

Accelerated carbonation: changes in water transport, porosity and phases of mortar due to different CO₂ pressures

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Abstract

Currently, the carbonation resistance of concrete is assessed on the basis of accelerated tests performed with high (unrealistic) CO₂ concentrations. It remains unclear whether these high concentrations reflect the processes occurring under natural conditions and enable the accurate prediction of field behaviour. To develop future test procedures with higher reliability, it is necessary to deepen the knowledge on the mechanisms of carbonation.

Thin slices of mortar were stored in a gaseous mixture of 2 % CO₂ and 98 % N₂ at atmospheric pressure or 5 bar. ¹H-NMR equipment was used to determine moisture profiles with a resolution of 0.2 mm. At 5 bar a drying front at the near-surface region of the mortar discs severely inhibited the progression of the carbonation reactions. This effect was prevented by exposure to alternating cycles of pressure and storage at atmospheric pressure (65%RH) which significantly increased the rate of carbonation, but was too severe to resolve the effect of cement type on carbonation resistance. Furthermore, the evolution of water beyond the carbonation front of mortar samples under accelerated concentration and at atmospheric pressure was clearly visible. This may lead to an overestimation of carbonation resistance of samples tested under accelerated conditions at the optimal relative humidity for natural carbonation (50 - 70% RH).

1 Introduction

The carbonation of concrete is a well-known phenomenon that has been intensively studied in the past, [1-8]. When CO₂ diffuses into the concrete structure, it dissolves and reacts with the phases of the hydrated binder C (*Cement notations: C = CaO, H = H₂O, S = SiO₂*), sulfate-containing phases (AFt and AFm) and C-S-H. Carbonation reactions lead to a decrease in pH and result in changes in the microstructure and the moisture content. The production of water by the carbonation reaction may reduce the available space for CO₂ diffusion [8]. In addition, it may be involved in moisture transport and promote the reaction of residual clinker [8].

It is well known that the decrease in pH produces a risk of corrosion. Therefore, knowledge of the carbonation rate is necessary to predict the durability of reinforced concrete structures. The carbonation rate can be determined by testing concrete specimens under natural conditions (0.03 to 0.07 vol.% CO₂) and determining the carbonation depth at different time intervals over several years. However, this procedure requires a very long time. To shorten the time for testing the carbonation process can be accelerated using increased CO₂ concentrations [9, 10].

Higher CO₂ concentrations lead to a higher carbonation rate than in natural conditions. However, the accelerated carbonation rate is generally significantly lower than the acceleration of the CO₂ concentration [9]. Hence, the carbonation resistance of samples tested under accelerated conditions may be overestimated compared to natural conditions.

The following reasons for this phenomenon are proposed in the literature [9].

- The moisture conditions in the pore structure and
- The different phase formation and pore structure produced by accelerated test methods

The carbonation reaction releases water changing the moisture condition of the pore structure and therefore reducing the carbonation rate. However, this effect has not yet been systematically investigated [9]. The accumulation of water could also lead to a change in the dependence of carbonation rate and ambient relative humidity so that the maximum carbonation rate occurs at a lower relative

humidity. Systematic investigations on the influence of moisture transport will be carried out in the course of this PhD thesis.

According to various authors (e.g. [11, 12]) carbonation at elevated CO₂ concentrations results in the carbonation of additional components of the hardened cement paste matrix. Thus, the pores of the cement paste at high CO₂ levels clog stronger than under natural conditions [9]. This might lead to a slower carbonation progress and consequently an overestimation of carbonation resistance. Castellote et al. [12] found that below a CO₂ concentration of about 3 vol.% the nanostructure of the C-S-H gel is preserved. Thus the chemical reactions occurring at these concentrations appear to be comparable to those under natural conditions. In this contribution, investigations with a CO₂ concentration of 2 vol.% are carried out in order to focus on the role of the moisture transport processes.

Besides the increase in CO₂ concentration, the transport of CO₂ can be accelerated by permeation of a gas mixture with natural or elevated CO₂ concentrations under pressure (“pressure carbonation”). Young et al. [13] found that with pure CO₂ gas, concrete carbonation was accelerated by increasing the pressure from 1 to 2 bar, but was not significantly changed by a further increase to 4 bar. According to a comparison of gas diffusion and permeation in concrete by Graef and Grube [14], the gas diffusion coefficient is $4 \cdot 10^{-8} \text{ m}^2/\text{s}$ for a concrete with a permeability coefficient of 10^{-16} m^2 . Increasing the air pressure on the concrete surface to 5 bar increases the diffusion of CO₂ by a factor of 10, but due to permeation, the CO₂ transport even increases by a factor 4000.

