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

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ABSTRACT

Carbonation of concrete at ambient CO_2 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 CO_2-concentration will accelerate the test but the validity of an increase CO_2 -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 CO_2 concentration will not change the carbonation process. Since carbonation occurs instantly, a zero CO_2 concentration at the carbonation front is maintained. Moreover, it has been concluded that all hydrated and unhydrated cement ultimately carbonate. This implies that the amount of carbonatable matter can be determined on the basis of the amount of calcium in the unreacted cement.

Keywords. Carbonation, Acceleration, CO_2 concentrations, Stability, Buffer capacity

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. Glass et al., 1991). 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 CO_2 concentration is however slow. Since the time available for testing is usually brief, acceleration of the test then is required. The easiest, and most straightforward way of accelerating the test is by increasing the CO_2-concentration as the increase in carbonation rate is proportional to the increase in CO_2-concentration (Visser, 2012).

The validity of acceleration by means of an increase of CO_2-concentration is however debated. Castellote et al. (2009) 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. 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.

In order to try to understand the effect of an increase in CO_2-concentration, this paper will look into more detail into the carbonation process, and, ultimately, the validity of the accelerated test at high concentration. 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 capacityof these phases and transient behaviour. After that conclusions are drawn with respect to the possibility of acceleration.

THE CHEMICAL EQUILIBIUM EFFECTS ON CARBONATION

Carbonation of concrete starts from the surface of the concrete, by penetration of CO_2 in gaseous form. After diffusion of the CO_2-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):

$$CO_2(g) \Leftrightarrow CO_2\,(\mathrm{l}) \tag{1}$$

Part of the CO_2 in the pore solution will become carbonic acid H_2CO_3:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \tag{2}$$

The carbonic acid dissociates in HCO_3^- and CO_3^{2-}. This brings about a decrease in pH, since the dissociation results in the formation of H_3O^+ according to:

$$H_2CO_3 + \mathrm{H_2O} \Leftrightarrow \mathrm{H_3O^+} + \mathrm{HCO_3^-} \tag{3}$$

$$HCO_3^- + \mathrm{H_2O} \Leftrightarrow \mathrm{H_3O^+} + \mathrm{CO_3^{2-}}$$

A good overview of these reactions can be found in, among others, Maekawa et al (2003).

In the pore solution of concrete, generally some calcium ions are dissolved. Because the solubility of $CaCO_3$ (and for that matter also of $MgCO_3$) is very low, the CO_3^{2-} reacts with Ca^{2+} -ions in the pore solution to calcium carbonate that precipitates into a solid compound (s):

$$CO_3^{2-} + Ca^{2+} \Leftrightarrow CaCO_3\,(\mathrm{s}) \tag{4}$$

From the above equations, together with electron neutrality, water constant and steuchiometric, the pH and the concentrations of the carbonatic acid and its dissociates can be calculated. These are shown in Figure 1. In additions, the solubility and precipitation boundaries shown for $CaCO_3$ and $Ca(OH)_2$. The principal driving force for carbonation is the formation of calcium carbonate. Since the $CaCO_3$ is practically insoluble above a pH of about 5 (CaCO3dissol line in Figure 1), the insolubility drives the reaction in eq.(4) totally to the right. Hence, as long as there is CO_3^{2-} or Ca^{2+} the reaction will continue. CO_3^{2-} is present in the pore water only at a pH above 8. Below this pH (CaCO3precip line in Figure 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 CO_2-concentration of the ambient air. This is due to the fact that the amount of dissolved CO_2 (eq. 1) in the pore water is proportional to the CO_2 concentration in the ambient air. Figure 2 shows that the pH of the water (with no other ions dissolved) is about 7 if the CO_2-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 CO_2 concentration above approx. 1 %, the pH drops below 5 and the solubility of calcium carbonate increases rapidly with further reduction in pH (Figure 1).

