

# Carbonation of concrete: the role of CO<sub>2</sub> concentration, relative humidity and CO<sub>2</sub> buffer capacity

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**Abstract** In this study, the effect of CO<sub>2</sub> concentration and ambient relative humidity (RH) on accelerated and natural carbonation of 18 concrete mixtures produced with nine different cement types is investigated. Increasing the CO<sub>2</sub> concentration from 0.045 to 1 and 4 % at 57 % RH does not alter the relative carbonation resistance between the concrete mixtures. The increase of RH from 57 to 70 and 80 % RH at 4 % CO<sub>2</sub> shows a water-to-cement ratio and cement-specific effect that affects the relative carbonation resistance between the concrete mixtures. The carbonation resistance at 4 % CO<sub>2</sub> and 57 % RH allows assessing the carbonation resistance of concrete in sheltered and with restrictions in unsheltered outdoor exposure. The carbonation resistance below 70 % RH is mainly governed by the CO<sub>2</sub> buffer capacity. However, in the accelerated tests at 80 % RH and in the unsheltered outdoor exposure capillary condensation is of increased importance.

**Keywords** Carbonation · CO<sub>2</sub> concentration · Relative humidity · Blended cement · Concrete

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## 1 Introduction

The issue of concrete carbonation has gained importance in recent years due to the increased use of mineral additions in ordinary Portland cement-based systems. Usually, accelerated tests are used to assess the carbonation resistance of concrete. The CO<sub>2</sub> concentrations used in such tests can vary widely from 0.03 to 100 % and the relative humidity (RH) generally ranges from 50 to 65 % [1–8]. The relatively narrow range of RH is due to the fact that the progress of carbonation reaches a maximum at a RH of about 60 % [e.g. 1, 9]. However, RH outdoors is usually higher [10, 11], particularly in unsheltered exposure where rebar corrosion in reinforced concrete can be a problem [12, 13]. The relation between the conditions in the accelerated tests and natural exposure has to be known in order to transfer the results to concrete structures and assess their carbonation resistance.

Increasing the CO<sub>2</sub> concentration in accelerated tests can change both the porosity and the resulting phases compared to natural carbonation [14–18]. In general, carbonation leads to a decrease of total porosity [19–23]. The decrease of porosity increases with increasing CO<sub>2</sub> concentrations [17, 19]. In the case of cements blended with siliceous additions the decrease in porosity is less pronounced with increasing degree of cement clinker replacement and a significant coarsening of the pore size distribution may be observed [21–23]. During carbonation the portlandite is converted to CaCO<sub>3</sub> releasing water and the

calcium–silicate–hydrate (C–S–H) is decalcified leading to a phase with a lower Ca/Si-ratio [14, 18, 20, 22]. In a first step, C–S–H is gradually decalcified and in a second step, calcium from the principal layers is consumed leading to the formation of amorphous silica [24]. With increasing CO<sub>2</sub> concentrations the degree carbonation of the portlandite increases and the decalcification of the C–S–H is more pronounced [17, 19] leading to complete disappearance of C–S–H in case of 100 % CO<sub>2</sub> [18]. Moreover, the amount of the different CaCO<sub>3</sub> polymorphs calcite, vaterite and aragonite seem to be influenced as well by the CO<sub>2</sub> concentration, although the results of different studies differ [15–17, 25]. However, a CO<sub>2</sub> concentration of 3 % results in similar reaction products as formed in natural carbonation [18]. As such, employing a CO<sub>2</sub> concentration in this range seems to be appropriate for accelerated tests.

So far, different empirical and physical models and combinations of both allow to assess the carbonation resistance of cement-based materials [19, 26–30]. Based on CO<sub>2</sub> buffer capacity per volume of cement paste and the inclusion of additional parameters like for example the pressure of CO<sub>2</sub> and the CO<sub>2</sub> diffusion coefficient, the carbonation depth as a function of time can be modelled [19].

However, in a much simpler approach the mass ratio between the amount of water used for concrete production and the reactive or reacted CaO ( $w/\text{CaO}_{\text{reactive}}$  and  $w/\text{CaO}_{\text{reacted}}$ ) per cubic meter of concrete can be used to assess the carbonation resistance of cementitious materials [23]. This term expresses the CO<sub>2</sub> buffer capacity per volume of cement paste and, as it is a mass ratio between water and solid, additionally contains information about porosity and microstructure. It shows a good correlation to the carbonation resistance of mortar and concrete produced with different cement types, water-to-cement ratios ( $w/c$ ) and paste volumes exposed to accelerated carbonation and to natural carbonation in sheltered conditions [23]. As such, it offers a simple approach for concrete producers to assess the influence of concrete mix design on the carbonation resistance. However, at a RH > 70 %, capillary condensation as an additional parameter seems to have a pore size-dependent and with it a cement-specific influence on carbonation resistance [23]. Cementitious materials with a relatively high amount of fine pores have a higher pore volume filled

with water due to condensation than a material with a coarser pore structure at identical RH [26, 31, 32]. As a result, carbonation of a mortar or concrete with a high amount of fine pores is slowed down more at a certain increase of RH than carbonation of mortar or concrete with a high amount of coarse pores [23]. As a result, the increase of RH may lead to a lower correlation coefficient between  $w/\text{CaO}$  and carbonation resistance. Moreover, accelerated carbonation performed at RH < 70 % may underestimate the carbonation resistance of concrete mixtures with very fine pore systems exposed to high RH at unsheltered outdoor exposure [23]. Consequently, more data about the cement-specific behavior as a function of the ambient RH are needed. Here, it has to be pointed out that rebar corrosion in carbonated concrete is usually only a problem at the high RH level characteristic of unsheltered exposure [12, 13].

The goals of this study are to investigate the influence of CO<sub>2</sub> concentration, ambient RH and CO<sub>2</sub> buffer capacity on accelerated and natural carbonation of concrete produced with different cement types. It expands the experimental matrix used in [23]. 18 concrete mixtures produced with nine different cement types are investigated. The influence of CO<sub>2</sub>-concentration is studied at three different CO<sub>2</sub> levels (0.045, 1.0 and 4.0 %) and constant RH of 57 %. The influence of RH is investigated at three different levels (57 %, 70 %, 80 %) and constant CO<sub>2</sub>-concentration of 4 %. Carbonation coefficients in sheltered and unsheltered conditions are determined after an exposure of 2 years to link the accelerated test to natural carbonation. Moreover, compressive strength and oxygen diffusion are measured.