The present study investigates the effect of elevated CO₂ concentrations at elevated pressures on moisture transport and porosity of mortars during carbonation.

2 Materials and investigations

2.1 Materials

Two different mortars were used in the investigations. The mortars were designed using the concrete-equivalent-mortar method and based on a concrete (cement content = 280 kg/m³, w/c = 0.50) fulfilling the requirements of European standards for the exposure class XC3 (corrosion of the reinforcement induced by carbonation at moderate humidity). The compositions of the resulting mortars are shown in Table 1. Standard siliceous sand was used. Both mortars had a w/c ratio of 0.50. For the mortar M1 ordinary Portland cement (CEM I 42.5 R) was used while the mortar M3 contained blast-furnace slag cement (CEM III/B 42.5 N-LH/HS/NA).

Table 1 Mortar composition and characteristics

Name	Cement [kg/m ³]	Water [kg/m ³]	Sand [kg/m ³]	Air void content [vol.%]	Raw density [kg/m ³]	28 day compressive strength [MPa]
M1	551.6	275.8	1371.8	2.5	2234	55.8
M3	547.6	273.8	1360.5	2.9	2227	55.9

From each mixture cylinders (height = 300 mm, diameter = 36 mm) were prepared. The cylinders were demoulded after one day and then stored in a saturated Ca(OH)₂ solution for at least 1 year.

To minimize the effect of possible transport processes, 3 mm thick discs were cut from the cylinders. To minimize compaction effects, the first 15 mm of material at the ends of the cylinders were discarded. The mortar discs were stored in climate chambers at 20° C and 65 % RH in a CO₂-free atmosphere until the mass change after two consecutive measurements was below 0.1 wt.%. As mentioned in the first section, water is necessary to enable the carbonation reactions, while too much water limits the reaction due to pore clogging. Hence, a relative humidity of 50 – 70 % offers optimal carbonation conditions [8, 9].

2.2 Experimental procedures

After drying, the discs were exposed to accelerated carbonation at 2 vol.% CO₂ and 20°C in three different conditions:

- P_{atm} : atmospheric pressure and relative humidity of 65 %
- $P_{5,c}$: 5 bar constant pressure

- $P_{5,alt}$: alternating exposure, : 6 hours at 5 bar followed by 18 hours at atmospheric pressure in a CO₂-free atmosphere at 65 % RH.

Eight discs were used for each individual combination of composition and condition. The storage at atmospheric pressure were carried out in a the CO₂ incubator KPK 120 from Mytron. An autoclave Berghof HR – 28L was used for the studies at elevated pressure. After different time intervals the moisture profile was determined with single-sided nuclear magnetic resonance (NMR) and the carbonation depth measured using a pH indicator test. This pH indicator remains colourless at pH values below 8.3 and is pink-fuchsia at a pH above 10. While this test is quick, easy and cheap, it has the disadvantage that the total depth of pH reduction is not detected [9]. The NMR test method is described in detail in [15-17]. The Magritek PM25 single-sided NMR MOUSE was used. The measurements were carried out using the CPMG pulse sequence [18]. A resolution of 0.2 mm, a repetition time of 500 ms, 256 scans and 256 echoes were used.

To determine the porosity, MIP (*Mercury Intrusion Porosimetry*) measurements were performed using an AutoPore III from Micrometitics. Note that the small gel pores are not detected by MIP. The results of the porosity measurements are always below the total porosity as assessed using equation 1.

$$\pi_{dens} = \left(1 - \frac{\rho_{bulk}}{\rho_{matrix}}\right) 100 \quad [\text{vol.}\%] \quad (1)$$

The bulk density ρ_{bulk} was determined by weighing and the matrix density ρ_{matrix} was determined with the helium pycnometer AccuPyc 1330 by Micrometitics.

3 Results and discussion

The carbonation depths determined with a pH indicator test are shown in Fig. 1. As expected, the carbonation depth of the samples with blast-furnace slag cement ("M3") is significantly faster in samples subjected to constant pressure. This is due to the reduced clinker content and therefore lower content of CH in the hydration products compared with ordinary Portland cement.

