

Accelerated carbonation testing of mortar with supplementary cementing materials - Limitation of the acceleration due to drying

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In the design stage of a concrete structure, decisions have to be made on how to fulfil the required service life and consequently, what concrete composition to use. Concrete compositions can be chosen on account of known performances but this will limit the choice of compositions and materials to those that have already been in use. Other methods may give a wider choice in concrete compositions, but mostly require proof which is generally obtained by means of testing. When limited time is available for testing, accelerated tests often are performed. If there is no good insight in the underlying principles of the effect of the acceleration, some serious mistakes in the service life designs will be made.

In this paper, an example of accelerated testing is shown for carbonation. Accelerated carbonation tests at 2 % CO₂ and natural carbonation tests at ambient CO₂-level have been executed. Based on the results, the resistance against carbonation has been calculated. Since this resistance is a material property, it should be similar in both tests. For two of the tested concrete compositions this proved to be the case, a third type of concrete made with fine cement it did, however, not. It was speculated that in the accelerated test, a different mechanism was becoming dominant for this concrete. Instead of the transport of CO₂, now drying out was thought to be dominant. The drying out is a necessary step in the carbonation process as during the carbonation a relatively large amount of water is generated that, when saturating the pore space, prohibits CO₂ to be transported to the carbonation front. A new simple model was derived for this case. The modelling gave a similar resistance against carbonation for the fine OPC as determined in the natural carbonation case where transport of CO₂ was the dominant step in the carbonation process. If this change in dominant step had not been made, a far too high resistance in carbonation would have been calculated, seriously overestimating the service life of this fine OPC concrete in structural applications.

Key words: Accelerated testing, modelling, carbonation, moisture, pore structure

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1 Introduction

In the design stage of concrete structures, decisions have to be made on how to fulfil the required service life and, consequently, what concrete composition to use. To ascertain the service life with respect to durability, concrete compositions can be chosen on account of known performances e.g. such as laid down in the standard EN 206 by means of deem-to-satisfy rules. However, these contain only a limited choice of concrete compositions and materials. Other ways of selecting a composition requires testing accompanied by either modelling with respect to the degradation mechanisms or by comparison with an already accepted concrete composition, in an equivalent performance procedure.

The available period of testing in the design stage is often limited, hence accelerated tests are preferred. Acceleration can be performed in two ways: increasing the driving force of the degradation process (e.g. concentration, temperature) or compressing time (e.g. using shorter freeze thawing or drying/wetting cycles). Acceleration can however lead to several unwanted effects. Among others, a different degradation process or parameter in the process may become dominant. There thus is often a maximum on the possible acceleration factor. Complicating things even more, concrete itself is an ageing material. Especially at young age, its properties have not yet been developed fully. This can also give rise to results that are not compatible with the long-term behaviour under natural test conditions and result in serious errors in the service life predictions.

One of the most important degradation mechanisms of reinforced concrete structures that seems to be easy to accelerate is carbonation. For many large infrastructural works requiring long service life, this test is prescribed due to the importance or high costs related to the damage due to corrosion that may arise after carbonation. In a brief research to investigate two concrete compositions for a new Dutch tunnel required to have a service life of 100 years, both accelerated (at 2% CO₂) and natural carbonation (at ambient CO₂) were performed in order to investigate whether also for concrete with supplementary materials (fly ash and blast furnace slag) acceleration was suitable. For comparison, also an OPC-concrete was tested. In this paper, these results are presented and discussed in light of the chosen acceleration parameters. In Section 2, firstly the theoretical background of testing for service life design, the carbonation modelling and possibilities for accelerated carbonation testing are discussed. In Section 3, the experiments and the results are

presented. Discussion of the results with respect to the chosen acceleration and its possible influence is given in Section 4. Section 5, finally, gives the conclusions.

2 Service life design for corrosion due to carbonation

2.1 The carbonation reaction and service life design

The most widespread degradation mechanism in reinforced concrete structures is corrosion of the reinforcement. Corrosion is initiated when the passivation layer on the reinforcement steel is broken. This can be brought about by carbonation of the surrounding concrete, which results in a drop in the surrounding pH, from the usually very high alkaline environment (pH about 13) to an environment with a pH of below 9 (e.g. Glass *et al.* [1991]).

