as a parameter that has to be measured, especially if we are facing indoor structures, where we have little experience.

The CO_2-uptake m_{CO2}, per unit surface area, can be described with

$$m_{CO_2} = d_c \cdot a_{CO_2} \quad [\text{kg } CO_2/\text{m}^2] \qquad (5)$$

or

$$m_{CO_2} = d_c \cdot C \cdot \frac{CaO}{C} \cdot \frac{(CaO)_{CO_3}}{CaO} \cdot \frac{M_{CO_2}}{M_{CaO}} \quad [\text{kg } CO_2/\text{m}^2] \qquad (6)$$

where $(CaO)_{CO3}/CaO$ is the degree of carbonation. Note that the parameter a appears twice in equation (5); it is obviously a very important parameter to quantify.

Part 2: Literature study on mechanisms/models

In the previous NIC-project, the chemical mechanisms involved in carbonation were thoroughly described. The physical parts should be improved, however, and more sophisticated models than the square-root of time model should be examined.

An extended literature survey has been performed to update the State-of-the-Art on carbonation models.

Degree of carbonation

A PhD project on measurement of carbonation, Möller (1994), was solely dedicated to quantifying the <u>degree</u> of carbonation, i.e. the <u>extent</u> of reaction by the calcium containing constituents $(CaO)_{CO3}/CaO$. An example of his results are shown in Figure 2.
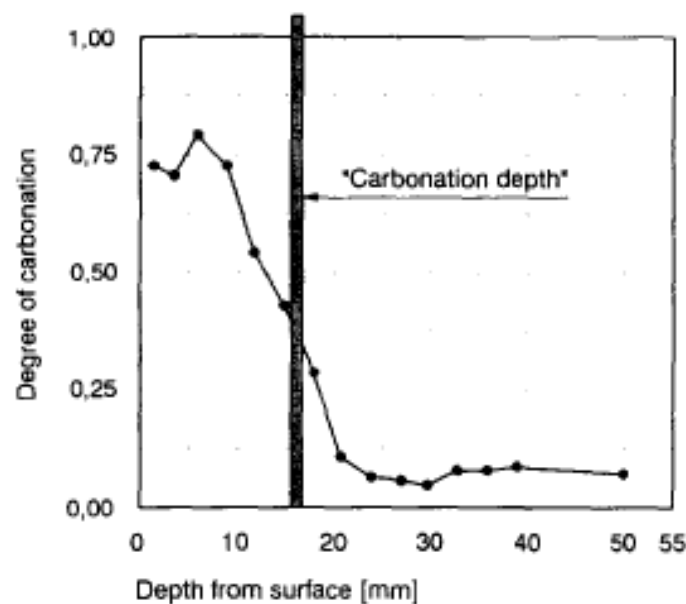
Fig. 2 The degree of carbonation as a function of depth for a 30 MPa concrete carbonated for eight years in laboratory climate, Möller (1994)

Möller (1994) measured a degree of carbonation of some 0.75! He did not obtain a sharp front but a carbonation profile with a certain slope around the depth of carbonation measured by phenolftalein, see figure 2.

Similar measurements were done already by Tuutti (1979) and later by Villain et al (2006, 2007). Besides those three studies, that kind of data is rare.

Micro-level models for carbonation

Models for carbonation are characterized at three levels: macro, meso and micro level, CEB (1997). The simple square-root of time model is a macro model. In a micro level model most chemical and physical processes are described as good as possible, utilizing the best of our present knowledge. All available models, however, are limited to include only a portion of all things that are affecting carbonation, e.g. they are based on some assumptions on what is regarded as less significant.