## 2 Materials and methods

### 2.1 Materials

The different cements used are shown in Table 1. Besides two ordinary Portland cements (OPC A and B), one blended with limestone powder (L30) and others blended with siliceous additions including ground granulated blast-furnace slag (GGBS/S22, S45, S66), microsilica (MS8) and fly ash (FA25, FA35) were used resulting in different CaO contents of the cements. Two concrete mixtures with a  $w/c$  of 0.40 (cement content of 380 kg/m<sup>3</sup>) and 0.65 (cement



**Table 1** Chemical composition and density of the cements

Cement type	Name	Mass%												$\rho$ (g/cm <sup>3</sup> )
		CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	LOI	
CEM I 52.5 N	OPC A	64.24	20.69	5.08	1.9	3.63	1.03	0.53	0.36	0.29	0.06	0.171	1.69	3.14
CEM I 52,5 R	OPC B	59.59	19.21	4.54	2.51	3.05	3.97	0.836	0.386	0.25	0.07	0.174	4.74	3.16
CEM II/B-S 42-5R	S22	59.03	25.01	6.47	1.62	3.15	2.71	0.605	0.397	0.42	0.13	0.132	0.35	3.13
CEM III/A 42.5 N	S45	53.74	27.09	6.92	1.27	4.00	4.43	0.67	0.41	0.59	0.12	0.107	0.70	3.05
CEM III/B 42,5	S66	47.31	31.86	8.35	0.82	3.58	6.59	0.75	0.44	0.79	0.15	0.061	0.35	2.99
CEM II/A-D 52.5 N	MS8	59.12	26.67	4.71	1.76	3.35	0.98	0.54	0.35	0.26	0.05	0.16	1.71	3.07
CEM II/B-LL 32.5R	L30	55.59	18.51	4.28	2.68	2.55	4.00	0.74	0.346	0.22	0.07	0.178	11.08	3.10
CEM IV/A 32,5 R	FA25	47.43	26.25	9.36	3.37	3.22	3.56	0.875	0.409	0.53	0.06	0.165	4.64	2.92
CEM IV/B 32,5 R	FA35	41.62	29.52	11.87	3.74	2.86	3.20	0.90	0.44	0.68	0.06	0.18	4.75	2.83

content of 280 kg/m<sup>3</sup>) were produced with each cement type (Table 2). As aggregates, alluvial sand containing a mixture of sandstones, limestone, siliceous limestone and gneiss and crushed gravel of the same lithology were used. The aggregate grading for the concrete with a  $w/c$  of 0.65 was 52 mass% 0/4 mm, 18 mass% 4/8 mm, 17 mass% 8/16 mm and 13 mass% 16/32 mm. For the concrete with a  $w/c$  of 0.40, the amount of 0/4 mm and 8/16 mm were changed to 47 and 22 mass%.

The concrete components were stored at  $20 \pm 1.5$  °C, the same temperature at which concrete production took place. Cement and dry aggregates were premixed and then 90 % of the mixing water was added. The rest of the mixing water was poured into the mixer together with the admixtures. The concrete was mixed for 90 s in a pan-type Eirich mixer.

A first set of samples was produced to determine carbonation resistance. The concrete prisms ( $120 \times 120 \times 360$  mm<sup>3</sup>) were demolded after 24 h and then stored in water for 48 h. Afterwards they were preconditioned at 20 °C and 57 % RH until 28 days of age. In the following, one prism per concrete mixture was stored in the lab exposed to CO<sub>2</sub> concentrations of 0.045 (only selected samples), 1 and 4 % at 20 °C and 57 % RH. Two further samples were stored outdoors in sheltered and unsheltered exposure. The sheltered exposure took place in a room, where the removed door allowed constant air circulation. The prisms in unsheltered conditions were stored on a roof, where they were placed on aluminum profiles to

prevent capillary suction from the roof. The average of temperature, RH and precipitation during the first year of outdoor exposure with the minima and maxima of the monthly average in parenthesis are 10.0 °C (3.1–21.5 °C), 75.5 % (64.2–83.5 %) and 76 mm (23–165 mm).

A second set of prisms was produced to investigate the influence of RH on accelerated carbonation. Production and curing until 28 days was identical to the first set of samples. Afterwards, one prism per mixture was exposed to 4 % CO<sub>2</sub> at 57, 70 and 80 % RH.

Five concrete cubes ( $150 \times 150 \times 150$  mm<sup>3</sup>) produced within the first set of samples were stored in identical conditions as the prisms used for carbonation until 28 days. Then three cores (diameter of 100 mm, height of 50 mm) were taken from two cubes to determine the oxygen diffusivity. They were conditioned at  $20 \pm 1$  °C and  $35 \pm 2$  % RH for 7 days and then dried in an oven at 50 °C for 7 days before the measurement started. The mass change during conditioning was recorded to obtain information about the drying behavior of the different concrete mixtures. Three cubes were used for compressive strength measurements at 2, 28 and 91 days. They were stored at 20 °C and >95 % RH until testing.

## 2.2 Methods

The protocol for the determination of the carbonation coefficient  $K$  is based on SN 505 262/1 [33].