A good overview of the chemical reactions in the carbonation process can be found, among others, in Thiery *et al.* [2007] and Maekawa *et al.* [2003]. To recapitulate very briefly: carbonation starts from the surface of the concrete, by penetration of CO₂. After diffusion of the gas into the concrete, it dissolves in the pore water as carbonic acid H₂CO₃ that dissociates in HCO₃⁻ and CO₃²⁻, the concentrations depending on the pH of the pore water, the ambient CO₂ concentration and the other species in the pore water, most notably the alkalis. The dissociation decreases the pH of the pore water since it also produces H₃O⁺. The dissolved Ca²⁺ reacts with the CO₃²⁻ to solid CaCO₃, which precipitates in the pore space. Both the reduction in pH after dissociation of H₂CO₃ and the decrease in calcium concentration after precipitation of the calcium carbonates are drivers for the dissolution of the Ca(OH)₂. The dissolution of Ca(OH)₂ is buffering the pore water solution to a more or less constant pH. In addition to the calcium hydroxide, calcium is dissolved from other calcium bearing cement phases as CSH, ettringite (AFt) and monosulphate hydrate (AFm). With progressive consumption of calcium from the easily dissolving compounds of the hardened cement paste and precipitation of the almost insoluble calcium carbonate, ultimately there will be no more compounds that are easily soluble. At this moment, the pH cannot increase anymore and a new equilibrium is set in equilibrium with CO₂ concentration at the surface. In this chemical reaction process, water is required to dissolve the CO₂ but it also liberates water that previously was held in, among others, the solid Ca(OH)₂.

In most situations, there exists a narrow reaction layer in which the bulk of the carbonation reaction occurs and which progresses from the surface of the concrete inwards. Between the surface and the reaction layer, the concrete is fully carbonated while at greater depths than the reaction front, the concrete is unaffected. Since the existence of a very narrow carbonation zone has been proven for a whole range of experimental conditions [see e.g. Peter *et al.* 2008 and references therein], the carbonation zone is usually modelled as a jump change of the concentration of the CO₂ in this zone. This is because the carbonation reaction consumes any new CO₂ molecule that arrives at a not fully carbonated spot. Thus, all carbonatable matter must be consumed first before the carbon dioxide molecules can penetrate further. For convenience sake, and because of the fact that the measuring method consists of spraying of phenolphthalein which changes colour at a pH of 8.2, this narrow zone is usually modelled as a sharp front and is called the carbonation front. Variations in this carbonation front are often found to be solely due to variations in microstructure of the hardened cement paste (local variations in amount of consumable matter, degree of saturation, micro cracks facilitating diffusion etc.).

The time which it takes for the carbonation front to reach the reinforcement bars and destroys their passivation layer, is called the (corrosion) initiation time. For a service life design, it is usually required that the time of corrosion initiation due to carbonation is longer than the required service life. The following stage of corrosion of the reinforcement can be fast and the consequences of possible failure due to undetected corrosion can be huge and necessary repairs costly. Hence, as serviceability limit state, the probability that the carbonation front reaches the reinforcement within the expected service life must be lower than some predefined probability is used.

2.2 Modelling carbonation ingress

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 CO₂. The ingress takes place by means of diffusion (according to Fick's law) if the pore diameters are larger than the mean free path [Arandigoyen and Alvarez, 2006]. Therefore, the carbonation rate is in general modelled by a simplified equation for the CO₂-flux q in the concrete specimen and further simplified by a linear decline of the concentration over its carbonation depth, i.e.

$$q = -D\nabla c = \frac{DA(c_s - c_{front})}{x}, \quad (1)$$

with

q = flow rate of CO₂ [kg/m²s]

D = diffusion coefficient [m²/s]

c_i = CO₂ concentration at the concrete surface ($i = s$) and at the front ($i = \text{front}$) [kg/m³]

A = area through which the transport is taking place [m²]

x = the location of the carbonation front [m]

Based on the assumption that the carbonation front cannot move on except when all carbonatable matter a has reacted within a reference volume, $A dx$, the total mass of CO₂, dM , that has to be transported to the carbonation front to transform this matter a , thereby progressing the carbonation front by dx , is given by

$$dM = aA dx, \quad (2)$$

with

dM = mass of CO₂ [kg]

a = amount of carbonatable matter per unit volume [kg/m³]

dx = unit progress of the carbonation front [m]

A = unit area [m²]

x = the location of the front [m]

Since this is similar to the flux that goes through this reference volume in a reference time dt to move from dx forward, substituting the above equation in the simplified form of Fick's first law (1) then gives

$$\frac{DA(c_s - c_{\text{front}})}{x} = aA \frac{dx}{dt}. \quad (3)$$

The boundary condition for the CO₂ concentration c_{front} at the carbonation front is that it is zero. Using the boundary condition and solving equation (3) by integration results in

$$x_c = \sqrt{\frac{2Dc_s t}{a}}. \quad (4)$$

This square-root time relationship is well known and seems to be reasonably applicable. Rewriting Eq. 4 to the time in which the carbonation front reaches the reinforcement at cover depth d_c

$$t_{ini} = \frac{R_{carb} d_c^2}{2c_s t}, \quad (5)$$

in which the resistance of the concrete to carbonation $R_{carb} \equiv \frac{a}{D}$.