Carbonation in a natural climate

The CTH Carbonation Model, Nilsson & Rodhe (1997a&b), is a micro-level model for carbonation in a natural climate. It is probably the most developed model when it comes to consider the effect of humidity variations and rain periods. It was developed during a CEB committee work to predict carbonation-induced reinforcement corrosion during varying climatic conditions. Numerous parameters were considered, such as the degree of carbonation, the moisture dependency of the diffusion coefficient for carbon dioxide, the cement content, curing, temperature and humidity variations in the surrounding air, environmental actions at concrete surfaces, duration of rain periods, moisture flow properties being dependent on carbonation, moisture flow in the concrete surface resulting in humidity variations with depth and time, etc.
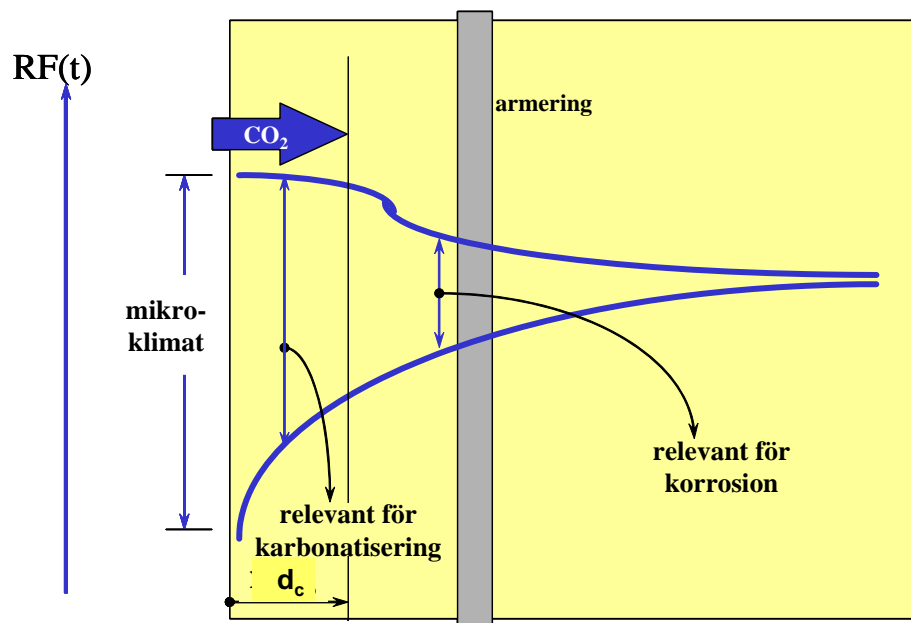

Fig. 3 Carbonation during moisture variations, in principle

The moisture variations at the concrete surface, due to variations in the air humidity, rain and running water at the surface, will give moisture profiles from the surface and inwards, that vary with time. The depth of penetration of these moisture variations depends on the properties of the concrete and the frequency of the surface humidity fluctuations, Nilsson (1996).

The carbonation process will only be affected by the moisture variations in the carbonated part of the concrete, cf. figure 3. That means that the diffusion coefficient for CO_2 is different

at different depths and varies with time. To be able to describe the flux of carbon dioxide through the carbonated part, the resistance R_{CO2} against diffusion of CO_2 is calculated

$$R_{CO_2} = \int_{x=0}^{x=d_C} \frac{dx}{D_{CO_2}(RH(x)} \tag{7}$$

The model first calculates the humidity variations, by considering the different material properties in the carbonated zone and the uncarbonated zone. Since e.g. the moisture sorption properties are different, the moisture content profiles will have a "step" at the carbonation front since carbonated concrete has lower moisture content, see figure 4. The corresponding carbonation process is shown in figure 5.
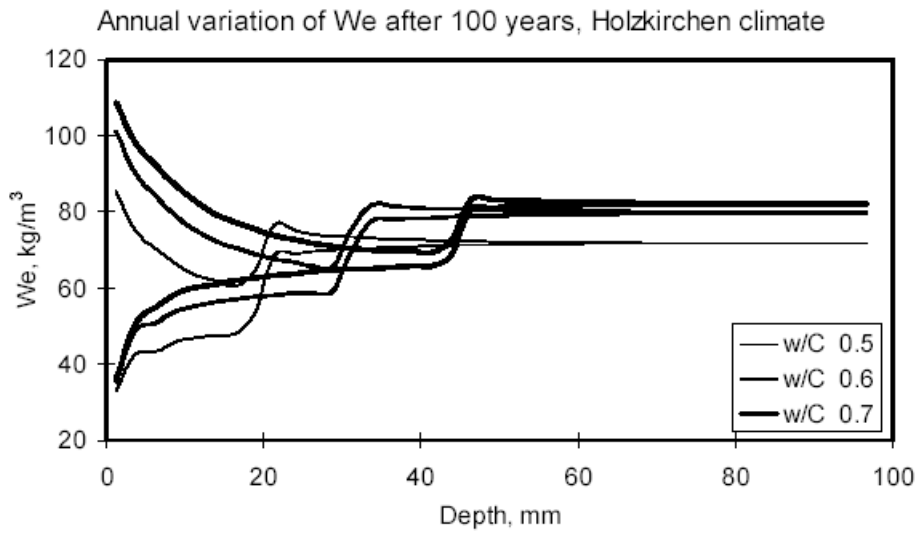

