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Karbonatizacija in absorpcija CO2 v beton

Carbonation and CO2 uptake in concrete

Karbonatisierung und CO2-Aufnahme von Beton

Carbonatation et absorption du CO2 dans le béton

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European foreword

This document (CEN/TR 17310:2019) has been prepared by Technical Committee CEN/TC 104 "Concrete and related products", the secretariat of which is held by SN.

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1 Scope

This document provides detailed guidance on the carbonation and carbon dioxide (CO_2) uptake in concrete. This guidance is complementary to that provided in EN 16757, *Product Category Rules for concrete and concrete elements*, Annex BB.

Typical CO_2 uptake values for a range of structures exposed to various environmental conditions are presented. These values can be incorporated into EPDs for the whole life cycle for either: a functional unit, one tonne or one m^3 of concrete, without necessarily having any detailed knowledge of the structure to be built.

In the rest of the document, the data will be given per m^3.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Carbonation, the uptake of carbon dioxide

4.1 Compounds, chemistry and notation

4.1.1 Carbon dioxide: Chemically expressed as CO_2 and present in the atmosphere as a gas. When CO_2 is dissolved in water, H_2O, it may form carbonic acid, H_2CO_3, where this may release carbonate, CO_3^{2-}, and bicarbonate, HCO_3^- ions.

4.1.2 Calcium hydroxide: Chemically expressed as $Ca(OH)_2$ and often called Portlandite. It is a product of the hydration of Portland cement and is always present in concrete. For simplicity, cement chemists often denote calcium hydroxide as CH. Calcium hydroxide is not very soluble in water but is does dissolve to the ions Ca_2^+ and $2OH^-$. The presence of calcium hydroxide in concrete is largely responsible for maintaining its alkaline environment, which is at a pH around 12,5. Around 25 % of hardened hydrated cement is $Ca(OH)_2$.

4.1.3 Calcium oxide: Chemically expressed as CaO. Portland cement clinker contains 61 % to 67 % CaO by oxide analysis, and where typically the assumed value is 65 %. Nearly all the calcium oxide in Portland cement is not present as calcium oxide but as part of more complicated compounds such as di-calcium silicates, tri-calcium silicates, tri-calcium aluminate and tetra-calcium alumina ferrite. Fortunately using the oxide analysis figure of 65 % CaO is sufficient for the calculation of potential carbonation without going into the more complex chemistry.

4.1.4 Calcium silicate hydrates, and other hydration products: When Portland cement reacts with water, that is when it hydrates, it forms calcium hydroxide and a larger proportion of complex hydration products where the bulk of these are made up of calcium and silica. The hydration products, or gel as described by concrete technologists, are called calcium-silica-hydrates, often simplified to CSH.

For a typical composition of hardened hydrated cement it is assumed 50 % is CSH, around 25 % is calcium hydroxide, 10% calcium monosulfoaluminate-AFm, 10 % ettringite-AFt leaving 5 % undefined.

4.1.5 Calcium carbonate: Chemically expressed as $CaCO_3$, normally present in concrete as calcite.

4.2 Carbonation

4.2.1 Carbonation reactions

The reaction between carbon dioxide and calcium hydroxide, to form calcium carbonate, $CaCO_3$, and water, H_2O, is called carbonation. The reaction can be expressed as a formula:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

This formula makes it appear that the reaction is simply carbon dioxide as a gas reacting with calcium hydroxide as a solid, but in reality the kinetics of the reaction are more complicated in that moisture must be present for the intermediate stages, where carbonate, CO_3^{2-}, bicarbonate, HCO_3^-, calcium Ca_2^+ and hydroxide $2OH^-$ ions interact.

In addition to carbonation of calcium hydroxide directly, the calcium-silicate-hydrates also carbonate. This is a complex reaction where CSH is made up of short silica chains bound together by calcium ions, Ca^{2+}, and hydroxide, OH^-, ions with the water more or less firmly bound. The makeup of CSH can be characterized by its calcium to silica ratio, expressed as either CaO/SiO_2 or Ca/Si, where the un-carbonated value is around 1,85. As carbonation lowers Ca^{2+} content of the pore solution this is compensated by the release of Ca^{2+} from the CSH [6], and its Ca/Si ratio drops to around 0,85. As the Ca/Si ratio falls below 1, and the pH is reduces to around 10, the CSH transforms into a silica gel but where there is always some calcium in the silica gel.