2.3 Acceleration of the carbonation ingress

The simplest way of acceleration is to increase the CO₂ concentration (c_s) of the ambient air. By Henry's law, the concentration of CO₂ in the pore water is directly related to the concentration of the CO₂ in the pore air. For higher c_s , more CO₂ molecules arrive at the carbonation front within a certain time period, dissolve and dissociate, and more calcium can react to calcium carbonate. This in turn increases the dissolution rate of the calcium from the hardened cement paste constituents. Thus, the calcium supply that can react is depleted faster and the carbonation front progresses faster. According to Eq. 4, the degradation rate is accelerated by an amount equal to the ratio of accelerated concentration divided by the natural concentration. E.g. using a concentration of 2% whereas natural CO₂-concentration is about 0.04 % thus increases the degradation 50-fold. As a result, the carbonation process theoretically can be accelerated as much as one wishes by increasing the concentration accordingly.

3 Experiments

3.1 Materials

Three different types of concrete were cast for the investigation, in which only the type of binder was varied. One concrete contained 100% Ordinary Portland Cement (OPC), the others contained either fly ash (FA) or blast furnace slag (BFS) as cement replacement (see Table 1). The slag was added by mixing blast furnace slag cement with OPC while FA was added as a pure component to the OPC. All FA and BFS were taken into account as binder.

Table 1: Concrete compositions used in the carbonation tests, with slag and fly ash percentage as OPC replacement

name in this paper	binder	slag (%)	fly ash (%)
fine OPC	CEM I 52.5 R	0	0
FAC	CEM I 52.5 R - fly-ash	0	30
BFSC	CEM I 52.5 R - CEM III/B 42.5	50	0

The choice of binders and cements were based on the available materials for a large infrastructural project. The concrete composition of all mixtures had a water-binder ratio (wbr) of 0.45 and a binder content of 340 kg/m³. River sand and gravel was used as aggregate, with a maximum diameter of 32 mm.

3.2 Carbonation test

Both Natural Carbonation (NC) and Accelerated Carbonation (AC) tests have been performed on the three types of concrete, given in Table 1. For each type of concrete, six concrete prisms (300 mm × 100 mm × 100 mm) were cast. After one day, the specimens were demoulded and stored in a fog room. At an age of seven days, the specimens were placed in a 20/65 climate room (temperature 20 °C and relative humidity 65%), at natural carbon dioxide concentrations (approximately 0.037 (V/V) % CO₂). At an age of 28 days, three concrete prisms were placed in a climate room with a CO₂ concentration of 2% (V/V) at a temperature of 20 °C and relative humidity of 65%. The other three specimens remained in the 20/65 climate room with a natural CO₂ concentration.

In the accelerated carbonation test, the carbonation depth was determined after 28, 62 and 152 days of accelerated carbonation at 2 (V/V) % CO₂. For the specimens in the natural carbonation test, the carbonation depth has been measured after 6 months, one year and three years of exposure, in the same way as for the accelerated test. The carbonation depth was determined according to point 4.2 of RILEM CPC-18: 'Measurements of hardened concrete carbonation depth' [Rilem, 1988].

Table 2: Carbonation depths (in mm) for the tested cements

age of testing (day)	CEM I		BFSC		FA	
	average	stdev	average	stdev	average	stdev
Natural carbonation						
183	0.2	0.3	1.1	0.5	1.4	0.5
365	0.4	0.2	1.2	0.7	1.7	0.5
1214	1.5	0.9	2.6	1.6	3.3	1.6
Accelerated carbonation						
28	0	0	3	0.6	3.7	0.7
63	0.1	0.2	4.3	0.7	5.3	1
154	0.4	0.3	6.9	1.7	8.8	2.2

3.3 Results

The results of the natural and accelerated carbonation tests are given in Figure 1 and Table 2. Both tests show the same ranking of carbonation depths: Portland cement concrete, blast furnace slag cement concrete and fly ash concrete. Note the difference in carbonation depth in the NC and AC test, i.e. 0 – 4 mm versus 0 – 10 mm respectively.