Fig. 4 Predicted moisture content profiles after 100 years of carbonation in a natural climate for three concrete qualities, Nilsson & Rodhe (1997b)
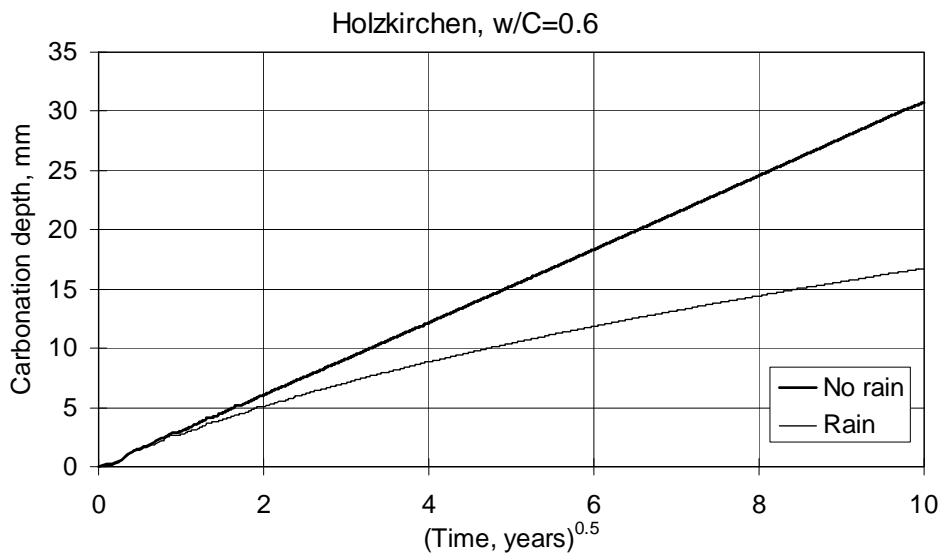

Fig. 5 Predicted depths of carbonation in a natural climate as a function of square root of time, without and with rain, Nilsson & Rodhe (1997b)

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Bakker (1964) developed a more simplified model for considering climatic variations. He separated the wetting periods from the drying periods, see figure 6.
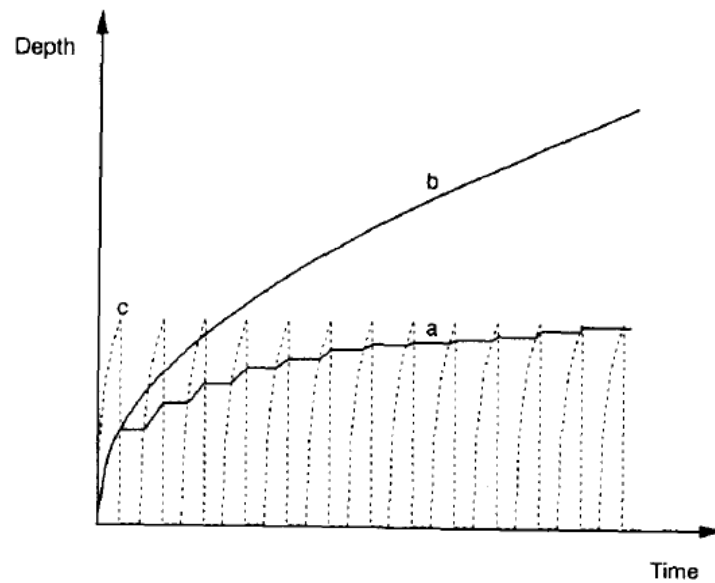

Fig. 6 Carbonation during wetting and drying (a) compared to carbonation if not wetted (b). The parameter (c) is the drying depth in each cycle. From Bakker (1964)

The effect of curing on carbonation

Curing will change the degree of hydration with depth. Consequently, the diffusion coefficient for CO_2 and the amount of carbonatable material will vary with depth.

