Supplementary material

Durability performance assessment of non-standard cementitious materials for buildings: a general method applied to the French context

Fact sheet 1 - Risk of steel corrosion induced by carbonation

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1 Introduction

This risk concerns concrete reinforced with ordinary black steel that is exposed to humid atmospheres.

The risk of corrosion by carbonation results from two successive physiochemical mechanisms. The first is concrete carbonation, which lowers pH. Carbonation occurs more or less quickly through the concrete cover depending on the concrete thickness and composition. The second is the active corrosion of steel that follows the dissolution of the passivation layer once low pH levels have reached the reinforcements. The development of corrosion requires a certain humidity level (reinforced materials in a constantly dry environment are not at risk).

2 Consequences

- Cracking, spalling of the concrete cover.
- Loss of bond between concrete and reinforcement.
- Reduction of reinforcement cross-section, leading to a loss of load-bearing capacity of the reinforced structure (ultimate state).

3 Physiochemical mechanisms

With Portland cement-based conventional concrete, reinforcements are passivated by the typically high pH of the interstitial pore solution (12.5 to 13.5). This passivation is compromised when the pH around the reinforcements drops sharply (pH < 10-11). This drop in pH is observed when the concrete cover is completely carbonated [1].

Concrete carbonation:

- Carbonation is a series of hydrate reactions (CH, C-S-H, etc.) between the cement paste and atmospheric carbon dioxide (Fig. 1).

  - $CO_{2(g)}$ penetrates by diffusion through non-saturated pores. Some of the $CO_{2(g)}$ dissolves into the interstitial solution, where it may react with hydrates.

  - When portlandite is present, it is the first hydrate to be carbonated. However, over time, each hydrate in concrete may be carbonated, ultimately forming a mix of carbonates, silica and alumina gel, and liberating water. These phases do not affect binding properties.

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- The dissolution of hydrates and the formation of calcium carbonate, CaCO₃, occur rapidly compared to mass transfer processes. This leads to a steep carbonation front.
- The pH of the pore solution drops below 9, which is why the carbonated crust can be identified with a coloured indicator (Fig. 2a).
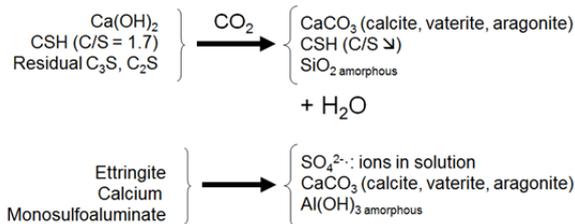
Figure 1. Typical carbonation reaction of hydrates, nature of *reactions may change with the nature of initial hydrate phases.*

- The apparent rate of concrete carbonation depends on the $CO_{2(g)}$ diffusivity and the amount of "carbonatable" hydrates (Fig. 2b):

  - The quantity of carbonatable hydrates rises with the degree of hydration, the quality of the cure, and the cement content and composition.
  - The maximum conversion degree from hydrates into $CaCO_3$ falls along with relative humidity. These reactions cannot take place in the absence of liquid water (see red line in Fig. 2b).
  - The carbon dioxide diffusion rate decreases when the cement matrix is more compact.
  - The carbon dioxide diffusion decreases when water saturation in the pores increases.
  - Higher $CO_{2(g)}$ concentrations increase the apparent rate of carbonation and they can influence the nature of the newly formed phases.

Steel corrosion in carbonated concrete:

Reinforcement corrosion is a set of electrochemical reactions between the iron in the reinforcements and the atmospheric oxygen in presence of water. In the absence of chlorides, the rate of corrosion becomes significant only after concrete carbonation and after the pH drop of the interstitial solution. This rate is influenced by two simultaneous processes, oxygen transport and iron oxidation:

- The diffusion rate of gaseous oxygen is also related to the microstructure of the carbonated concrete, it decreases with increasing water content.
- The electrochemical reaction rates at the interface between reinforcement and concrete increase in line with the humidity present in the material.

The water saturation level in the porosity of concrete, which depends on relative humidity, determines the optimum carbonation and corrosion rates for each of the two processes (see Fig. 2b). Water content is influenced by water mass transfer properties (capillary flow and vapour diffusion), by the water absorption capacity of the porous

network, and by climatic conditions (relative humidity, rain, wind, sun). In very dry or humid environments, corrosion rate is quite low.
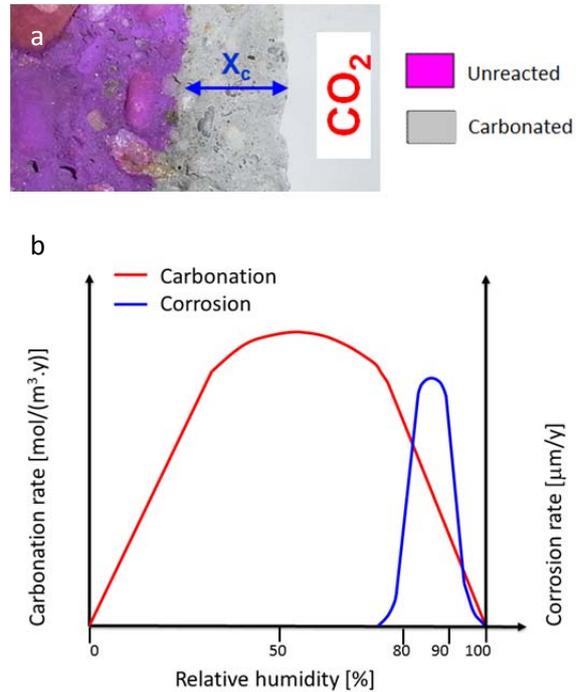
Figure 1. Carbonation depth measurement using a coloured indicator (a) and carbonation and corrosion rates based on relative humidity (b).