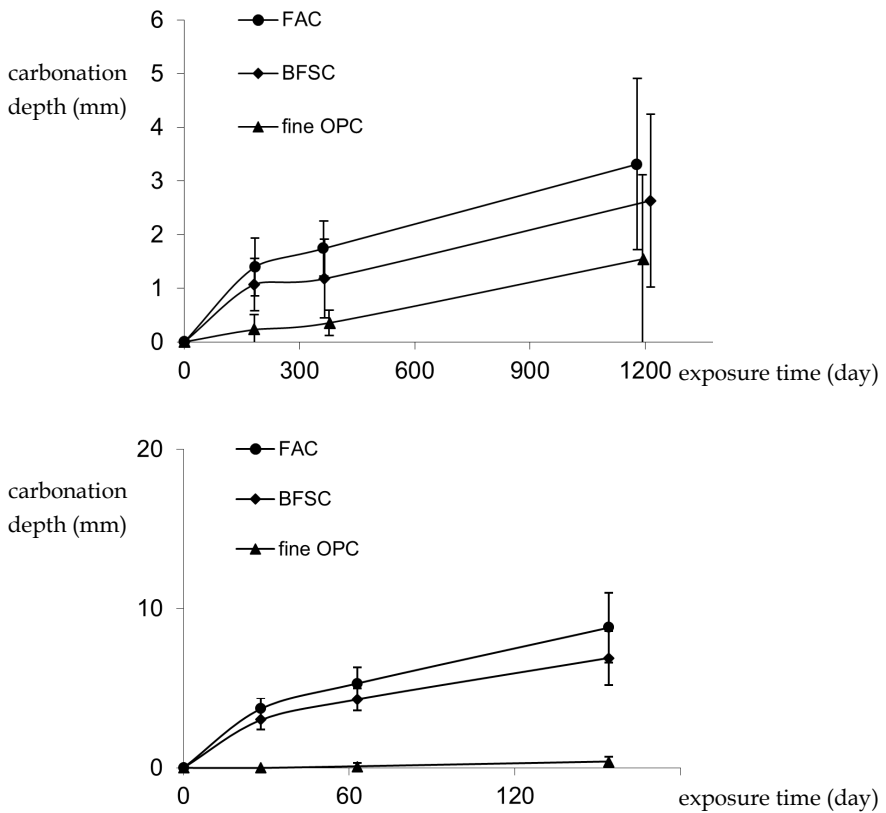


Figure 1: Carbonation depths after exposure under natural carbonation (top) and accelerated carbonation (bottom)

After exposure in the AC test for 154 days, the capillary porosity of the carbonated specimens were determined with Polarization and Fluorescence Microscopy (PFM). It was observed that on account of the capillary porosity, the degree of hydration of the fine OPC in the noncarbonated zone was high, whereas the hydration in the noncarbonated zone of the BFSC and the FAC was medium. In addition, the capillary porosity for the fine OPC in

the carbonated zone was reduced as compared to the noncarbonated concrete, while for the BFSC and the FAC an increase of the capillary porosity was observed.

4 Discussion

4.1 Comparing carbonation resistance under natural and accelerated conditions

In Figure 2, the results of the natural and accelerated tests are compared as a function of the concentration-independent variable $\sqrt{2c_s t}$. On account of equations (4) and (5)

$$x_c = \sqrt{\frac{1}{R_{\text{carb}}}} \sqrt{2c_s t} . \quad (6)$$

The curves should become straight lines with a slope being similar to $\sqrt{1/R_{\text{carb}}}$. Since this is a material variable, the lines for the accelerated and natural carbonation tests should be similar, and the resistance against carbonation should be the same. It can be seen in Figure 2 that the lines for concrete made with BFSC and FAC agree very well. For fine OPC, there is no agreement between the accelerated and natural carbonation test results.

The carbonation resistance, R_{carb} , can be determined by means of least-square approximation of Eq. 6 to the data. The results are given in Table 3. The resistance against carbonation for both the FAC and BFSC is relatively small, indicating the ease with which the concrete carbonates. On the other hand, the resistance of the OPC is, as far as could be estimated from the NC-test, two orders of magnitudes higher. For the AC-test of the fine OPC concrete, no stable results were found for the least squares fitting (LSQ) modelling.

Table 3: R_{carb} (in $(\text{kg CO}_2/\text{m}^3)/(\text{mm}^2/\text{yr})$) determined by means of least square approximation to Equation 4, for the natural carbonation test (NC) and accelerated carbonation test (AC)

concrete	binder	NC	AC
fine OPC	CEM I 52.5 R	$[1.2 \cdot 10^{-2}]$ (*)	--(**)
coarse OPC	CEM I 32.5 R	-	$1.2 \cdot 10^{-3}$
FAC	CEM I 52.5 R - fly-ash	$4.2 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$
BFSC	CEM III/B 42.5 - CEM I 52.5 R	$6.8 \cdot 10^{-4}$	$7.0 \cdot 10^{-4}$

(*) the least square fitted profile mostly ignores the last data point since the standard deviation of the measurement is high, profile on two data points

(**) the least square procedure is unstable, hence any solution fits equally well