Carbonation is the neutralization of the natural alkalinity of hydrated cement in concrete, reducing the pH from around 12,5 to below 9 and possibly as low as 8. The pH of freshly exposed surfaces of concrete can be assessed by the application of an indicator. Phenolphthalein is particularly useful as it remains clear when sprayed onto concrete where the pH is below 9, but is purple for higher pH, as shown in Figure 1. The concrete shown in Figure 1 is a high quality concrete and indicates that the pH is above 9 except for the very outer surface of the concrete.

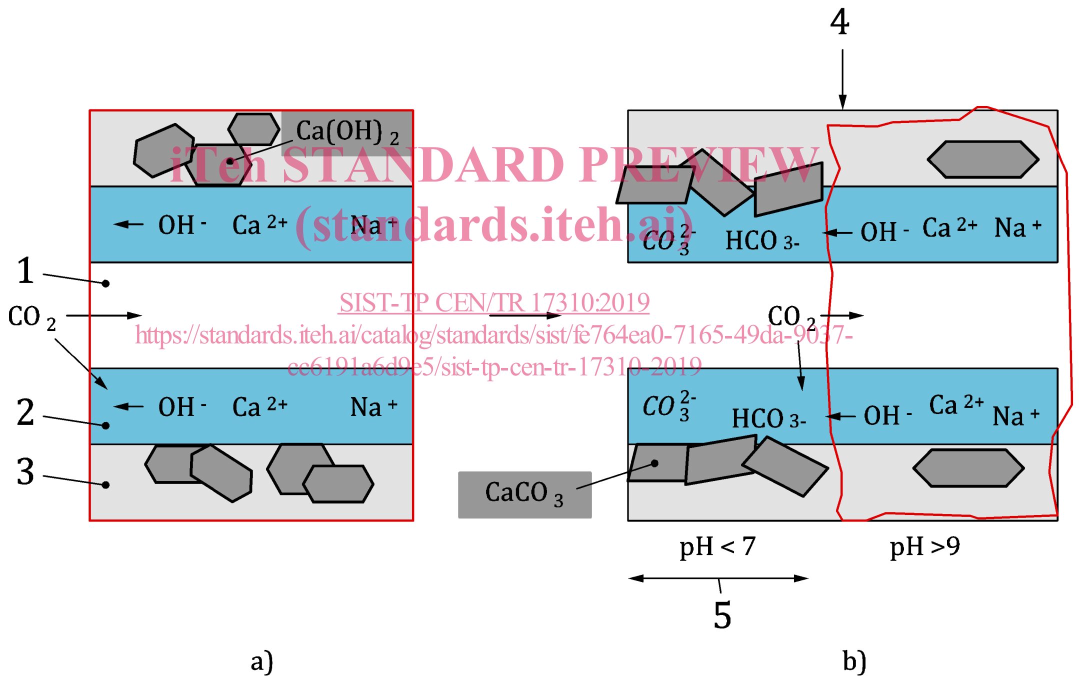
Figure 1 — Phenolphthalein indicator as used on a freshly exposed surface of good quality concrete

4.2.2 Process of carbonation

Carbonation starts at the concrete surface as this is where it is first exposed to carbon dioxide gas in the atmosphere. Carbonation also occurs where concrete is in contact with water containing soluble carbon compounds such as carbonic acid, bicarbonate and carbonate ions. Carbonation under water is slower than in air because ion diffusion through water is slower than CO_2 gas through concrete pores. There are two simultaneous processes:

- the transport and dissolution of any CO_2 gas and soluble carbon compounds into the concrete from the surface;
- the reaction of the soluble carbon compounds with the hydrated cement to produce calcium carbonate. The precipitated calcium carbonate is normally calcite but may be vaterite or aragonite.

The demarcation between carbonated concrete and uncarbonated concrete is called the carbonation front, and the depth of the carbonation is generally assumed to be the distance from the surface of the concrete to the purple zone revealed by the application of phenolphthalein. Figure 2 is a diagrammatic representation of carbonation through concrete.



a) uncarbonated concrete showing an air void, pore solution and hydrated cement

b) the progression of CO_2 through air void and pore solution to carbonate concrete

Key

1	air void in pore	4	carbonation front
2	pore solution	5	carbonation depth
3	hydrated phases		

NOTE The red line is the limit of the phenolphthalein colour change.