The effect of curing on carbonation can be treated in a similar manner as moisture variations. A simplified version of the CTH Micro Level Carbonation Model was recently used in predicting the effect of curing on carbonation for the Årsta Bridge in Stockholm, Nilsson (2004). This was done by developing that model to consider curing giving different carbon dioxide diffusion coefficients and amount of carbonatable material at different depths.

The effect of curing on the degree of hydration is shown in figure 7, estimated from moisture measurements during curing.

The estimated diffusion coefficients as a function of curing is shown in figure 8.
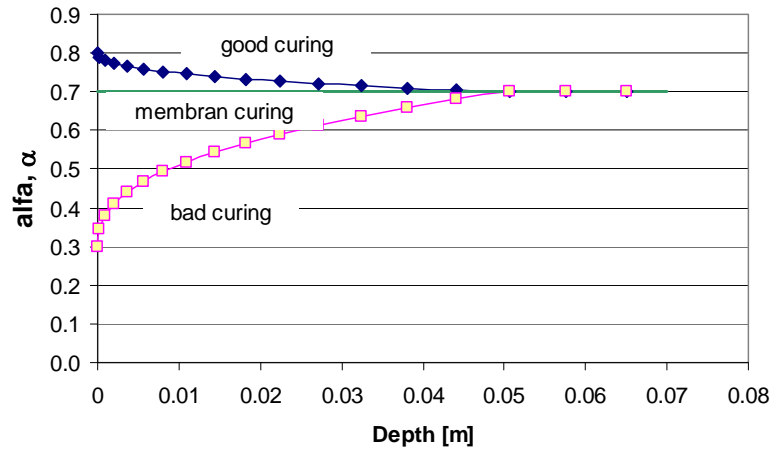
Fig. 7 Predicted profiles of degree of hydration from various types of curing, Nilsson (2004)
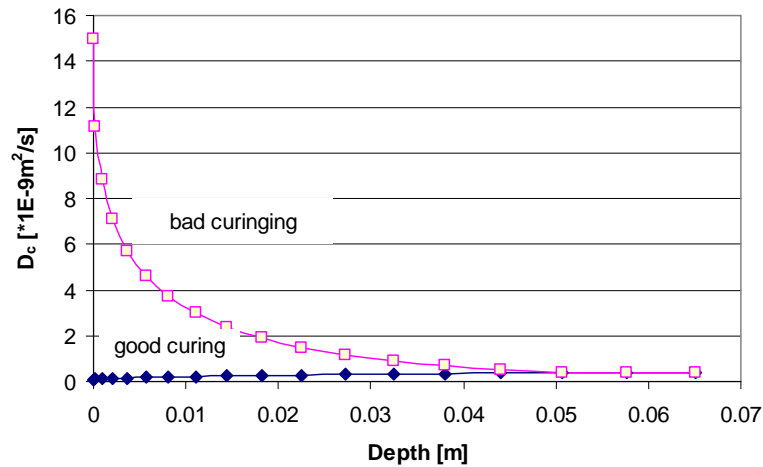

Fig. 8 Estimated diffusion coefficients as a function of depth for various types of curing, Nilsson (2004)

Such effects could be very relevant for carbonation of indoor structures where early drying is expected, creating profiles of degree of hydration.

The effect of microstructural changes and other ions on carbonation

Further detailed studies of the components of the carbonation process were performed by i.e. van Balen (2004), Ishida et al (2004). Ishida et al (2004) include the effect of porosity reduction with degree of carbonation, without really identifying the mechanism behind it. Bary & Sellier (2004) describe the diffusion of CaO from depths beyond the carbonation front, adding $CaCO_3$ into the carbonated layer, as a mechanism which reduces porosity.

Meso-level models for carbonation

Meso-level models for carbonation are models that calculate the depth of carbonation with a more or less simple formula. The square-root of time model could be regarded as the most simple meso-level model, but it simply lacks input parameters, however.

The most developed meso-level model for carbonation is the DuraCrete Carbonation model, where the depth of carbonation is described by this equation

$$d_C = \sqrt{\frac{2 \cdot k_1 \cdot k_2 \cdot k_3 \cdot D_c \cdot c}{a_{CO_3}}} \cdot \sqrt{t} \cdot \left(\frac{t_0}{t}\right)^n \qquad (8)$$

Compared to the simple square-root of time model the DuraCrete Carbonation Model has a number of features: The parameter in front of the square-root of time is quantified in terms of diffusion coefficient D, concentration c of CO_2 and amount a of carbon dioxide required to carbonate a unit volume. A number of factors k are used to compensate for another climate, another test method and for another kind of curing. The square-root of time factor is multiplied by a time-factor with an age exponent n, being dependent on the environmental conditions. All parameters were quantified in the DuraCrete project.