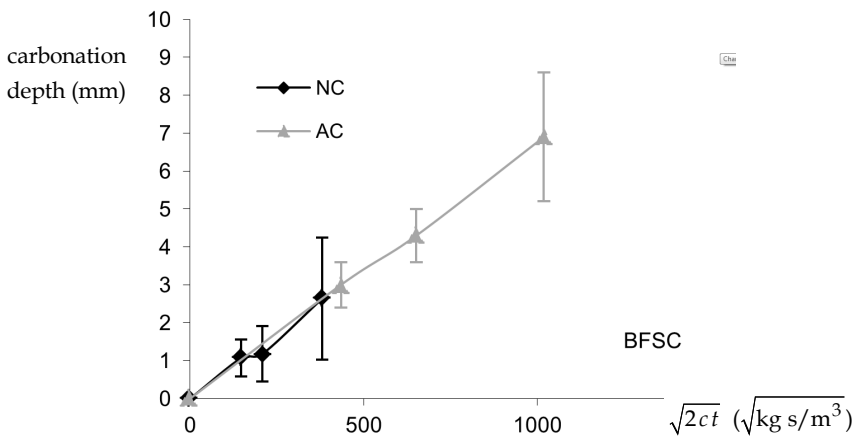
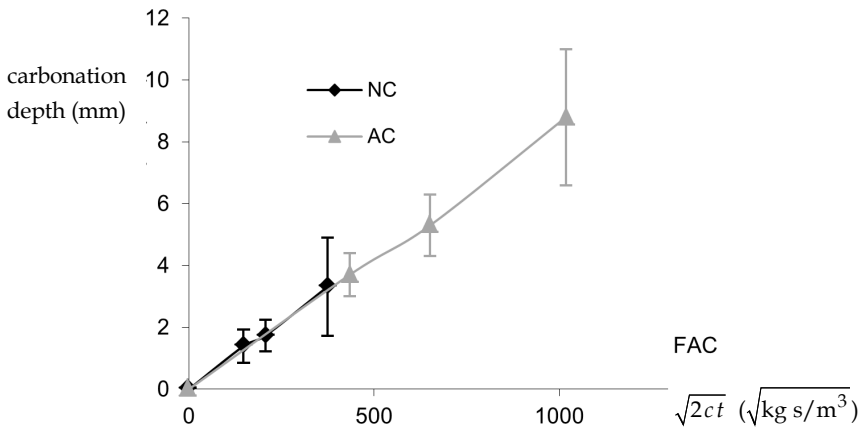
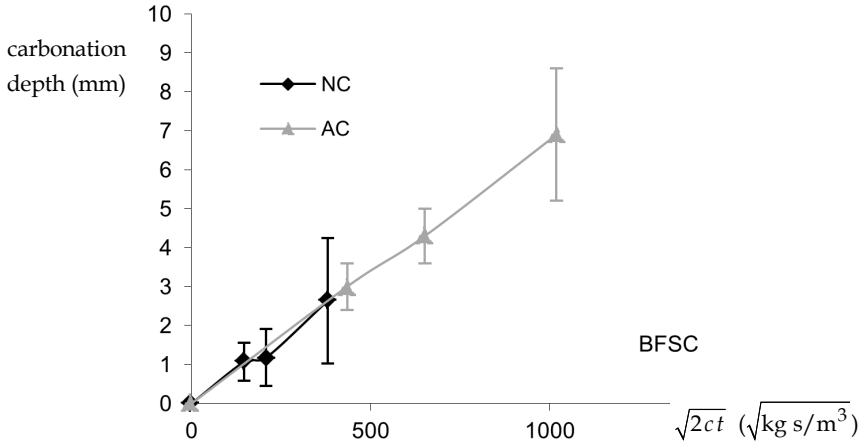


Figure 2: Comparing natural and accelerated carbonation test

Figure 3 shows that there is hardly any difference in carbonation depth in the natural and accelerated test for the fine OPC concrete at a certain exposure time. This implies that despite a much higher CO₂-concentration in the accelerated test, the carbonation does not proceed any faster than in the natural carbonation test. This proved to be a feature of the fine OPC alone. For comparison, a coarse OPC concrete (CEM I 32.5 R) with the same composition as the fine OPC concrete (CEM I 52.5 R) has been tested in acceleration as well, up to an age of three year. This concrete has the desired square root t behaviour and thus fits the model very well. The results of the LSQ-modelling are also given in the table above. The behaviour of the fine OPC cannot be modelled by the simple square-root equation as given in Eq. 6.