**Table 2** Mix design of the concrete

Concrete/ cement (–)	Aggregate (kg/m <sup>3</sup> )	$m_{s/g}$ (–)	Cement (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	$w/c$ (–)	SP <sup>a</sup> (kg/m <sup>3</sup> )	CaO <sub>reactive</sub> (kg/m <sup>3</sup> )	CaO <sub>reacted,ACC</sub> <sup>b</sup> (kg/m <sup>3</sup> )	CaO <sub>reacted,US/S</sub> <sup>c</sup> (kg/m <sup>3</sup> )
OPC A	1906	1.06	280	182	0.65	1.4	176	142 (81 %) <sup>d</sup>	158 (90 %) <sup>d</sup>
OPC A	1901	0.90	380	152	0.40	4.1	238	171 (72 %)	183 (77 %)
OPC B	1907	1.06	280	182	0.65	1.1	159	129 (81 %)	143 (90 %)
OPC B	1903	0.90	380	152	0.40	5.2	216	155 (72 %)	166 (77 %)
S22	1905	1.06	280	182	0.65	0.4	165	124 (81 %, 41 %)	142 (90 %, 60 %)
S22	1900	0.90	380	152	0.40	3.8	223	150 (72 %, 36 %)	165 (77 %, 51 %)
S45	1899	1.06	280	182	0.65	0.0	147	99 (81 %, 41 %)	117 (90 %, 60 %)
S45	1891	0.90	380	152	0.40	3.0	200	120 (72 %, 36 %)	143 (77 %, 51 %)
S66	1894	1.06	280	182	0.65	2.8	129	75 (81 %, 41 %)	95 (90 %, 60 %)
S66	1885	0.90	380	152	0.40	2.3	176	91 (72 %, 36 %)	110 (77 %, 51 %)
MS8	1900	1.06	280	182	0.65	1.4	161	131 (81 %, 41 %)	145 (90 %)
MS8	1894	0.90	380	152	0.40	3.4	219	158 (72 %, 36 %)	169 (77 %)
L30	1903	1.06	280	182	0.65	0.3	126	102 (81 %, 41 %)	113 (90 %)
L30	1897	0.90	380	152	0.40	2.3	171	123 (72 %, 36 %)	132 (77 %)
FA25	1888	1.06	280	182	0.65	0.6	127	102 (81 %, 41 %)	114 (90 %)
FA25	1877	0.90	380	152	0.40	4.2	172	124 (72 %, 36 %)	132 (77 %)
FA35	1880	1.06	280	182	0.65	0.9	110	90 (81 %, 41 %)	99 (90 %)
FA35	1866	0.90	380	152	0.40	4.9	149	108 (72 %, 36 %)	115 (77 %)

$m_{s/g}$  mass ratio between sand and gravel

<sup>a</sup> Superplasticizer

<sup>b</sup> Reacted CaO of concrete exposed to accelerated carbonation

<sup>c</sup> Reacted CaO of concrete exposed to natural carbonation

<sup>d</sup> Assumed degree of hydration for cement clinker (first number in parenthesis) and GGBS (second number in parenthesis)

According to this standard, a CO<sub>2</sub> concentration of 4 % is to be used. This is close to 3 % CO<sub>2</sub> that results in similar phases during carbonation as natural carbonation [18]. Because a concentration of 4 % is close to 3 %, the former seems to be a reasonable CO<sub>2</sub> concentration for testing accelerated carbonation. Before moving the concrete prisms to the different exposure conditions at the age of 28 days, the initial carbonation depth was determined. An approximately 50 mm thick slice was split off from the prisms. Phenolphthalein was used to spray the freshly-broken surface. The carbonation depth was measured on five points per side, resulting in 20 measurements per age and prism. Afterwards, the carbonation depth of the samples stored in carbonation chambers was measured after an exposure of 7, 28, 63 and additionally of 126 days for the concrete exposed to 70 and 80 % RH. The carbonation depth of the concrete exposed outdoors was determined after an exposure of 2 years using the same technique

as for the samples stored in the carbonation chambers. The carbonation coefficient  $K$  was determined by calculating the regression of the carbonation depth as a function of the square root of time (Eq. 1):

$$K = \frac{(d_K - A)}{\sqrt{t}} \quad (1)$$

where  $K$  is the carbonation coefficient in mm/ $\sqrt{y}$ ,  $d_K$  the carbonation depth in mm,  $A$  the initial carbonation depth in mm after curing and  $t$  the time in years.

In regard to natural exposure, specimens of all concrete mixtures were exposed at two different sites in sheltered and unsheltered exposure resulting in very similar values with a correlation coefficient of  $R^2 = 0.90$  in the case of sheltered and  $R^2 = 0.97$  in case of unsheltered exposure. In the following, only the data from one of the sites are presented.

Based on the variation of the carbonation depth in the specimens, the standard error of the carbonation coefficient  $K$  has been calculated. The following



**Table 3** Results of the concrete (production set 1, see Table 4)

Concrete/cement	w/c (–)	Flow (cm)	$f_{c,2}$ (MPa)	$f_{c,28}$ (MPa)	$f_{c,91}$ (MPa)	$D_O$ ( $10^{-8}$ m/s <sup>2</sup> )
OPC A	0.65	51	18.0	37.6	43.5	2.80
OPC A	0.40	46	47.0	75.6	84.8	0.92
OPC B	0.65	45	26.0	46.5	50.8	2.58
OPC B	0.40	32	58.2	83.8	94.1	0.64
S22	0.65	46	16.4	38.8	47.4	1.08
S22	0.40	47	44.4	83.9	92.7	0.37
S45	0.65	49	11.6	36.0	44.7	0.76
S45	0.40	53	28.4	69.1	78.5	0.36
S66	0.65	48	6.4	31.5	39.9	0.43
S66	0.40	44	19.5	65.8	72.2	0.09
MS8	0.65	49	17.1	44.5	50.1	0.80
MS8	0.40	43	43.7	84.5	92.8	0.18
L30	0.65	45	12.0	25.5	28.9	4.88
L30	0.40	48	28.5	47.5	55.0	1.35
FA25	0.65	48	10.9	26.3	33.6	2.12
FA25	0.40	31	35.0	62.6	77.4	0.46
FA35	0.65	47	10.0	28.0	34.4	0.97
FA35	0.40	46	30.0	66.7	78.3	0.23

$f_{c,X}$  compressive strength after  $X$  days,  $D_O$  oxygen diffusion coefficient after 28 days

standard errors are given as an example for the range carbonation coefficients  $K$  presented in the paper:  $4.5 \pm 0.3$ ,  $22.7 \pm 0.7$  and  $55.3 \pm 1.8$  mm/ $\sqrt{y}$ . In a Round Robin test with 18 participating laboratories the carbonation coefficient  $K$  was between 1.49 and 6.70 mm/ $\sqrt{y}$  and the coefficients of repeatability and comparability showed a range of 2.2–10.1 % and 8.8–19.5 %, respectively [34].

A thermogravimetric analysis of the amount of calcite formed in the cement paste of the different concrete mixtures during carbonation as for example performed by [14, 22, 35] was not possible due to the limestone present in the aggregates. However, the calculation of the  $CaO_{\text{reactive}}$  and the assessment of the  $CaO_{\text{reacted}}$  (Table 2) as described and discussed in paragraph 3.7 allows an estimation of the  $CaO$  available for carbonation.

The oxygen diffusion coefficient  $D_O$  was determined as described in [36–38] on three cores (diameter of 100 mm, height of 50 mm). An oxygen flow was applied on one side of the cores and a nitrogen flow on the other side, with identical gas pressure on both sides. The oxygen content in the nitrogen flow was determined until equilibrium was reached.