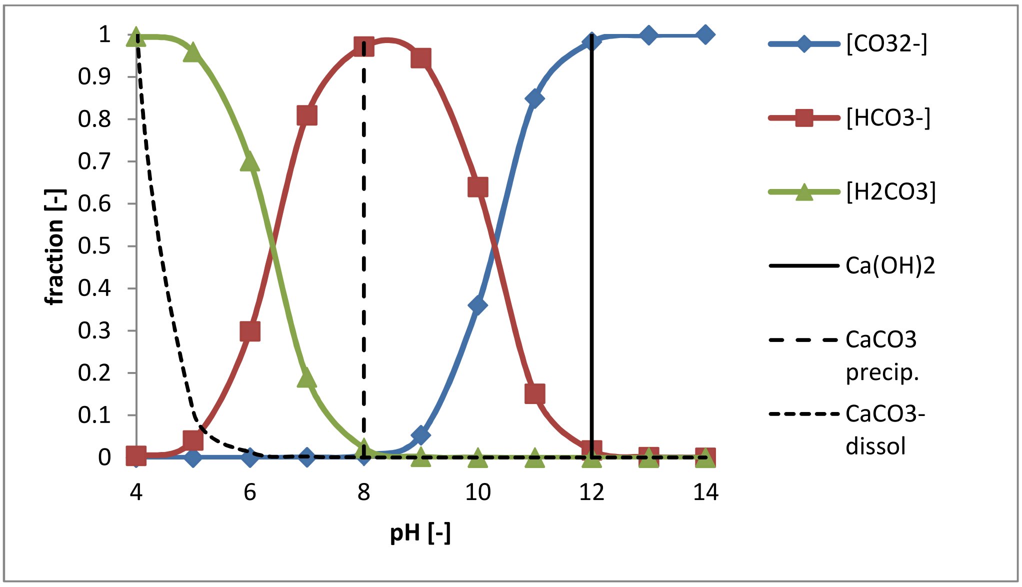

Figure 1. Normalized distribution of the CO_2 phases and precipitation / dissolution boundaries for $CaCO_3$ and $Ca(OH)_2$

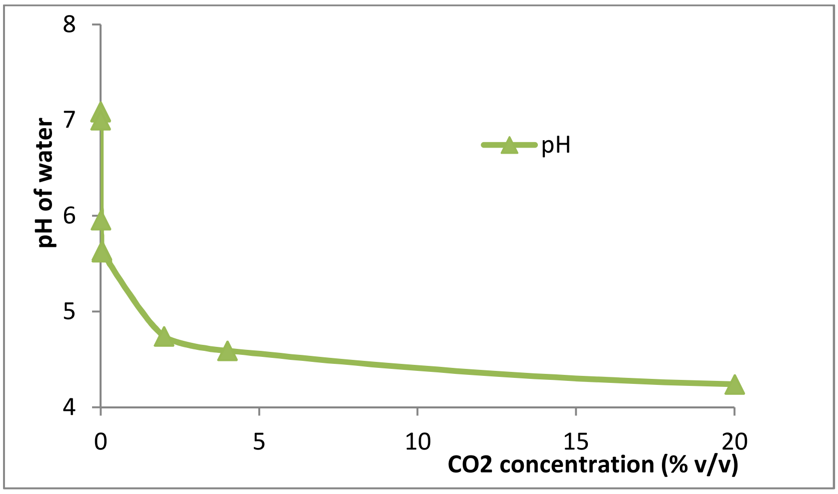

Figure 2. Change in pH with CO_2 concentration (open system)

The CO_2-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 CO_2-concentration (Figure 2). Secondly, it determined the amount of CO_3^{2-} (per mol/l) in the pore solution which becomes higher with an increase of CO_2 concentration. The pH at which the CO_3^{2-} disappears remains however the same (see Figure 3).

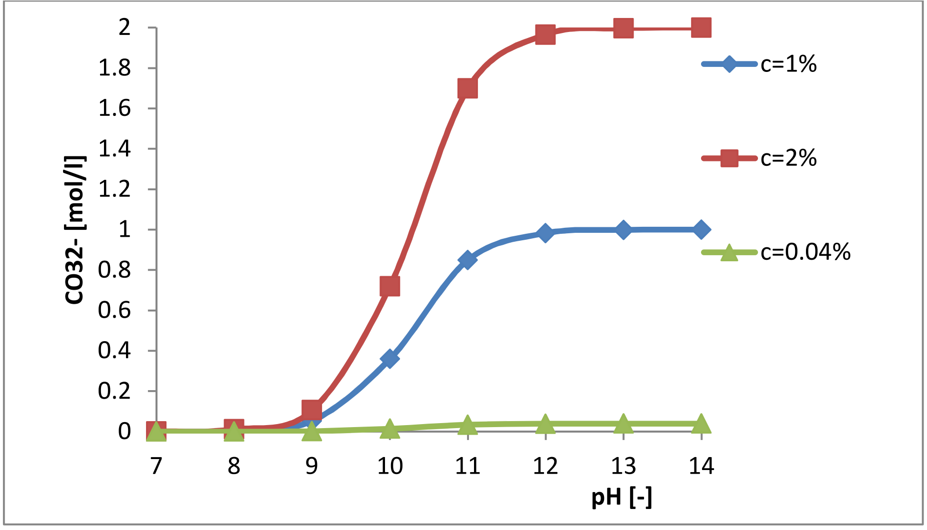

Figure 3. Concentration of CO_3^{2-} for various concentrations of CO_2 in the ambient air