Figure 2 — Progression of carbonation through concrete

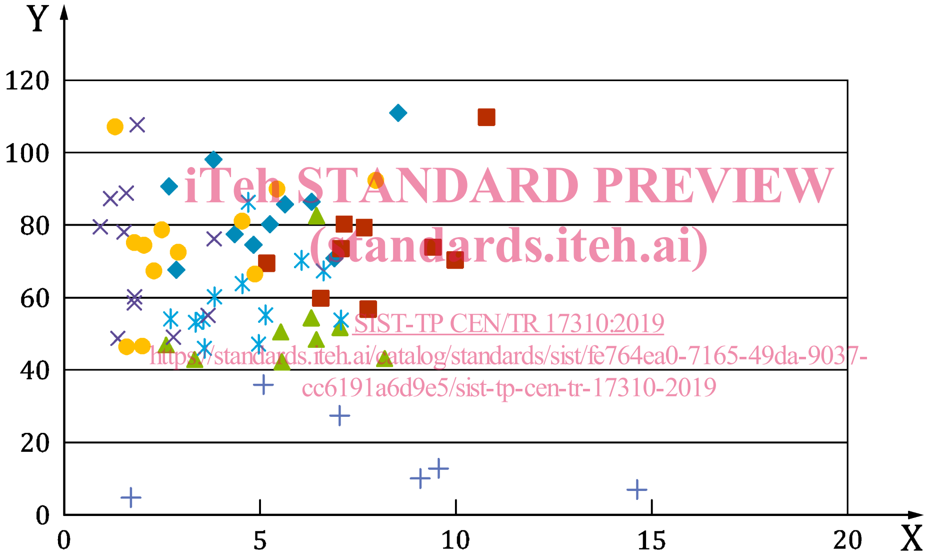
4.2.3 Degree of carbonation

It is important to note that the phenolphthalein colour change corresponds to areas of low pH, where some of the calcium hydroxide and CSH has carbonated but not that they have totally carbonated. The degree of carbonation is generally defined as the percentage of reactive CaO present in hydrated cement in concrete that is converted to $CaCO_3$, or the CO_2 bound in concrete related to the CO_2 emitted during calcination in the carbonated zone of the concrete (not taking into account CO_2 emitted by fuel),both giving the same results.

This figure has to be distinguished of the percentage of CO_2 bound in the total functional unit related to the CO_2 emitted by carbonation, this percentage taking into account the not carbonated zone.

In practice the degree of carbonation can only be determined by sophisticated techniques such as thermogravimetric analysis (TG).

There is no precise relationship between carbonation depth as determined by phenolphthalein and the degree of carbonation expressed as the amount of CO_2 as percentage of calcination emissions (Figure 3).



Key

X k (mm/year^{0,5})

Y degree of carbonation (%)

◆ outdoor non sheltered – 0,6

▲ indoor – 0,6

✳ outdoor sheltered – 0,45

+ old samples

■ outdoor sheltered – 0,6

× outdoor sheltered – 0,45

● indoor – 0,45

Figure 3 — Relationship between carbonation rate and the degree of carbonation for interior, sheltered and non-sheltered concrete, after [13]

NOTE Due to the low content in clinker of CEM III the carbonation degree is higher than 100 % because the slag carbonates. It happens also with other mineral additions. The degree of carbonation is only with respect to emissions due to the clinker.

It is known from a reviews of laboratory testing, such as those by Parrot, 1987, that the depth of carbonation is a maximum where the relative humidity is around 60 %. At lower RH the lack of moisture inhibits the ability of CO_2 to dissolve and react, whereas at higher RH there is so much moisture that it prevents the permeation of CO_2 gas through the concrete pore system. For Northern-Europe external sheltered exposure approximates to RH 60 %, and so it is not surprising that the measurements shown in Figure 3 confirm the highest depth and degree of carbonation. It is expected that drier internal conditions or wetter un-sheltered exposure will give lower depths of carbonation.

Tables 1 and 2 show semi quantitative x-ray diffraction of a cement paste taken from indoor concrete (Table 1) and outdoor concrete (Table 2) [4]. The measurements are taken at various depths as tabulated, where the results are semi quantitative because the materials are identified from spot counting sample areas without reconciling with the actual proportions in the concrete. The depth of carbonation was determined using phenolphthalein indicator on a split concrete cylinder, where for indoor concrete the depth of carbonation is at 35 mm, and for outdoor concrete around 20 mm. In the tables carbonated is indicated as ‘Carb.’, at the carbonation front ‘Carb. Front’ and where it is assumed the concrete is at a depth largely uncarbonated identified as 'intact'.