Afterwards, the oxygen diffusion coefficient  $D_O$  was calculated according to [36].

The compressive strength of the the concrete cubes was measured according to EN 12390-3 [39].

### 3 Results

#### 3.1 Overview of the results

Concrete strength development and strength at 28 days both depend on cement type (Table 3). The cement types OPC A, OPC B, S22 and MS8 with the highest clinker content reach the highest strength at 2 and 28 days. The lowest values are shown by concrete L30.

The concrete produced with cement containing siliceous mineral additions exhibits lower oxygen diffusion coefficients  $D_O$  than concrete OPC (Table 3). Concrete S66 reaches the lowest values, while the use of limestone powder in the case of concrete L30 results in the highest oxygen diffusivity of all mixtures.

The carbonation results (Table 4) are described and discussed in detail in the following paragraphs.

**Table 4** Carbonation coefficients of the concrete production sets 1 and 2

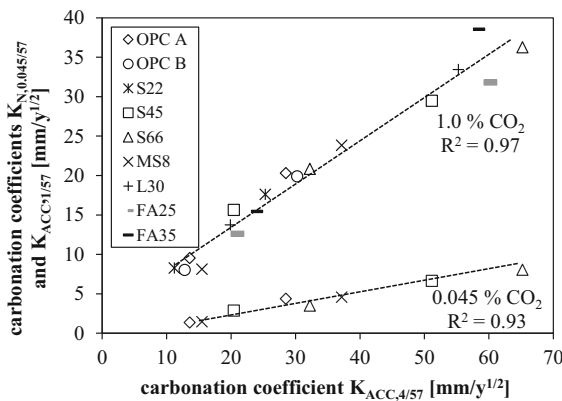
Concrete/cement	w/c (–)	First production set (mm/ $\sqrt{y}$ )					Second production set (mm/ $\sqrt{y}$ )		
		$K_{ACC,4/57}$	$K_{ACC,1/57}$	$K_{ACC,0.045/57}$	$K_{N,US}$	$K_{N,S}$	$K_{ACC,4/57}$	$K_{ACC,4/70}$	$K_{ACC,4/80}$
OPC A	0.65	28.5	20.3	4.4	1.6	4.5	30.1	22.2	11.0
OPC A	0.40	13.6	9.5	1.4	0.1	0.4	15.6	6.4	0.2
OPC B	0.65	30.3	19.9	–	2.0	4.4	27.5	20.4	9.4
OPC B	0.40	12.8	8.0	–	0.4	0.6	10.6	3.5	0.1
S22	0.65	25.3	17.6	–	2.8	4.4	31.3	25.0	11.7
S22	0.40	11.2	8.3	–	0.5	0.9	9.9	4.4	0.2
S45	0.65	51.2	29.5	6.6	2.6	6.8	49.4	43.9	23.3
S45	0.40	20.4	15.6	2.9	0.4	2.6	20.1	12.8	2.3
S66	0.65	65.2	36.3	8.0	4.2	8.3	57.7	53.0	29.3
S66	0.40	32.2	20.8	3.5	1.2	3.2	24.3	17.4	1.4
MS8	0.65	37.2	23.8	4.6	1.9	5.0	32.6	22.9	8.7
MS8	0.40	15.5	8.1	1.5	0.3	0.9	11.1	1.3	0.6
L30	0.65	55.3	33.4	–	3.7	6.9	71.0	69.9	53.2
L30	0.40	19.9	13.7	–	1.1	1.7	30.6	22.5	5.3
FA25	0.65	59.2	31.8	–	3.2	8.0	59.5	48.0	37.8
FA25	0.40	20.0	12.6	–	0.4	2.4	21.5	15.6	2.1
FA35	0.65	58.5	38.6	–	2.8	7.2	62.4	56.8	43.3
FA35	0.40	24.0	15.4	–	0.7	2.9	26.8	19.2	2.6

$K_{ACC,XY}$  coefficient of accelerated carbonation with  $X = CO_2$  content and  $Y = RH$  both given in %,  $K_N$  coefficient of natural carbonation in sheltered (S) and unsheltered (US) conditions

### 3.2 Influence of $CO_2$ concentration on carbonation

There is a linear relationship of the carbonation coefficients  $K_{ACC}$  determined at the different  $CO_2$  concentrations (Fig. 1). The carbonation coefficient

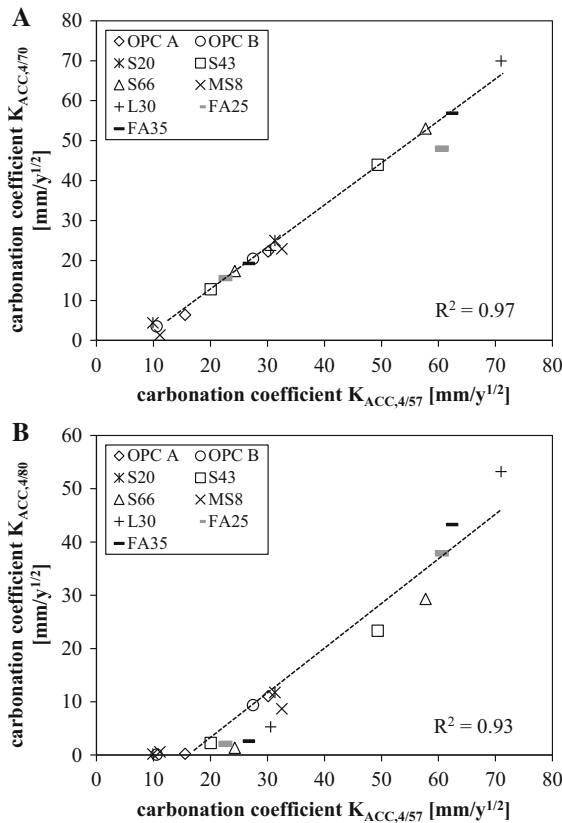
$K_{ACC}$  decreases with decreasing  $CO_2$  concentration. The gradient of the linear regression of all data points in Fig. 1 of 0.61 (A) and 0.12 (B) corresponds approximately to the square root of the quotient of the  $CO_2$  concentrations used in the accelerated tests agreeing with other studies [1, 12].