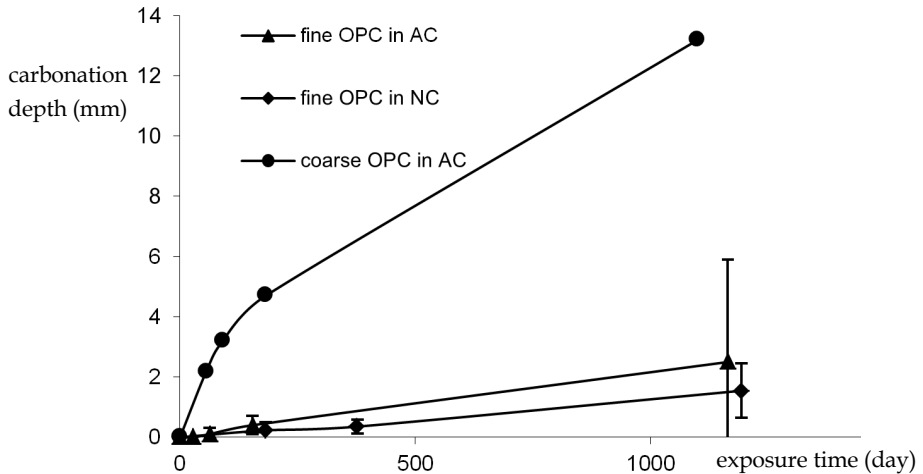


Figure 3: Comparing fine OPC in natural and accelerated carbonation tests and coarse OPC (CEM I 32.5 R) in accelerated test

4.2 Possible causes of mismatch between modelling and testing

PFM analysis of the thin sections indicated a noticeable difference in the pore structure of the carbonated zones of the fine OPC concrete and the concretes with supplementary cementing materials. Analysis were made with respect to the change in capillary porosity and expressed as apparent wcr, defined as the wcr of a (non-carbonated) concrete of similar composition and similar age. The apparent wcr of the FAC and BFSC were found to have increased from 0.45 to 0.50 while that of the OPC had decreased from 0.45 to 0.40.

This is generally attributed to the fact that the high Ca(OH)_2 content in the OPC forms a large amount of CaCO_3 that has about 11% larger volume than the calcium hydroxide and therefore clogs up the pore space, reducing its porosity. However, there is sufficient evidence that also the other hydration phases carbonate [Castellote *et al.* 2009, Anstice *et al.* 2005, Borges *et al.* 2010], leading to a shrinkage of the CSH. Meier *et al.* [2007] and Peter *et al.* [2008] found from their numerical modelling that the rate of carbonation of the other constituents (CSH etc.) in carbonation was dependent on the relative reaction rates of these other constituents. Since that of Ca(OH)_2 is much faster than all the other phases, this phase dominates the progress of the carbonation front in OPC. The others were found to be of only of secondary effect and hardly influenced the carbonation depth. For the FAC and BFSC, the content of Ca(OH)_2 is much lower than for OPC. Firstly less calcium hydroxide is formed because the fraction of the clinker is lower (the total binder content was kept constant). Secondly, especially the fly ash consumes calcium hydroxide in its hydration. The carbonation of the other hydration phases are therefore likely to be dominant for these concrete compositions, since coarsening of the pore space is observed.

In relation with the above observation, ageing thus can have a different effect for the three types of concrete. For OPC, the two largest ageing effects with respect to carbonation are expected to be an increase in calcium hydroxide content and a reduction of capillary pores. After the start of the carbonation tests, however, it is also expected that for the fast hydrating fine OPC, these variables do not change that much anymore. The analyses of the thin section does not supplement any evidence: the carbonated zone is too small to observe any change in capillary porosity with depth. Nevertheless, ageing effects for this cement are expected to be negligible. For the BFSC, it is expected that at the start of the test at 28 days, the calcium hydroxide content would not increase much anymore. Further densification of the hardened cement paste will occur mostly due to on-going slag hydration. For the fly ash, on the other hand, a reducing calcium hydroxide content and a reducing capillary porosity will develop. Since the coarsened carbonated capillary pore space will facilitate the transport of the CO_2 , it is expected that the reduction of the Ca(OH)_2 content will be dominant.

From the differences in the resistance against carbonation (Table 3), it can be seen that indeed the resistance against carbonation decreased from OPC to BSFC to FAC. Due to the slower reaction of slag (> 2 days) and fly ash (> 30 days) [see e.g. Neville 2003], it can be assumed that if ageing would be a factor of importance in the testing, a difference would

have been observed between the responses of the natural carbonated and accelerated carbonation test. This is not the case. Nor are there any nonlinear effects in particularly the accelerated carbonation test that is performed at ages between 28 days to 180 days. Ageing therefore has no effect on the resistance against carbonation, for these particular materials and tests. This is contrary to the increase in resistance to chloride penetration with age that has been measured for the same materials [Visser and Polder, 2006]; see also [Osterminski *et al.* 2012, Polder 2012].