Experimental evidence for the low pH and occurrence of the various carbonic acid dissocated ions comes from Rochelle and Milodowski (2012) and Pu et al. (2012), who have reported ultimate pH values of respectively 7.3 (at super saturation) and 7.2 (at 5% CO_2). Rochelle and Milodowski (2012) also report an initial high pH > 13 decreasing to 7.3 at which pH all CO_3^{2-} has been converted to HCO_3^- (all OH^- has disappeared of course as well). Quite some cations are still available, however. These balance mostly the HCO_3^-. Pu et al. (2012) show linearly decreasing pH with time of carbonation, up to a pH of 7.5 – 8 after which the pH decrease much slower to an apparent constant value of 7.2. This pH of 7-8 coincides with the disappearance of CO_3^{2-}. In addition the pH of 7.2 coincides with the maximum pH at zero CO_2 concentration.

THE STABILITY OF THE CEMENT PHASES

From Figure 1, it can be deduced that all hydrated and unhydrated cement phases that are not stable below a pH of 8 will be decalcified. This is in accordance with the many researches in the literature that found that basically all calcium containing cement phases will carbonate (see among others Borges et al., 2010, Castellote et al., 2009, Thiery et al., 2010 and Gervais et al., 2004). Thiery et al. (2010) concluded from their XRD-analysis that portlandite, ettringite and aluminates disappeared from the XRD-diagrams, even at natural carbonation conditions. Lagerblad (2005) states that at a pH of 9.2 (at which the phenolphthalein change colour) none of the original hydrated cement phases are present any more. Monosulphate (AFm) decomposes at a pH of 11.6 into ettringite (AFt) and alumium oxide phases while ettringite (AFt) decomposes at a pH of 10.6, in sulphate ions and aluminium hydroxide ions. The first might precipitate into gypsum, the second into some stables aluminium hydroxide, e.g. $Al(OH)_3$ (Lagerblad, 2005).

The mechanism of decomposition of the CSH phases upon carbonation is not fully understood. It is thought that for OPC cement, the CSH consists of short silica chains bound together with Ca^{2+} and OH^- (Lagerblad, 2005). This CSH will carbonate firstly by removal of the interlayer calcium of the CSH (Borges et al., 2010). The excess of negative charge is eliminated by adsorption of the cations (mostly alkalis) in the pore water (e.g. Castellote et al., 2009), Anstice et al., 2005). When no more cations are present to maintain charge equilibrium, condensation of neighbouring Si-OH groups to Si-O-Si then polymerizes the CSH, and results in a reduction in C/S ratio (see e.g. Taylor, 1997). Rochelle and Milodowski (2012) state that for CSH there may be both a cascade of reactions or alternatively, the CSH may react directly. The cascade reaction goes in different stable steps from the jennite-form of the CSH (C/S=1.5) to a tobermorite form (C/S=0.8) to silicagel (no more calcium). The CSH thus may decompose in various stages.

The exact pH at which the phases are stable will likely changes with the exact composition of the pore solution, due to the so-called common ion effect. Given a certain chemical composition of the cement, it is mostly the amount of free potassium and sodium that determines the exact pH at which the phases become unstable. An example for $Ca(OH)_2$ is given in Figure 4. It can be seen that the pH increases from ca. 12.6 when there are no alkalis present to 14 at high concentrations of alkalis.