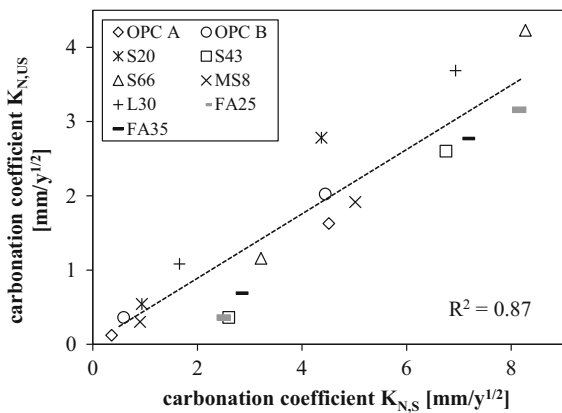
**Fig. 1** Carbonation coefficient  $K_{ACC}$  at 1 %  $CO_2$  (higher values) and  $K_{ACC}$  at 0.045 %  $CO_2$  (lower values) both at 57 % RH as a function of the carbonation coefficient  $K_{ACC}$  at 4 %  $CO_2$  and 57 % RH

### 3.3 Influence of relative humidity on carbonation

The carbonation coefficient  $K_{ACC}$  decreases with increasing RH (Fig. 2). While the decrease is moderate going from 57 to 70 % RH (Fig. 2a), it is very pronounced at 80 % RH (Fig. 2b). The decrease is more pronounced for the concrete with a low w/c of 0.40 and low carbonation coefficients  $K_{ACC,4/57}$  than for the concrete with a high w/c of 0.65 and high carbonation coefficients  $K_{ACC,4/57}$  (Fig. 2b). The carbonation coefficient  $K_{ACC}$  of concrete S45, S66, FA25 and FA35 with a w/c of 0.40 decreases close to the level of concrete OPC A, OPC B and MS8, whose carbonation coefficients  $K_{ACC}$  are in comparison considerably smaller at 57 % RH. On the other hand, concrete L30, FA25 and FA35 with a w/c of 0.65

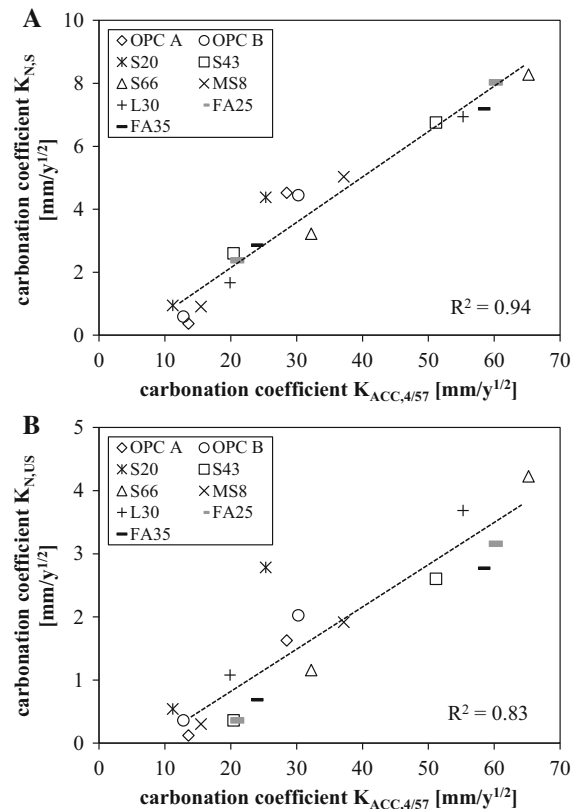


**Fig. 2** Carbonation coefficient  $K_{ACC}$  at 70 %  $CO_2$  (a) and  $K_{ACC}$  at 80 % RH (b) as a function of the carbonation coefficient  $K_{ACC}$  at 57 % RH at 4 %  $CO_2$



**Fig. 3** Carbonation coefficient  $K_N$  at unsheltered (US) and sheltered (S) exposure

remain nearly unchanged going from 57 to 70 % RH and show a smaller decrease than concrete OPC at 80 % RH.



**Fig. 4** Carbonation coefficient  $K_N$  in sheltered (a) and  $K_N$  in unsheltered exposure (b) as a function of the carbonation coefficient  $K_{ACC}$  at 57 % RH at 4 %  $CO_2$

### 3.4 Natural carbonation

The carbonation coefficient  $K_N$  is approximately 2.5 times lower in the unsheltered exposure compared to the sheltered one (Fig. 3). No systematic change compared to concrete OPC in regard to cement type or  $w/c$  is evident going from the sheltered to the unsheltered exposure.

### 3.5 Accelerated carbonation compared to natural carbonation

The correlation between carbonation coefficient  $K_{ACC,4/57}$  and carbonation coefficient  $K_{N,S}$  is excellent ( $R^2 = 0.94$ /Fig. 4a). The gradient of the linear regression for concrete OPC is slightly higher compared to the other concrete mixtures. This applies as well to the comparison of carbonation coefficients  $K_{ACC,4/57}$  and  $K_{N,US}$  (Fig. 4b/ $R^2 = 0.83$ ). The correlation of carbonation coefficients  $K_{N,S}$  and  $K_{N,US}$  with  $K_{ACC}$  is the



highest at 57 % RH and decreases with increasing RH to 70 % ( $R^2 = 0.83$  and  $0.82$ ) and to 80 % RH ( $R^2 = 0.74$  and  $0.72$ ).

### 3.6 Relation of carbonation with other concrete properties

There is a relatively good correlation between concrete compressive strength and the carbonation coefficient  $K_{ACC,4/57}$  ( $R^2 = 0.73$ /Fig. 5). This seems to apply in particular for a compressive strength higher than 40 MPa. However, between 32 and 39 MPa there can be a difference in the carbonation coefficient  $K_{ACC,4/57}$  by a factor of 2.5 (concrete OPC A and S66).

Both oxygen diffusion coefficient  $D_O$  and carbonation coefficient  $K_{ACC,4/57}$  increase with increasing  $w/c$  (Tables 3 and 4). However, there is no correlation between the two parameters ( $R^2 = 0.13$  (not shown)).