The CTH Carbonation Model was used in the CEB committee work to calibrate the CEB Meso-level carbonation model and later in the EU-DuraCrete project to further calibrate the environmental factors in the DuraCrete Carbonation model. The results are shown in figure 9.
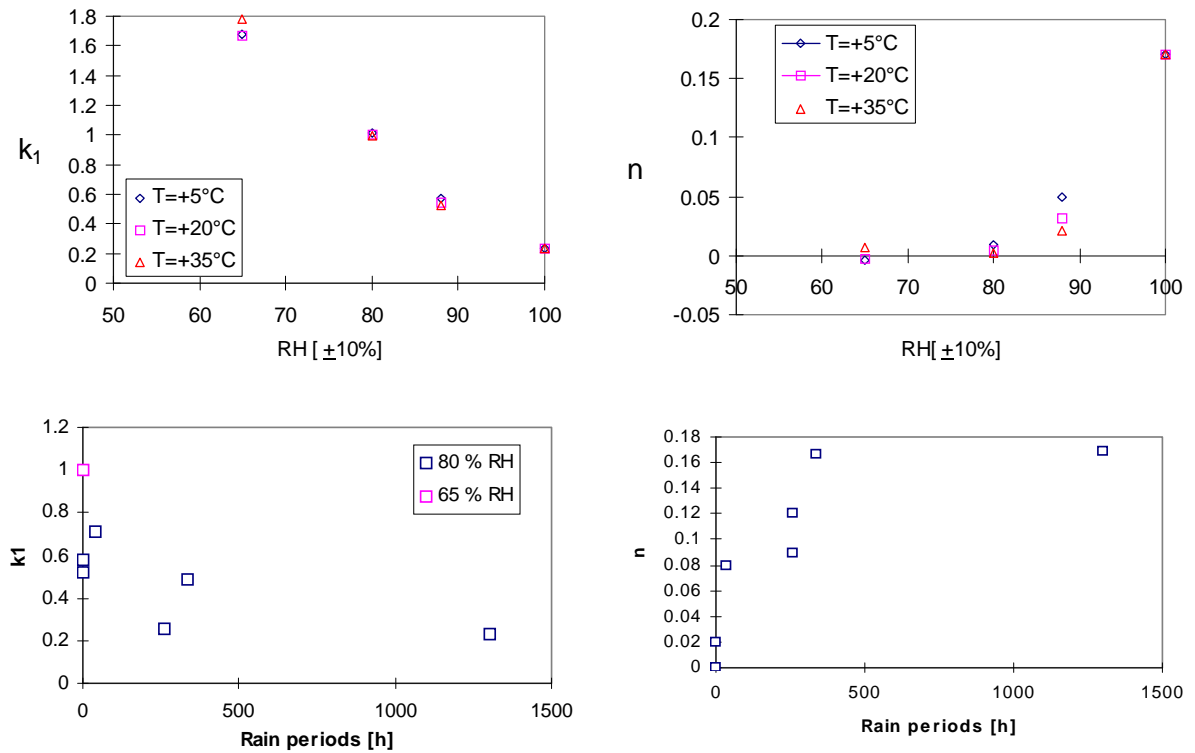

Fig. 8 Quantification of the environmental parameters k_1 and n in the CEB Meso-level and DuraCrete Carbonation Models, CEB (1997)

Conclusions on carbonation models for CO$_2$-uptake

From the additional literature study one may draw these conclusions.

During service-life
- Existing models should be applicable; re-alkalization and CaO-diffusion are, however, not considered.
- Existing models require new data, *D* and *a* for modern binders and *a* for different environmental conditions, especially indoors.
- How far to go in further development depends on what parameters are believed to be important and what accuracy is needed.

Accelerated carbonation of crushed concrete
- No models for this application have been found
- Existing models may very well be applicable, after some development.

CO$_2$-diffusion and -convection in hollow spaces between particles could be added in a simple way.

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