



Influence of the carbon dioxide concentration on the resistance to carbonation of concrete

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HIGHLIGHTS

- The pH of the pore water in equilibrium with the CO₂ concentration of the ambient air (max. pH = 7).
- At this pH all (un)hydrated cement become unstable.
- Carbonation of concrete thus will ultimately go to completion.

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ABSTRACT

Carbonation of concrete at ambient CO₂ concentration is a slow process. This makes the testing of the resistance of concrete against carbonation often too slow to be applicable for service life assessments of new structures. Raising the CO₂-concentration will accelerate the test but the validity of an increase CO₂-level is debated. If not valid, the service life can be seriously underestimated. In this paper, the effects of accelerating on the carbonation process are discussed.

It is shown that a change in CO₂ concentration will not change the carbonation process. Since carbonation occurs instantly, a zero CO₂ concentration at the carbonation front is maintained. Moreover, it has been concluded that all hydrated and unhydrated cement ultimately carbonates. This implies that the amount of material that can carbonate can be determined on the basis of the amount of calcium in the unreacted cement.

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1. Introduction

Corrosion of the reinforcement is without doubt the most widespread degradation mechanism in reinforced concrete structures. Corrosion is initiated when the passivation layer on the surface of the reinforcement steel is broken. This can be brought about by carbonation of the surrounding concrete. Carbonation results in a decrease in the pH in the surrounding concrete, from a high alkaline environment (pH about 13) to below 9 (e.g. [1]). This destroys the passivation layer.

To prevent corrosion due to carbonation within the service life, concrete structures are required to have a concrete cover with sufficient thickness and resistance against carbonation. The resistance against carbonation of the concrete is either known from previous applications or has to be determined by testing. For new concrete compositions, testing often is the only option. Testing the resistance against carbonation under ambient CO₂ concentration is however slow. Since the time available for testing is usually brief, acceleration of the test is required. Since the carbonation rate is

usually derived from Fick's first law, an apparent easy and straightforward way of accelerating the test is by increasing the CO₂-concentration. The carbonation rate formula derived from Fick's first law states that the increase in carbonation rate is proportional to the increase in CO₂-concentration [2].

The validity of acceleration by means of an increase of CO₂-concentration is however debated. The carbonation rate model derived from Fick's law takes only (to first order) the transport of CO₂ into account. Changes in, for instance, chemical reaction or transport mechanisms at higher concentration, are not included. Castellote et al. [3] have for instance shown that accelerated testing at 3%, 10% and 100%, as compared to 0.03% (approx. natural condition), may change the conditions for carbonation critically resulting in different reaction products at higher concentrations. Bernal et al. [20] state that the pH at higher CO₂-concentration given rise to lower pHs in the concrete, giving rise to different carbonation end products. Another cause that may compromise the validity of accelerated testing is the rate of drying [2]. Since CO₂ can only penetrate concrete at a reasonable rate through the pore air, the concrete has to be dried out sufficiently before testing. On the other hand, also the carbonation process itself produces water [2]. For low permeable materials, therefore, the evaporation

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of pore water may be the controlling factor in the carbonation process rather than the diffusion of CO₂. As a consequence, different resistances against carbonation might be measured during accelerated conditions that either underestimates or overestimates the time to corrosion of the reinforcement, and with this, the service life of the structure.

Discrepancies between the measured resistance against carbonation for accelerated and natural carbonation tests [2] greatly hampers the introduction of performance based concrete design for carbonation. The literature as discussed above given two major different explanations for this discrepancies: difference in CO₂-reactions and change in dominant transport mechanism. In this paper, the effect of CO₂ concentration on the reactions will be reconsidered. Although very extensive models are available in literature is available (e.g. [4,17]), they do not clarify the possible effects of higher CO₂ concentration in this aspect sufficiently. In this paper these effects will be clarified. It does so on experimental evidence from literature supplemented with chemistry and physics on four aspects: chemical equilibrium, stability of the (hydrated) cement phases, buffering capacity of these phases and transient behavior. Special attention will be given to the change in pH of the pore water as a function of CO₂ concentration and its effect on the stability of the cement pastes. After that conclusions are drawn with respect to the possibility of acceleration.