Table 1 — Semi quantitative x-ray diffraction of a cement paste taken from indoor concrete

Material identified	(0 to 5) mm Carb.	(5 to 10) mm Carb.	(10 to 15) mm Carb.	(15 to 40) mm Carb. front	(40 to 50) mm Intact
Alite	11	0	0	0	0
Alite+Belite	513	250	92	98	72
Portlandite, CH	0	291	1 037	1 794	2 115
Calcite	827	529	761	456	121
Quartz	3 707	4 125	4 309	2 234	1 335
Feldspar	1 010	1 310	1 289	865	828

Table 2 — Semi quantitative x-ray diffraction of a cement paste taken from outdoor concrete

Material identified	(0 to 7) mm Carb.	(7 to 16) mm Carb.	(16 to 25) mm Carb. front	(25 to 50) mm Intact
Alite	0	0	0	0
Alite+Belite	59	66	121	123
Portlandite, CH	0	0	912	2 443
Calcite	2 382	2 919	1 179	0
Quartz	3 201	2 318	2 871	2 138
Feldspar	1 059	869	2 084	736

The materials identified are alite, alite+belite, portlandite, calcite, quartz and feldspar. Alite and alite+belite are compounds found in unhydrated Portland cement, where there will always be some of these materials present in concrete however old, although the amount will reduce with time if there is water present for continued hydration. Portlandite and calcite are as described before, where a comparative reduction in portlandite and an increase in caltite means the concrete is carbonatining. Quartz and feldspar are minerals from the aggregate.

From Table 1 it is evident that the carbonated zone as indicated by phenolphthalein contains significant amounts of both portlandite, and unhydrated cement grains as shown by the presence of alite and alite+belite. In outdoor concrete some unhydrated cement is present close to the surface but the portlandite is carbonated to the carbonation front.

The measurements indicate that the degree of carbonation in the drier indoor concrete is significantly lower than the wetter outdoor concrete.

From wider research it is evident that outdoor concrete, generally with a lower depth of carbonation than drier indoor concrete, the degree of carbonation is higher at around 75 % to 90 % [2], [4], [7], [15].

4.2.4 Effect of carbonation on cement paste structure

The transformation of portlandite to calcite represent a volume change of 11 %, but the theoretical volume change from transformation of CSH to calcite is less certain and will depend on the water content. It is known that the volume changes do not affect the mechanical stability of the carbonated zone, it is stable and hard. Cracks induced by carbonation are rare although there may be microcracks. Normally the calcite precipitated just fills the available space in the capillary system and thus densifies the cement paste locally.

In general the effect of carbonation on porosity will depend on the locations and mode of calcite precipitation as well as the type of cement. As diffusion and transport in cement paste is mainly through the capillary pores then precipitation in these pores will diminish flow.

There is evidence that concrete made with Portland slag cement produces a coarser pore system when carbonated, then that of a pure Portland cement concrete. As the slag cement paste contains less calcium hydroxide and more CSH it will affect the carbonation front, and generally increase the rate of carbonation.

Although the carbonation may appear to be quite simple in practice the process is complex in that the concrete quality, cement type and carbonation will affect the structure, and changes in the structure will affect the rate and degree of carbonation.

4.2.5 Carbonation rate

The rate at which concrete carbonates reduces with time. This is because carbonation is a diffusive process, that is as carbonation progresses the carbon dioxide has further to travel to carbonate the interior of the concrete In addition the precipitation of calcite may reduce the penetrability of the concrete. For all practical purposes this can be described by the following expression:

$$d_c = k\sqrt{t} \tag{2}$$

where

d_c = depth of carbonation;

k = rate;

t = time.

The rate of carbonation, "k", includes the effects of transport and reaction and enable the depth of carbonation to be calculated at any time. To calculate the amount of CO_2 combined within the concrete other models are required to cover transport and reaction separately.

The rate of carbonation is influenced by many factors. Apart from the amount of CO_2 in the atmosphere it also depends on; the size, geometry and interconnectivity of pores, as well as t the type of cement or binder, the relative humidity and other factors.

4.2.6 Carbonation rate controlling factors

4.2.6.1 Humidity and temperature

A very dry concrete does not carbonate as water is needed for ions to form and subsequently react with carbon hydroxide or CSH and form calcite. In normally dry concrete, say RH around 50 % to 85 %, the rate of carbonation depends largely on gas diffusion where the driving mechanism in stagnant air is the difference in partial pressure between the surface and the interior of the concrete. The CO_2 gas then dissolves in the pore water and consumed at the carbonation front. In wetter concrete, say RH > 85 %, the rate of carbonation is controlled by ion diffusion in the pore solution, and this is slower than the permeation of CO_2 as a gas. Figure 4 shows the influence of relative humidity, water/cement (w/c) ratio, and temperature upon depth of carbonation at sixteen years, after [5].