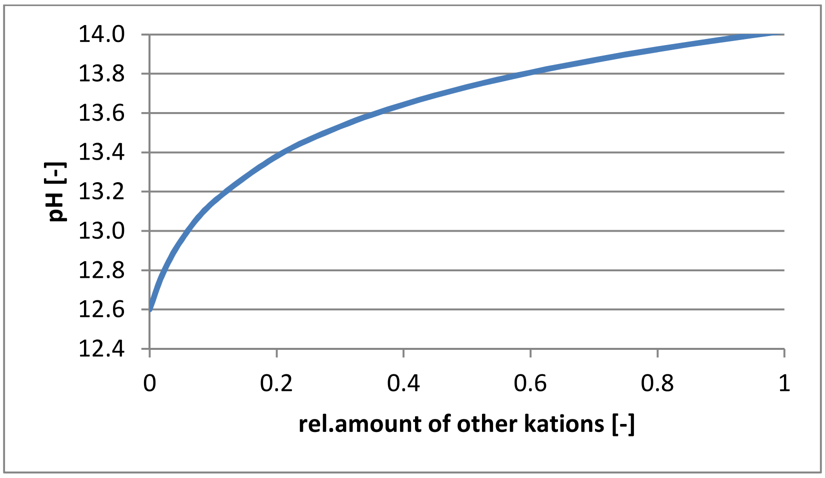

Figure 4. Dissolution pH of $Ca(OH)_2$ as a function of the amount of cations in the pore water

The equilibrium conditions for (synthetic) CSH with various C/S-ratios has been investigated by Hong and Glasser (1999). Some results are shown in Figure 5, together with the dissolution pH for $Ca(OH)_2$ for the same alkali concentrations. The result of Hong and Glasser (1999) shows that the pH of CSH in the high C/S range (1.8) is similar to that of the dissolution pH of the $Ca(OH)_2$ and that due to the common ion effect the pH of the pore water increases similar, namely from 12.6 to 13.4. A different situation arises when there are hardly any cations available and the C/S ratio of the CSH decreases: the dissolution pH of the calcium hydroxide remains the same (12.6) while the dissolution pH of the CSH at successively lower C/S ratios decreases from 12.6 to a PH of 11 at a C/S-ratio of 0.85. Nevertheless, the common ion effect is so large that at high alkali concentrations, even for a C/S ratio as low as 0.85, the pH is also 13.4.

Despite all the different hydrated cement phases, the only reaction product formed from the CO_2-dissolution in the water is $CaCO_3$ although it may be present in various polymorphs: calcite, aragonite and varetite (see e.g. Rochelle and Milodowski, 2012, and Borges et al., 2010). Decalcification of the cement hydrates leads, ultimately, to silica-, alumina- and ferrite-gels. In addition to the hydration phases, also the unreacted cement clinkers and other compounds carbonate: e.g. the calcium containing clinker minerals goes directly to calcium carbonate and silica-, alumina- and ferrite-gels (Rochelle and Milodowski, 2012).

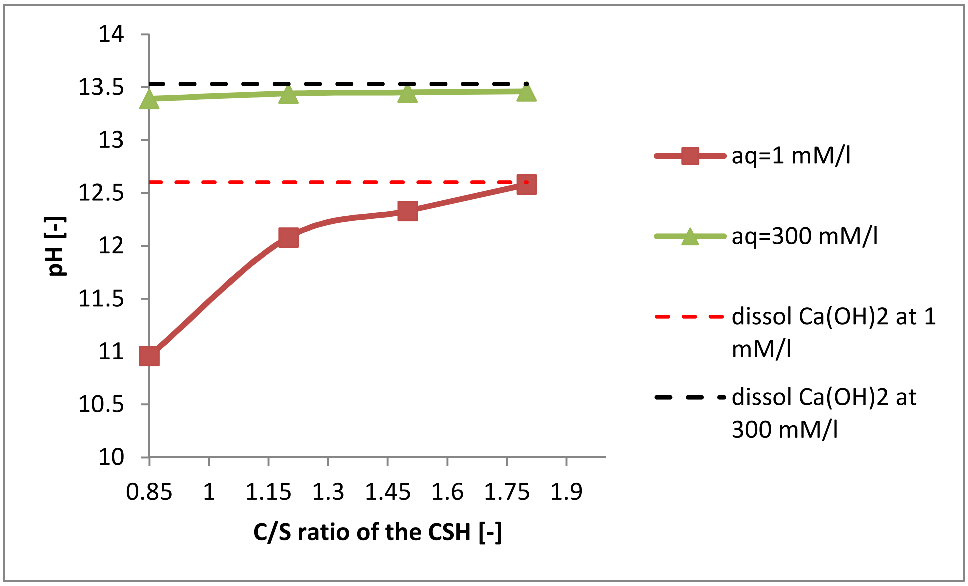

Figure 5. Influence of the alkali-concentration (Na^+-based) on the pH of the pore water as a function of the C/S ratio (data CSH from Hong and Glasser, 1999)

In summary, the stability/decomposition pH boundaries of the different cement phases are given Table 1. It should be realized that the actual pH boundaries at which the various cement phases, and especially the CSH-phases will become unstable will depend on the exact composition. Also the given C/S boundaries are approximations.