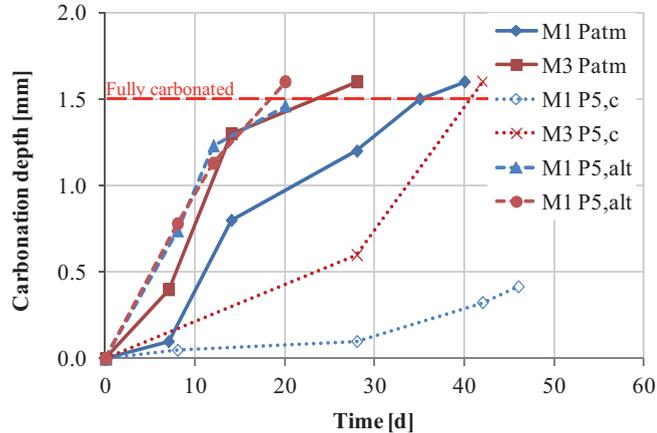


Fig. 1 Effect of storage conditions and cement type on evolution of carbonation depth at 2 vol.% CO₂. Continuous storage at atmospheric pressure, P_{atm} or at 5 bar, $P_{5,c}$. Alternating storage $P_{5,alt}$, cycles of 6 h at 5 bar and 18 hours atmospheric pressure 65 % RH and 0% CO₂

It is apparent that pressure affects the rate of carbonation decisively, irrespective of cement type, carbonation being slower at the higher pressure. The series M1 P5,c carbonates much slower than the samples M1 P_{atm}. While the samples M3 P5,c are completely carbonated after 42 days, the samples M1 P5,c are merely carbonated at the edge. Compared with the series with continuous CO₂ exposure at atmospheric pressure, subjecting samples to alternating cycles of pressurization and atmospheric pressure is an effective procedure to increase the carbonation progress. However, the carbonation depths for the samples made with Portland and blast-furnace slag cement indicate that this exposure cycle is so severe that all effects of mortar composition are completely suppressed.

The porosities measured with MIP π_{MIP} and helium pycnometry, calculated with Eq. (1), π_{dens} before and after accelerated carbonation at atmospheric pressure or 5 bar are shown in Table 2 for the

mortars with ordinary Portland cement (M1). Due to carbonation, the porosity decreased in all samples, the largest decrease occurring for 5 bar. The porosity determined by helium pycnometry is, as expected, generally higher than that determined by MIP. However, the difference in porosity determined by MIP and helium pycnometry for the samples subjected to 5 bar compared with the untreated samples is very small indicating a reduction in the amount of finer pores (< 2 nm diameter) during the carbonation reactions.

Table 2 Porosities (mean of two measurements) and change in porosity $\Delta\pi$ due to different exposures to 2 vol.% CO₂ at atmospheric pressure P_{atm} and 5 bar $P_{5,c}$

Sample	π_{MIP} [vol.%]	$\Delta\pi_{MIP}$ [vol.%]	π_{dens} [vol.%]	$\Delta\pi_{dens}$ [vol.%]
M1 before exposure	17.8	-	18.7	-
M1 P_{atm} 35d exposure	12.8	-5.0	14.2	-4.5
M1 $P_{5,c}$ 35d (partially carbonated)	11.3	-6.5	11.7	-7.0

Fig. 2 shows the water content profiles determined at different time intervals for the mortar with ordinary Portland cement. The near surface zones at the top and at the bottom of the samples (0-0.2 and 2.8 - 3.0 mm) were not considered, since experience has shown that large variations arise due to the rough and uneven surfaces.

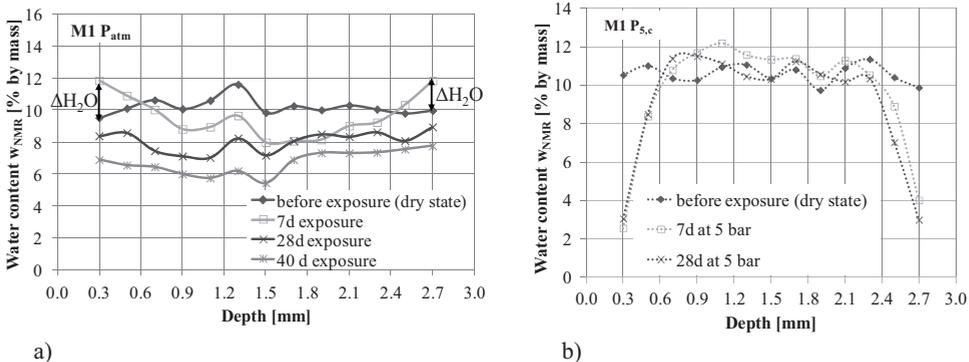


Fig. 2 Water content determined by single-sided NMR for ordinary Portland cement mortar samples before and after exposure to 2 vol.% CO₂ (a) at atmospheric pressure, P_{atm} , (b)