## 4 Discussion

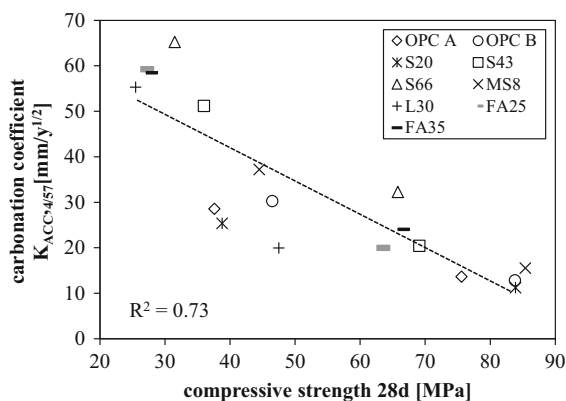
### 4.1 Influence of $CO_2$ concentration on carbonation

The changes in the ranking of the concrete in regard to its carbonation resistance going from 4 to 1 and 0.045 %  $CO_2$  are only minor (Fig. 1). This indicates that  $CO_2$  concentrations up to 4 % are suitable for ranking the carbonation resistance of concrete produced with different cement types and  $w/c$ . As already discussed in the introduction the chosen  $CO_2$  concentration influences the resulting porosity, phases

formed and degree of carbonation [14–25]. Even, when the resulting microstructure and products formed due to carbonation at low  $CO_2$  concentrations of 0.03 and 3 % are very similar [18], it cannot be excluded that an increase to 4 % changes this situation. Nevertheless, it is clear from the presented data that an increase from 1 to 4 %  $CO_2$  has little effect on the ranking of the concrete mixtures.

### 4.2 Influence of relative humidity on carbonation

The carbonation coefficients determined at the different RH of 57, 70 and 80 % clearly indicate that the response of a concrete to carbonation at increased RH is both dependent on cement type and  $w/c$ . The reason for this behavior is likely caused by capillary condensation. As total porosity and pore size decrease with decreasing  $w/c$  [40, 41], the percentage of pores filled with water due to capillary condensation, which slows down carbonation, is higher for the concrete with low  $w/c$  [26, 31, 32]. Additionally, the pore size distribution at a given  $w/c$  is cement-specific. Mortar and concrete with siliceous additions like GGBS and pozzolans result in a higher amount of fine pores [23, 42–45] and with it a higher percentage of pores filled with capillary condensed and adsorbed water at a given RH [46, 47]. Consequently, the concrete containing siliceous additions used in this study is expected to show a more pronounced decrease of the carbonation coefficient  $K_{ACC}$  at 80 % RH than concrete OPC. This applies in the case of the lower  $w/c$  as indicated by concrete S45, S66, FA25 and FA35, but is not supported by the concrete produced with the higher  $w/c$ . There, the concrete with siliceous additions shows either a comparable behavior as concrete OPC or even a smaller reduction of carbonation coefficient  $K_{ACC}$ . A possible reason for this behavior is the short duration of curing of only 3 days and subsequent exposure to 57 % RH. Concrete produced with slow hydrating siliceous additions dries faster than a pure OPC [10, 48]. The drying affects hydration and results in a higher porosity and coarser pore structure compared to concrete with longer curing [49]. Moreover, the air permeability of cement paste containing GGBS is increased more than the one of concrete produced with OPC with a shortening of curing time [50]. As a result, the short curing may have had a stronger influence on the concrete with siliceous additions and high  $w/c$  than on the other mixtures,



**Fig. 5** Carbonation coefficient  $K_{ACC,4/57}$  as a function of compressive strength





resulting in a relatively coarse pore system and less pronounced effect of capillary condensation on carbonation at high RH. In any case, the wide range of cement types and  $w/c$  used for the experimental matrix in combination with the short curing makes it difficult to distinguish between the effects of hydration, pore structure and capillary condensation on the carbonation at different RH.

#### 4.3 Accelerated carbonation compared to natural carbonation

The decreasing correlation of carbonation coefficients  $K_{N,S}$  and  $K_{N,US}$  with the carbonation coefficients  $K_{ACC}$  at increasing RH is surprising, as 70 and 80 % RH are closer to natural conditions than 57 % RH. The major reason has to be the difference between constant RH and dynamic conditions as present in natural exposure. In the latter not only capillary condensation, but also capillary suction (unsheltered exposure), drying and the kinetics of these processes are additionally involved. The lowest and highest monthly average of RH during the first year of outdoor exposure are 64 and 87 % RH, as recorded by the meteorological station located only 50 meters away from the exposure site [23]. The daily minima can go down to 30 % RH and the maxima to 100 % RH due to fog or rain. As such, the specimens stored in natural exposure were exposed to periods that are more favorable for carbonation than constant 80 % RH at accelerated carbonation. This is confirmed by the carbonation coefficients  $K_{ACC,4/80}$  of the concrete mixtures, with the lowest values that are in the same order of magnitude as the carbonation coefficients  $K_{N,US}$  of the corresponding concrete mixtures despite the much higher  $CO_2$  concentrations in accelerated conditions. Apparently, an increased RH in accelerated tests is not able to improve the comparability and transferability of the results to natural conditions. In spite of this, the correlation between the carbonation coefficients  $K$  determined in accelerated and natural conditions remains reasonable. In principle, an assessment of the carbonation resistance of concrete in natural conditions by the accelerated test performed at 4 %  $CO_2$  and 57 % RH seems possible. However, it has to be pointed out that this applies to the curing regime as performed in this study. If longer curing is used, concrete produced with siliceous additions seems to be more affected by the increase RH in natural exposure [23]. This can result

in a better performance of such concrete in natural conditions than indicated by the accelerated test.

#### 4.4 Relation of carbonation with other concrete properties

Compressive strength and carbonation are dependent on microstructure, total porosity and as such the amount of hydrates formed resulting in a certain correlation between these two parameters.

It is evident that the oxygen diffusivity has no direct relation to the carbonation resistance confirming the results of [23]. However, it has to be taken into account that this refers to the diffusivity of oxygen. The diffusion coefficient of  $CO_2$  is about ten times lower than the one of oxygen in OPC mortars [51]. So far, to the authors' knowledge, no  $CO_2$  diffusion coefficients of mortar or concrete produced with different cement types have been published. As such, the relation between  $O_2$  and  $CO_2$  diffusion coefficients in concrete produced with different cement types and  $w/c$  is unknown.