Table 1. Summary of the stability of the cement phases

Stage	pH	stable phases
1 (non-carbonated)	>12.6	$Ca(OH)_2$, CSH (Ca/Si > 1.8 or at high common ion effect), AFt, AFm
2	11.6 – 12.6	CSH (Ca/Si< 1.8), AFt, AFm
3	10.5 – 11.6	CSH (Ca/Si< 1.05), AFt, $Al(OH)_3$
4	10.0 – 10.5	CSH (Ca/Si< 0.85), $Fe(OH)_3$, $Al(OH)_3$
5 (fully carbonated)	< 10	SiO_2 with some CaO, $Fe(OH)_3$, $Al(OH)_3$

BUFFERING CAPACITY OF THE CEMENT PHASES

The completeness of the carbonation process, i.e. the amount of a cement phase that actual carbonates, will depend on the buffering capacity of the cement phases. This is easiest seen for the calcium hydroxide. Dissolution of CO_2 in the pore solution decrease its pH to the point where this cement phase become unstable and dissolve into:

$$Ca(OH)_2\,(\mathrm{s}) \Leftrightarrow \mathrm{Ca}^{2+} + 2\mathrm{OH}^{-} \tag{5}$$

This will restore the pH that has initially decreased due to the formation of H_3O^+ when the carbonic acid dissociates. From eq. (2) to (4) it can be seen that for every Ca^{2+} that becomes bound in the $CaCO_3$, two H_3O^+ are formed. Hence, at the dissolution of $Ca(OH)_2$ where two OH^- ions are formed, the net change in pH due to dissolution of $Ca(OH)_2$ and precipitation of $CaCO_3$ is zero. The net result of the chemical reaction (eq. (2) to eq. (5)) can be summarized as follows:

$$Ca(OH)_2\,(\mathrm{s}) + CO_2(\mathrm{aq}) \Leftrightarrow H_2O + CaCO_3\,(\mathrm{s}) \tag{6}$$

It thus is a neutral reaction, in which water is liberated. The reaction is completely to the right: it will continue until all $Ca(OH)_2$ is depleted. This reaction moreover does not affect the pore solution composition: if there is a common ion effect on the dissolution, it will be maintained. In short, it can be said that carbonation of calcium hydroxide will always be completed at its dissolution pH due to its buffering capacity.

If $Ca(OH)_2$ is the only buffering cement phase, the pH will decrease almost immediately after it has become depleted. It will moreover decrease continuously with each new CO_2 molecule dissolving in the pore solution, forming two H_3O^+-ions with each CO_3^{2-}at a pH > 8. Ultimately, the pH will drop so much that only HCO_3^- will form below a pH of about 8 and no further carbonation will occur. It the other cement phases will not buffer the pore solution in the same way as the calcium hydroxide (eq. (6)), it can be expected that there will be conditions that carbonation is not complete. Almost without exception, the experimental evidence indicate that ultimately, all cement phases will reduce to gels and calcium carbonate (see Table 1). This can only be brought about if also the other phases buffer the pore solution as well.

There is sufficient experimental evidence from XRD that ettringite and other aluminate and ferrite phases are extremely susceptible to carbonation and always disappear completely, regardless the CO_2 conditions or the type of cement or Secondary Cementing Materials used (see e.g. Hyvert et al. 2010 for results at among other 0.03% and 50% CO_2). This can be explained only if carbonation for these phases is neutral at well. This means that the decomposition of ettringite and monosulphate should result in 2 OH^- per calcium ion to maintain a constant pH in the same way as for the calcium hydroxide. Hence, writing in a similar way as for $Ca(OH)_2$ in eq. (5) the net reaction, the carbonation of ettringite results in:

$$\begin{aligned} &Ca_6Al_2(SO_4)_3.(OH)_{12}.26H_2O(s) + 3CO_2(\mathrm{aq}) \Leftrightarrow \\ &\qquad 3(CaSO_4.2H_2O)(s) + 3CaCO_3\,(\mathrm{s}) + 2(\mathrm{Al(OH)_3.3H_2O})(\mathrm{s}) + 14\,\mathrm{H_2O} \end{aligned} \tag{7}$$