Meier *et al.* [2006] observed another effect that may change the carbonation rate considerable, namely the amount of water released in the carbonation process. Relatively large amounts of water are released, not only from the reaction with $\text{Ca}(\text{OH})_2$ but also with the other hydrates. E.g. for CSH, the removal of Ca^{2+} creates a charge imbalance that is compensated through the formation of Si-O-Si from Si-OH groups [see e.g. Borges *et al.*, 2010]. Most of this water will strongly decrease the carbonation rate since the transport of the carbonic acids and dissociated ions (in the pore water) is extremely slow compared to the transport of CO_2 through (pore) air. Diffusion of CO_2 in water is a factor 10^4 lower than in air [Thiery *et al.*, 2007]. For the BFS and FAC with their coarse pores after carbonation, the water liberated in the carbonation process can evaporate quickly enough (apparent $w_{cr} = 0.5$) as can be concluded from the fact that the carbonation rate is equally fast in the natural carbonation and the accelerated carbonation test. For the fine OPC cement, the carbonated hardened cement paste is becoming denser due to the precipitation of a large amount of CaCO_3 . A smaller capillary porosity (apparent w_{cr} decreasing from 0.45 to 0.4) probably combined with a finer pore sizes as well, makes evaporation of water much slower. The overall degree of saturation of the remaining pores will be much higher since capillary condensation is pore size dependent [see e.g. Bear and Bachmat, 1991, Cerny and Rovnanikova, 2002]. At an RH of 65% as in the accelerated carbonation test, it is expected that the pores still can sufficiently dry out to allow carbonation. However, much slower drying out of the pores may seriously reduce the carbonation rate for the fine OPC. The principle is schematized in Figure 4. If the above explanation is correct, the carbonation process for the fine OPC cannot go further until the pores are sufficiently dried out to allow for diffusion of CO_2 through the vapour phase in the most recently carbonated layer [Maekawa *et al.* 2003]. There might even exist a fully saturated thin zone at the carbonation front. In the limit case that the drying out is indeed this slow, the diffusion of CO_2 (at least in the accelerated test) will be completely stopped at the water saturation front until it

dries out. In order to model this effect on the carbonation rate, it is assumed that the CO₂ concentration in the carbonated zone is constant throughout the whole carbonated layer.

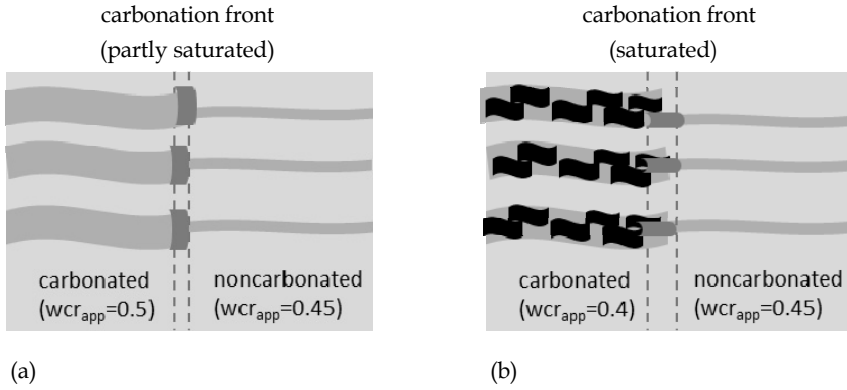


Figure 4: Schematized principle of the carbonation process

(a) increased capillary porosity due to carbonation shrinkage and improved transport of gasses for FAC and BFSC

(b) decreased capillary porosity due to the formation of calcium carbonate and hampered transport of gasses, most notably water vapour, in the carbonated zone for OPC.

The CO₂ concentration then decreases only over this very thin fully saturated layer in which the material has just previously been carbonated.

$$q = DA(c_{out} - c_{in}) \quad (7)$$

This first order approach thus is equal to Fick's law over a membrane, with c_{out} the CO₂ concentration at the outside of the water saturated layer, being thus equal to the surface CO₂ concentration, and c_{in} being equal to zero again. Since the amount of carbonatable matter remains the same, as is the condition for the movement of the front, equation (3) becomes instead

$$[DAc_s] = aA \frac{dx}{dt} \quad (8)$$

Solving this by integration results in

$$x_c = \text{Offset} + \frac{Dc_s t}{a} = \text{Offset} + \frac{c_s t}{R_{carb}} \quad (9)$$

If it is assumed that the mismatch between the AC and NC test for the fine OPC is due to the fact that in the AC test the fine OPC cannot dry out fast enough, Eq. 9 will apply for the AC test results of the fine OPC. Least square modelling of this equation to the AC-data of the fine OPC, results in a calculated carbonation resistance of $1.2 \cdot 10^{-2} \text{ (kg/m}^3\text{)/(mm}^2\text{/yr)}$. This value is the same as the value calculated for the natural carbonation test, see Table 2. This is a strong indication that indeed the drying out of the fine OPC in the AC-test is too slow for the AC-test to be applicable. However, the test can still be used, provided that the results are interpreted using a different model (Eq. 9) .