#### 4.5 Relation of carbonation with $CO_2$ buffer capacity

The carbonation coefficient  $K$  of mortar and concrete produced with different cement types is mainly governed by the  $CO_2$  buffer or binding capacity per volume of the cement paste [23]. The CaO present in the hydrates will be transferred into  $CaCO_3$  upon carbonation. Because the degree of hydration in a concrete is usually not known, the entire reactive CaO in a binder can be taken into account assuming complete hydration. The buffer capacity per volume of cement paste can be taken into account by the  $w/CaO_{reactive}$ . As the term is a mass ratio between water and solid, it additionally contains information about porosity and microstructure. As a mass ratio the  $w/CaO_{reactive}$  is independent of the cement paste volume per cubic meter of concrete and independent of the total cement content per cubic meter of concrete. If only the CaO that already has reacted and is part of hydrates is considered, the buffer capacity is expressed as  $w/CaO_{reacted}$ . This requires an assessment of the degree of hydration. The degree of hydration depends on curing [1, 52–55] and likely, there is gradient in the degree of hydration as a function of depth from the concrete surface as pointed out in [23]. Moreover, the



degree of hydration can change during exposure [55], if the environment provides sufficient moisture. For the cements used in this project, the chemical analysis provides the amount of CaO in the cements (Table 1) and the Rietveld analysis (not shown) quantifies the amount of limestone present. The amount of CaO in the limestone has to be subtracted from the total CaO content as only a small part of it participates in the formation of monocarbonate [56]. The degree of hydration is assessed taking into account the data published in literature on pure and blended Portland cements [57–61]. The degree of cement clinker hydration increases with increasing  $w/c$  [57]. GGBS hydrates slower and to a lesser degree than cement clinker [58, 60], but the difference in degree of hydration compared to cement clinker decreases with ongoing hydration and time [58, 61]. However, the hydration behavior of different batches of GGBS can differ significantly depending on their composition [59, 61]. The main purpose to assess the  $w/\text{CaO}_{\text{reacted}}$  is to take into account that the CaO present in the GGBS is available for carbonation to a lesser extent than the CaO present in cement clinker due to the differences in degree of hydration. All the concrete samples were exposed to the same curing conditions until the age of 28 days. It can be expected that the degree of hydration does not change significantly in the samples exposed to 57 % RH after pre-conditioning. Although, the storage in the carbonation chamber at 70 and 80 % RH for 126 days must have resulted in further hydration, the  $w/\text{CaO}_{\text{reacted}}$  was kept constant for all accelerated tests to simplify the comparison. However, for the exposure in sheltered and unsheltered outdoors conditions an increased degree of hydration of the cement clinker and of the GGBS was assumed, due to the relatively high RH and the duration of exposure of 2 years (Table 2). Again, no distinction in the degree of hydration between sheltered and unsheltered outdoor exposure were made to keep the approach relatively simple.

The degree of hydration for the cement clinker in the acceleration chamber was assumed to be 72 % for a  $w/c$  of 0.40 and 81 % for a  $w/c$  of 0.65. The assumed degree of GGBS hydration was lower by a factor of 2 than the one of the cement clinker. At a  $w/c$  of 0.40 and 0.65 a cement clinker hydration of 77 and 90 % were assumed for the natural exposure. The degree of hydration of GGBS was calculated as being 1.5 times lower taking into account the higher degree

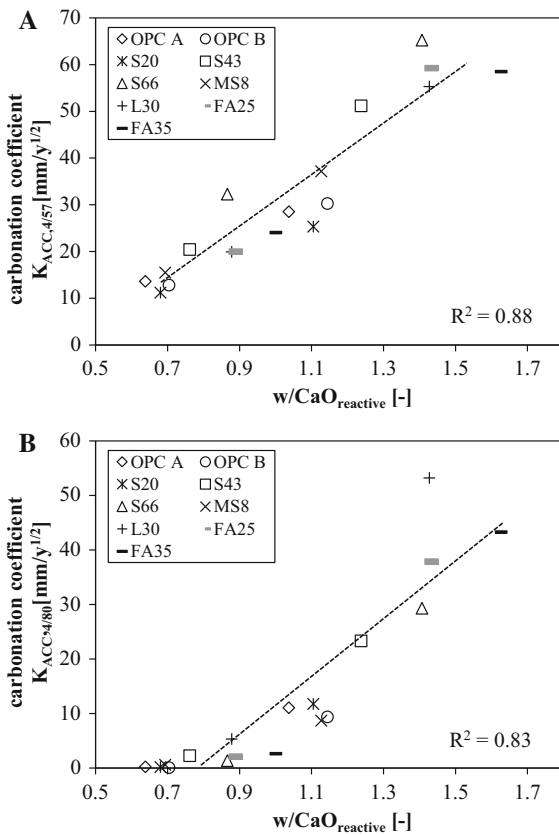
of hydration compared to the accelerated tests resulting from the outdoor storage for 2 years. As the CaO content of microsilica (0.3 mass% CaO) and fly ash (2.4 mass% CaO) are very low and therefore their contribution to the buffer capacity is insignificant, their degree of hydration was not taken into account.

Of course, this approach requires simplifications and assessing a degree of hydration is related to a high uncertainty. Moreover, the hydrates carbonate only partially and the amount of  $\text{CaCO}_3$  formed in the carbonated zone increases with increasing  $\text{CO}_2$  concentration [18, 35]. The reaction products formed in natural carbonation and carbonation at low  $\text{CO}_2$  concentration up to 3 and 4 % include a low-calcium C–S–H and residual portlandite is present as well [18, 35, 62]. Consequently, not all CaO in hydrates reacts and adds to the  $\text{CO}_2$  buffer capacity. However, the only partial carbonation of the hydrates affects all concrete mixtures used in this study in the same way and should therefore not have an impact on the applicability of the  $w/\text{CaO}$  as it is confirmed by the following comparisons.

The  $w/\text{CaO}_{\text{reactive}}$  and the  $w/\text{CaO}_{\text{reacted}}$  correlate well with the carbonation coefficient  $K_{\text{ACC},4/57}$  ( $R^2 = 0.88$  and  $0.87$  (not shown)/Fig. 6a). With the increase of RH to 80 % the correlation declines for both coefficients ( $R^2 = 0.83$  and  $0.58$  (not shown)/Fig. 6b). A similar behavior is observed in natural carbonation. The  $w/\text{CaO}_{\text{reactive}}$  and the  $w/\text{CaO}_{\text{reacted}}$  show a good correlation with the carbonation coefficient  $K_{\text{N},\text{S}}$  ( $R^2 = 0.90$  and  $0.87$  (not shown)/Fig. 7a). In the unsheltered exposure the correlation gets worse ( $R^2 = 0.83$  and  $0.79$  (not shown)/Fig. 7b). Generally, the concrete produced with mineral additions exhibits lower carbonation coefficients  $K_{\text{N}}$  for a given  $w/\text{CaO}_{\text{reacted}}$  compared to concrete OPC.