Corrosion leads to the creation of an expansive oxide layer on the surface of the steel. This expansion causes internal stresses that can lead to cracking of concrete around the reinforcement. Cracks that reach the surface of concrete significantly accelerate the diffusion of oxygen, carbon dioxide, and water.

This second stage of the phenomenon, the corrosion of the reinforcements themselves, is generally not taken into account when designing structural performance. Nevertheless, it may be taken into account if very low corrosion rates are justified

4 Main models

As of 2015, there is no complete standardised model for prediction carbonation depth in concrete (x_c), although several models have been published.

The Papadakis AIChE 1989 [2] model is an example of an analytic model to analyse carbonation depth x_c in laboratory test in constant atmospheric conditions over time (t):

$$D_a = \frac{D_g \cdot C_{CO2,g}}{C_{Ca,s}} \tag{1}$$

$$x_c = \sqrt{D_a}\sqrt{t} \tag{2}$$

where D_a is the apparent diffusion coefficient in the carbonated front, D_g is the CO_2 diffusion coefficient in the

carbonated layer, $C_{CO2,g}$ is the CO_2 concentration in the atmosphere, and $C_{Ca,s}$ is the total calcium concentration in the carbonatable hydrates per volume of concrete. Numerical models have also been published [3-5] that incorporate variable relative humidity in the environment and even simultaneous drying of the material. The relationship with on-site behaviour can be established with models like *fib* Model Code [6]. The reader may refer to J. Mai-Nhu's thesis [7] for a more exhaustive review of existing models.

5 Main parameters

Material parameters:

- Material transport properties.
- The amount of carbonatable material in the product (the amount of portlandite in particular).
- Curing length and conditions. A moist and sufficiently long cure creates a well-hydrated product with reduced porosity and transport properties.

Environment parameters:

- Relative humidity, rain, cycle, wind, sun exposure, and temperature: these parameters influence the concrete drying rate as well as hydration rate.
- Ambient atmospheric CO_2 and O_2 concentration.

6 Testing method stages

Testing methods involve exposing samples to a given relative humidity and partial pressure CO_2.

The key stages are:

- Curing length and conditions (temperature, under water, in a watertight bag or at 100% RH).
- Length and conditions of initial drying (T, RH). This stage helps reducing the water content of concrete and thereby accelerating CO_2 diffusion. The duration of this drying step may not be enough to create a homogeneous water content profile.
- Duration and conditions for the carbonation test itself (T, RH, %$CO_{2(gaz)}$).
- At selected time intervals, the carbonation front is highlighted by spraying a 0.5% phenolphthalein solution on a fresh cross-section, which is perpendicular to the CO_2 penetration surfaces.

The important quantities of interest are carbonation depth after a given time period or the apparent diffusion coefficient of the carbonation front (see section 4).

N.B.: pure phenolphthalein (CAS No. 77-09-8) is classified as a CMR product (Carcinogenic, Mutagenic, Reprotoxic) in category 1B (strong presumption (conclusive animal tests)) and it must be used in a professional context in line with the regulations in force. Ordering a 0.5% phenolphthalein solution from a supplier avoids having to handle this substance in its pure state. The solution is diluted enough to avoid classification as a CMR product. There are also other products that may be used as substitutes.

7 Reference testing methods

Tests listed in national regulations valid in place of use for conventional concrete:

Name	Cure	Dry-ing	Carbona-tion	Dura-tion	Com-ment
DD CEN/TS 12390-10: 2007 [8]	Under water until C_s reaches half of targeted C_s	-	natural [CO_2] RH=65%	2 years	Used in CUAPs.
EN 13295:2004 [9]	Under water, unspeci-fied duration	-	[CO_2]=1% RH=55%	> 80 d	Test for repair mortar.
XP P18-458: 2008 [10]	Under water 2 d	14 d, 45°C	[CO_2]= 50% RH=55%	44 d	
Cur - Rec-ommenda-tion 48 [11]	Under water 3 d	-	[CO_2]=2% RH=65%	Be-tween 91 d and 365 d	
GBJ82-85 [12]	In air 28 d RH=70%. T=20°C	-	[CO_2]= 20% RH=70%	56 d	
ISO/DIS 1920-12: 2014 [13]	Under water 28 d	14 d, RH= 50-70%	[CO_2]=3% RH=55% T=22°C	70 d	

Alternative test:

FPr CEN/TS 12390-12: 2012 [14]	Under water 28 d	14 d RH=50-65% T=20°C	[CO_2]=4% RH=55%	112 d	Proposed standard (pending)

Carbonation depth can be measured using standards NF EN 14630:2007 [15] or RILEM CPC 18 [16]. Based on carbonation depth measurements at dates, the diffusion rate of the carbonation front can be calculated (see section 4).

8 Performance assessment

Assessment method:

- *comparative assessment:* the carbonation depth is measured on the candidate concrete, then is compared to the values obtained from a standardised reference product using the same testing method.
- *absolute assessment:* currently, there is no absolute threshold value that has been defined for the testing methods.

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