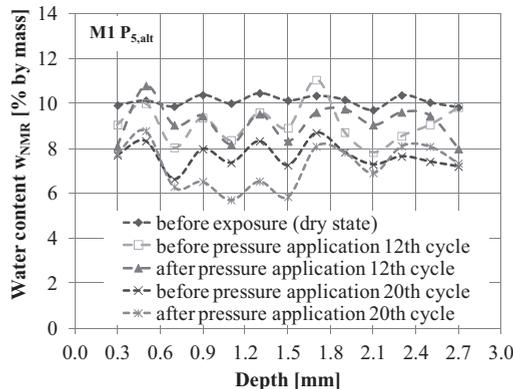


Fig. 3 Water content determined by single-sided NMR for ordinary Portland cement mortar samples before and after exposure to alternating exposure, 6 h at 5 bar and 2 vol.% CO₂ and 18 h at atmospheric pressure without CO₂, $P_{5,alt}$

Fig. 2a shows the moisture profiles of the samples that were exposed to accelerated carbonation at atmospheric pressure. After 7 days (carbonation depth with phenolphthalein approx. 0.1 mm), a higher water content is measured in the near surface region (0.3 and 2.7 mm). This clearly shows that water is released inside the specimens during carbonation. The overall water content then decreases during exposure and becomes, perhaps, somewhat flatter which is obviously due to drying and redistribution of moisture by water vapour diffusion. This suggests that the water formed during carbonation has already evaporated. At the same time the pore space is reduced by the carbonation reactions, so that fewer pores are present in which the equilibrium moisture condition is reached.

The moisture profiles of the series M1 P₅, c show a very low moisture content in the surface regions of the samples after 7 days and 28 days of continuous pressure application. Thus the samples are clearly dried by the permeation of the dry gas, leading to a lack of water for the carbonation reaction.

The moisture profiles for the samples M1 P_{5,alt} subjected to alternating carbonation are presented in Fig. 3. As expected, the carbonated areas show lower moisture contents, suggesting a denser material structure. The water content of the edge regions of the samples directly after applying gas pressure is slightly lower than before. Moreover, the sharp drying front as observed for the samples M1 P_{5,c} is not apparent. However, this exposure condition seems to completely suppress concrete technological effects. Hence, the exposure to alternating pressure cycles is in its current form not suitable for the evaluation of the carbonation resistance of mortars.

4 Conclusions and outlook

At present, accelerated carbonation tests are conducted at different CO₂ concentrations using different storage conditions of the specimens. Based on the results, the resistance against carbonation is assessed. If this carbonation resistance is a material property, it should relate to the carbonation of concrete in field conditions. However, this is not generally the case and there is therefore need for research to improve the transferability of results obtained under accelerated laboratory conditions to field exposure. Therefore, this contribution considers the effect of accelerated carbonation on the moisture transport and porosity of mortar.

Based on the present results, the following conclusions may be drawn:

- Single-sided NMR is a valuable tool to investigate moisture transport processes occurring during carbonation non-destructively.
- Accelerated carbonation (2 vol. % CO₂) at atmospheric pressure leads to an increase in moisture content beyond the carbonation front. This may lead to an overestimation of carbonation resistance of samples tested under accelerated conditions. Since the optimum relative humidity for carbonation under natural conditions is between 50 – 70 %, the relative humidity for carbonation under accelerated conditions could be lowered to compensate the formation of additional moisture in the pore system. Future work will focus on this aspect.
- The acceleration of carbonation by applying a dry gas pressure of 5 bar significantly reduces the amount of water for the carbonation reactions. The rate of carbonation can be increased by alternating the gas pressure application with storage at 65% RH and atmospheric pressure (0% CO₂). This provides moisture for the carbonation reactions and enhances CO₂ permeation. However, this cyclic method is so severe that the effect of mortar composition on the carbonation rate is suppressed. Further investigations with different times and pressures for the alternating cycles will be carried out.
- The present investigations with exposure at constant pressure as well as the observations in the literature indicates that there is an optimum pressure to accelerate carbonation between atmospheric pressure and 5 bar. Further investigations will be carried out in order to define this optimal pressure value.

5 Acknowledgements

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References

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