In which it has been speculated that at the end of the carbonation reaction, all sulfate will have formed gypsum and all aluminum will form an (amphoteric) aluminum gel, in accordance to Table 1. In a similar way, the reaction of the other aluminum and ferrite hydration products can be written down. It can be expected that the pore solution will change somewhat. Some sulphate as well as aluminum hydroxides might stay in solution in the form of $Al(OH)_4^-.2H_2O$ and $Al(OH)_5^{2-}.H_2O$, as long as the pH remains high.

For CSH, being not well crystallized, the carbonation process cannot be seen in the XRD, but similar reaction process is likely to occur, since other microscopic techniques such as BSEM and Si-NMR shown mostly silica gel at the end of the carbonation process (e.g Castellote et al., 2009, Rochelle and Milodowski, 2012). For the same reason as for the Al-and Fe- phases, the reaction should be neutral. Rochelle and Milodowski (2012) has written the carbonation process of CSH in a cascade process at successively lower C/S ratios in the following way:

$$2(Ca_9H_2Si_6O_{18}.(OH)_8.6H_2O)(jennite)+8CO_2(\mathrm{aq})\Leftrightarrow \\ 2(Ca_5Si_6O_{16}.(OH)_2.9.5H_2O)(tobermorite)+8CaCO_3\,(\mathrm{s})+4.5\ \mathrm{H_2O} \tag{8}$$

Which indeed is a neutral reactions as with every Ca^{2+} also 2 OH^- are produced. In the next step, the tobermorite is further decalcified resulting in:

$$2(Ca_5Si_6O_{16}.(OH)_2.9.5H_2O)(tobermorite)+5CO_2(\mathrm{aq})\Leftrightarrow \\ 6Si\,O_2\,(\mathrm{s})+5CaCO_3+11\ \mathrm{H_2O} \tag{9}$$

which is also neutral. In this two-step cascading carbonation process of the CSH, the C/S ratio of the CSH decreases from 1.5 to 0.83 to 0. It should be remarked that there may be more or different equilibrium situations in between, since the exact equilibrium will depend on the exact form of CSH. The equilibrium will be affected among other on the amount of cations and/or aluminum that sometimes are taken into the CSH-phases. In addition, sometimes some Ca-containing silica gel is observed as well.

TRANSIENT EFFECTS IN CARBONATION

The carbonation process requires not only an assessment of its equilibrium situation(s) as discussed above, but needs to be investigated in its transient state as well. The carbonation process starts with diffusion of CO_2 into the concrete (according to Fick's law, Arandigoyen and Alvarez, 2006). Since the diffusion is much faster in air than in water, most of the transport occurs through the pore air (Saeki et al., 1991). At the interface between the pore air and the pore solution, an equilibrium in CO_2 will establish as discussion in the previous section (eq. 1). For the initial high pH (>12.6) in hardened cement pastes, the dissociation reaction lies completely towards CO_3^{2-}. According to Meier et al. (2006), experimental evidence has shown that the dissolution and precipitation reactions are very fast in comparison to the ingress of CO_2. Thus, initially, the CO_2 concentration at the pore air – water interface remains zero. Equilibrium cannot be establish as each CO_3^{2-} is consumed immediately and thus more CO_2 has to dissolve in the pore water. As long as there remain buffering cement phases (i.e. H_3O^+ consuming phases), the CO_2 concentration cannot rise at the pore air/solution interface. The carbonation reaction thus is occurring at a zero concentration. This has as consequence that as long as the CO_2-molecules at the interface do not arrive too fast, the carbonation process will go to completion regardless the CO_2-concentration at the surface. Since most experimental results in literature show that regardless the concentration, ultimately only silica gel remains, another conclusion is that all cement phases do buffer the pore solution, otherwise in each and every research, for instance the same CHS of the same C/S ratio would have been found.