5 Conclusions

Accelerated testing of carbonation is only representative of the behaviour in reality if the processes of carbonation in the concrete are not changed. The square root t model that is usually applied for both natural carbonation tests and accelerated testing is found to be not always applicable. On the basis of the observed change in porosity in the thin sections and the results of the numerical modelling of Meier *et al.* [2006], it is speculated that the carbonation of very dense concrete with a high content in carbonatable matter may not follow the square root t behaviour. This is because there is so much water produced which needs to evaporate first before carbonation becomes possible and the carbonation front can move on. Since the porosity and pore sizes in the carbonated zone may be small, this can be a slow process compared to the diffusion of carbon dioxide into the concrete.

A simple analytical model has been derived taking as condition that the progress of the carbonation front is no longer the slowest step in the whole reaction process. Instead, it is the progress of the drying front. Therefore, the concentration of the CO_2 in the carbonated concrete is assumed constant and similar to the applied CO_2 -concentration. Consequently, the progress of the carbonation front can be described as linearly progressing.

The model has been applied to the results of a very fine Portland cement concrete for which the results of the accelerated carbonation test deviated from that of the natural carbonation test (according to the conventional model). Applying the new model to the accelerated test results gave a similar resistance against carbonation for the fine OPC as determined in the natural carbonation case where transport of CO_2 was the dominant step in the carbonation process. If the AC results would be interpreted following the conventional (square root of time) model, a far too high resistance in carbonation would

have been calculated, seriously overestimating the service life of this fine OPC concrete in structural applications.

Literature

- Al-Kadhimi, T.K.H., Banfill, P.F.G., Millard, S.G. and Bungey, J.H. 1996, 'An accelerated carbonation procedure for studies on concrete', *Adv.Cem.Res.* 30[8]: 47-59
- Arandigoyen, M. and Alvarez, J.I. 2006, Carbonation process in lime pastes with different water/binder ratio, *Mater.Construcc.* 56 [281]: 5-18 (ISSN 0465-2746)
- Bear, J. and Bachmat, Y. (1991), *Introduction To Modelling Of Porous Materials*, Kluwer Ac. Press
- Borges, P., Costa, J. *et al.* 2010 'Carbonation of CH and C-S-H in composite cement pastes containing high amounts of BFS', *Cem.&Concr.Res.* 40: 284-292
- Cerny, R. and Rovnanikova, P. 2002, *Transport Processes in Concrete*, Spon Press, London
- Castellote, M., Fernandez, L., Andrade, C. and Alonso, C. 2009, 'Chemical changes and phase analysis of OPC pastes carbonated at different CO₂ concentrations', *Mat&Struct.* 42: 515-525
- Glass, G.K. and Page, C.L. and Short, N.R. 1991, 'Factors affecting the corrosion rate of steel in carbonated concrete', *Corros.Sci.* 32: 1283-1294
- Maekawa, K. Ishida, T. and Kishi, T. 2003, Multi-scale modelling of concrete performance. Integrated material and structural mechanics, *J.Adv.Concr.Techn.* 1[2]: 91-126
- Meier, S.A., Peter, M.A., Muntean, A. and Bohm, M. 2007, 'Dynamics of the internal reaction layer arising during carbonation of concrete', *Chem.Engrg.Sc.* 62: 1125-1137
- Neville, A.M. 1993, *Properties of Concrete*, Pearson / Printice Hall
- Osterminski, K., Polder, R.B., Schiessl, P. 2012, "Long term electrical resistivity of concrete", *HERON*, Vol. 57 (2012) No. 3, pp. 211-230
- Peter, M.A., Muntean, A., Meier, S.A. and Bohm, M 2008, Competition of several carbonation reactions in concrete: a parametric study, *Cem&Concr.Res.* 38: 1385-1393
- Polder, R.B. 2012, Effects of slag and fly ash in concrete in chloride environment – Research from the Netherlands, *HERON*, Vol. 57 (2012) No. 3, pp. 197-210
- Sisomphon, K. and Franke, L. 2007, 'Carbonation rates of concretes containing high volume of pozzolanic materials', *Cem&Concr.Res.* 37: 1647-1653
- RILEM 1988, CPC 18: Measurement of hardened concrete carbonation depth, Rilem

- Thiery, M., Villian, G., Dangla, P. and Platret, G., 2007 'Investigation of the carbonation front shape on cementitious materials: effect of the chemical kinetics. *Cem&Concr.Res.* 37: 1047-1058
- Visser, J.H.M. and Polder, R.B. 2006, Concrete binder performance evaluation in service life. In: *Concrete Durability and Service Life Modelling* (eds. K. Kovler), pp. 330-340.