2. The chemical equilibrium effects on carbonation

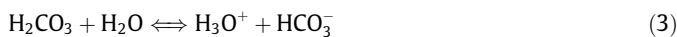
Carbonation of concrete starts from the surface of the concrete, by penetration of CO₂ in gaseous form. After diffusion of the CO₂-gas into the concrete, part of it dissolves in the pore solution and an equilibrium establishes over the interface between the pore air (g) and the pore solution (l):



The concentration of CO₂ in the pore water can be calculated from Henri's law, with Henri's constant $k = 140 \text{ MPa/mol}$ at 20 °C and 1 atm (from [18]). Part of the CO₂ in the pore solution will become carbonic acid H₂CO₃:



The carbonic acid dissociates in HCO₃³⁻ and CO₃²⁻. This brings about a decrease in pH, since the dissociation results in the formation of H₃O⁺ according to:

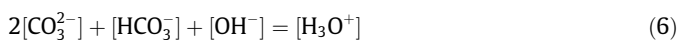


Because it is difficult to distinguish between dissolved CO₂ and H₂CO₃, the ionization constants of Eq. (2) and (3) are usually considered (i.e. measured) together:



With a $K_{a1} = [\text{H}_3\text{O}^+][\text{HCO}_3^-]/[\text{CO}_2]_l$, $\text{p}K_{a1} = 6.36$ [19] and the square brackets denoting concentrations. For the second dissociation step, Eq. (4), the ionization constant $K_{a2} = [\text{H}_3\text{O}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$, $\text{p}K_{a2} = 10.33$ [19]. A good overview of these reactions can be found in, among others, Maekawa et al. [4].

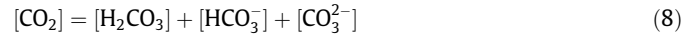
In order to determine the concentration of the carbonic acid dissociates three more equation are required to solve the five unknowns. These are the equation for electron neutrality:



the water constant:



With $\text{p}K_w = 14.164$ at 20 °C at 1 atm and the steuchiometric relation:



The five Eqs. (1)–(8) are sufficient to calculate the pH of the pore water and the concentrations of the carbonic acid and its dissociates. These are shown in Fig. 1. In additions, the solubility and precipitation boundaries shown for CaCO₃ and Ca(OH)₂. In the pore solution of concrete, generally some calcium ions are dissolved. Because the solubility of CaCO₃ (and for that matter also of MgCO₃) is very low ($\text{p}K_{sp} = 8.55$ and 7.47 respectively [19]), the CO₃²⁻ reacts with Ca²⁺-ions in the pore solution to calcium carbonate that precipitates into a solid compound (s):



Since this equation depends on the CO₃²⁻ concentration, the calcium concentration in the pore water has become a function of the pH. In a similar way, the dissolution of Ca(OH)₂ can be calculated, with $\text{p}K_{sp} = 5.26$ [19], see Eq. (10).

The principal driving force for carbonation is the formation of calcium carbonate. Since the CaCO₃ is practically insoluble above a pH of about 5 (CaCO₃dissol line in Fig. 1), the insolubility drives the reaction in Eq. (9) totally to the right. Hence, as long as there is CO₃²⁻ or Ca²⁺ the reaction will continue. CO₃²⁻ is present in the pore water only at a pH above 8. Below this pH (CaCO₃precip line in Fig. 1) the carbonation process thus stops.

Because the pores of concrete are in open contact with the ambient air (open system), the pH in the pore water will always try to become in equilibrium with the CO₂-concentration of the ambient air. This is due to the fact that the amount of dissolved CO₂ (Eq. (1)) in the pore water is proportional to the CO₂ concentration in the ambient air. Fig. 2 shows that the pH of the water (with no other ions dissolved) is about 7 if the CO₂-concentration is zero, but drops rapidly with an increase in concentration. At a concentration of 100%, the pH has dropped to approximately 4. At a CO₂ concentration above approx. 1%, the pH drops below 5 and the solubility of calcium carbonate increases rapidly with further reduction in pH (Fig. 1).

The CO₂-concentration in the ambient air this determined two important aspects in concrete in equilibrium with this concentration. Firstly, it determines the ultimate pH of the pore solution, which decreases with increase of CO₂-concentration (Fig. 2). Secondly, it determines the amount of CO₃²⁻ (per mol/l) in the pore solution which becomes higher with an increase of CO₂ concentration. The pH at which the CO₃²⁻ disappears remains however the same (see Fig. 3).

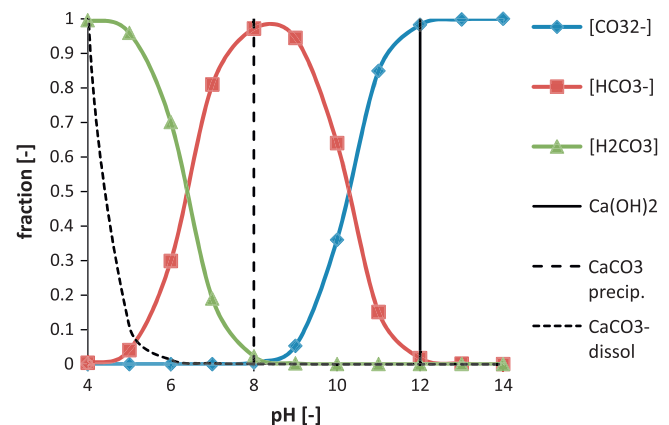


Fig. 1. Normalized distribution of the CO₂ phases and precipitation/dissolution boundaries for CaCO₃ and Ca(OH)₂ (calculated).

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