The good correlation of the  $w/\text{CaO}_{\text{reactive}}$  and  $w/\text{CaO}_{\text{reacted}}$  with the carbonation coefficients  $K_{\text{ACC},4/57}$  and  $K_{\text{N},\text{S}}$  (Figs. 6a, 7a) clearly shows that the buffer capacity governs carbonation resistance at low RH agreeing with the results of [23, 62]. As already discussed previously, the amount of pores filled with water by capillary condensation at increase RH is  $w/c$ - and cement-specific. As such, the influence of the buffer capacity as a chemical parameter decreases and the influence of capillary condensation as a physical parameter increases, resulting in a worsening of the correlation between carbonation coefficients  $K$  and  $w/\text{CaO}$ . This is clearly indicated by





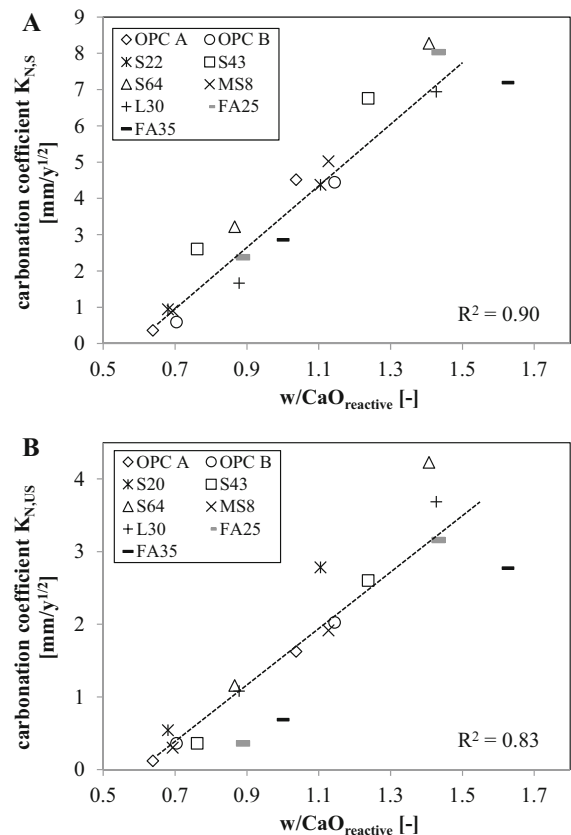
**Fig. 6** Carbonation coefficients  $K_{ACC,4/57}$  (a) and  $K_{ACC,4/80}$  (b) as a function of the  $w/CaO_{reactive}$

the worsened correlation between the carbonation coefficient  $K_{ACC,4/80}$  and  $w/CaO_{reactive}$  (Figs. 6b). In principle, the same applies going from sheltered to unsheltered exposure, even if the effect is less pronounced (Fig. 7b).

In spite of the relatively high degree of uncertainty in its assessment as described in the first part of this paragraph, the  $w/CaO_{reactive}$  is confirmed to be a useful tool to predict the carbonation resistance of concrete produced with different  $w/c$  and cement types.

## 5 Conclusions

The influence of CO<sub>2</sub> concentration and RH on accelerated carbonation was studied using concrete produced with two different  $w/c$  and nine different cements. The relation to natural carbonation was assessed by investigating the same concrete mixtures exposed to sheltered and unsheltered conditions.



**Fig. 7** Carbonation coefficient  $K_{N,S}$  (a) and  $K_{N,US}$  (b) as a function of the  $w/CaO_{reactive}$

Measurements of compressive strength and oxygen diffusion  $D_O$  extended the data set. The following conclusion can be drawn for the range of concrete mix designs and the curing used in this study:

- Increasing the CO<sub>2</sub> concentration from 0.045 to 1 and 4 % at 57 % RH has no significant influence on the ranking of the different concrete mixtures in regard to their carbonation resistance. Consequently, an acceleration of carbonation by an increase of CO<sub>2</sub> concentration up to a level of 4 % seems to be feasible.
- Increasing RH from 57 to 70 and 80 % at a CO<sub>2</sub> concentration of 4 % decreases the carbonation coefficient  $K_{ACC}$  due to an increasing amount of pores filled with water. Moreover, the ranking of the different concrete mixtures in regard to carbonation resistance is changed, likely as a result of the  $w/c$  and cement-specific pore size distribution.

- The carbonation coefficient  $K_N$  in sheltered exposure is about 2.5 higher than in unsheltered exposure.
- The carbonation coefficient  $K_{ACC,4/57}$  correlates well with the carbonation coefficients  $K_{N,S}$  ( $R^2 = 0.94$ ) and  $K_{N,US}$  ( $R^2 = 0.83$ ) permitting to assess the carbonation resistance of concrete in natural exposure by the accelerated test. However, prolonged curing (>3 days) may worsen the correlation, possibly leading to an underestimation of carbonation resistance of concrete containing slow hydrating siliceous additions in unsheltered outdoor exposure.
- Increasing RH in the accelerated test conducted at 4 %  $CO_2$  to 80 % RH worsens the correlation of the carbonation coefficients  $K$  at accelerated and natural exposure. Consequently, an increase of RH in accelerated testing does not improve the transferability of the results to natural carbonation. Apparently, constant RH and dynamic conditions with changes of RH involving capillary condensation, capillary suction (unsheltered exposure) and drying influence carbonation in a different way.
- The carbonation coefficients  $K$  show a certain correlation with the compressive strength, while there is no correlation with the oxygen diffusivity coefficient  $D_{O_2}$ .
- The  $w/CaO_{reactive}$  governs carbonation resistance with good correlation to the carbonation coefficients  $K_{ACC,4/57}$  ( $R^2 = 0.88$ ) and  $K_{N,S}$  ( $R^2 = 0.90$ ). Therefore, the carbonation resistance of concrete produced with different cements can be assessed with this chemical parameter. Increasing RH to 80 % in the accelerated test and going from the sheltered to the unsheltered conditions in natural exposure worsens the correlation, as carbonation is increasingly influenced by the physical parameters capillary condensation, capillary suction and drying.

In order to improve the understanding on the effect of degree of hydration, hydrates formed, pore structure, capillary condensation and drying on carbonation, more in-depth research is needed. However, it has to be kept in mind that the transferability of the results obtained with accelerated carbonation tests to natural conditions will always be significantly influenced by

the duration of curing and the climate-specific conditions in natural exposure.

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