A second deduction can be made for the cascade of carbonation reactions. The first cement phases will dissolve in response to maintain a constant pH. According to Table 1, the first phases are the calcium hydroxide and the CSH. If there is a common ion effect, this dissolution will occur at progressively lower pH due to the uptake of the alkalis in the decalcifying CSH which reduces the common ion effect in the pore water. At a pH of 12.6, the common effect is zero, and further dissolution will progress at this pH. If the C/S ratio becomes below 1.85 (or perhaps 1.5, the boundaries are not well known), the dissolution pH of the CSH is lower than for the $Ca(OH)_2$ (see Figure 5). Thus first all $Ca(OH)_2$ has to disappear before the pH can become lower and the CSH can carbonate further. Otherwise the CSH carbonates at the same time. Similar 'hold-up' levels may be found at the stability/decomposition pHs for AFm at 11.6 and AFt at 10.6 (see table 1). Even the CSH may decrease in discrete steps and thus carbonate at discrete pHs as well, as suggested by Rochelle and Milodowski (2012). Ultimately, however, also the CSH is carbonated fully. The pH of this point is not known, but it will be below a pH of 10 (Table 1) and above a pH of 8 (Figure 1).

Once there are no more buffering cement phases at a certain depth, the pH drops very rapidly upon further transport of CO_2 ions. At this point, equilibrium between the CO_2 concentration in the pore air and the pore solution can finally establish. When the CO_2 concentration in the pore solution in dissociated form (Figure 1) starts to rise, the pH drops below approx. 7. At this point no more carbonation takes place anyway.

CONCLUSIONS

In summary, the following conclusions can be drawn from the assessment of the carbonation process discussed above. Considering all experimental evidence, there is only one plausible carbonation process, stemming from full buffering of all cement phases:

- carbonation of each hydrated cement phase will occur at that pH below which the phase become unstable;
- because the equilibrium pH for the pore water at any CO_2 concentration will be lower than a pH of 7, all hydrated cement phase eventually become unstable;
- all phases react with the CO_2 in a neutral way so that the reaction can go to completion as long as CO_2 arrives at the reaction front;
- all calcium is consumed (neglecting possibly a very small portion remaining in the highly polymerized silicagel), meaning that the amount of carbonatable matter can actually be determined on the basis of the amount of calcium in the cement prior to batching.

The effect of a high CO_2 concentration will not change the carbonation process at all, since carbonation will occur instantly, thereby maintaining a CO_2 concentration of zero at the reaction front (or rather: a zero CO_3^{2-}concentration). The only effect of the high CO_2-concentration is a faster transport of the CO_2 molecules to the pore air – pore solution interface and thus a faster reaction process.

The answer on the question about the validity of acceleration by means of an increase of CO_2-concentration thus can be answered positive: acceleration is allowed and does not the chemical process whatsoever. The results of Castellote et al. (2009) fuelling this debate might have been due to incomplete carbonation. They showed that at 10% and 100% CO_2, indeed only a polymerized (Ca-modified) silica gel remained whereas at 0.03 % and 3 % not only silica gel but also CSH at a lower C/S ratio was left. The change in C/S ratio of this carbonated CSH compared to the uncarbonated concrete was from 1.87 to 1.2. According to Figure 5, at a C/S ratio of 1.2, the pH is about 12. Since this is well above the pH of about 7 at which the CO_2 concentration in the pore water can increases, as well as above the pH of 10 below which the silica gel is reported to occur, their time of testing might have been too brief.

Although no change in the carbonation process will occur due to the acceleration, some other side effects at acceleration are known. Some have been listed by Visser (2012). Among others, a change in dominant transport mechanism may occur. Due to a large water production upon carbonation, the rate of evaporation (water vapour transport) may become dominant over the CO_2 diffusion ingress. This may give rise to underestimation of the resistance against carbonation. Another one has been given by Thiery et al. (2007), who found no more CSH in their carbonated specimens, while $Ca(OH)_2$ remained in abundance. These were found to be coated with $CaCO_3$, preventing further dissolution. This might be due to a too fast, massive $CaCO_3$ production. Saeki et al. (1991) have investigated back diffusion of hydroxide at very low CO_2-reaction rates as a reason for massive precipitation of $CaCO_3$ close to the concrete surface. This slows down or even may prevent further CO_2-diffusion in the concrete and forms another natural defence against carbonation. If this massive precipitation is not occurring in the accelerating testing, there will again be a mismatch between the natural and accelerating test. Hence, despite the fact that the carbonation process itself does not change, higher CO_2 concentrations still may involuntary give rise to other effects, ultimately under- or overestimated the service life of the concrete structure.

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