

# Carbonation resistance of mortar produced with alternative cements

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Received: 18 December 2017 / Accepted: 2 August 2018  
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**Abstract** The use of alternative cements with lower CO<sub>2</sub> emissions during production compared to ordinary Portland cement (PC) is only sustainable, if the durability and with it the service life of components and structures produced with them are not compromised. In this project, the carbonation resistance of mortars produced with calcium sulfoaluminate cement (CSA) and three different slag-based cements is studied in accelerated conditions and natural exposure. Additionally, the diffusion coefficients of oxygen ( $D_{O_2}$ ) and carbon dioxide ( $D_{CO_2}$ ) are measured (the latter one only on carbonated mortars) and the change in mortar porosity due to carbonation is determined. Mortar PC used as reference and mortar CSA display the lowest carbonation coefficients, both in accelerated conditions and natural exposure. The three systems based on slag display higher carbonation coefficients. After carbonation, the diffusion coefficient  $D_{O_2}$  is increased for all mortars except for mortar PC, whose total porosity is decreased as well, in contrast to all other mortars. The diffusion coefficients  $D_{O_2}$  and  $D_{CO_2}$  show a linear relationship in the carbonated mortars.

**Keywords** Carbonation · Diffusion · Mortar · Alternative cement

## 1 Introduction

As cements with reduced clinker content and alternative cements permit a reduction of CO<sub>2</sub> emissions during production compared to plain Portland cement (PC), they are increasingly used. However, the sustainability is only improved if the durability and thus the service life of components and structures produced with them is not compromised. One of the main potential durability problems of concrete produced with alternative cements is carbonation. In carbonated concrete, the pH is decreased and rebar corrosion can occur when the environment provides sufficient moisture [1, 2], significantly decreasing service life. The CO<sub>2</sub> binding or buffer capacity per volume of cement paste is the most important parameter for the carbonation resistance of mortar and concrete produced with PC-based cements [3–5]. In general, the carbonation resistance of PC-based mortar and concrete is higher compared to those produced with alternative binders [6–10]. However, there are studies where this general assessment is questioned [11–14]. One reason for this could be the conditions used to determine carbonation resistance. Usually, the carbonation resistance of mortar and

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concrete is determined in accelerated conditions using different test procedures with  $\text{CO}_2$  levels differing from 3 to 100% [15–21]. However, the degree of carbonation of the hydrates increases with increasing  $\text{CO}_2$  concentration [22–24]. Therefore, it is questionable, whether data obtained with accelerated carbonation at increased  $\text{CO}_2$  concentration can be transferred to carbonation at natural concentration [11, 12, 23, 25]. In the case of concrete produced with PC-based cements, the ranking list of different concrete mixtures in regard to carbonation resistance is the same in the range of  $\text{CO}_2$  concentrations from 0.045 to 4.0% [5]. This indicates that  $\text{CO}_2$  concentrations up to 4% are suitable to assess the carbonation resistance of these materials. In the case of alternative cements, the data base available up to this point is insufficient for reaching any conclusions.

Another important point for understanding and modelling the carbonation of mortar and concrete produced with alternative binders is the kinetics of gas diffusion in such systems. In order to carbonate the hydrates,  $\text{CO}_2$  needs to diffuse through the already-carbonated material. Moreover,  $\text{O}_2$  diffusion in the carbonated layer is also important for durability, as its presence is a prerequisite for steel bar corrosion [1].

The goal of this project is to clarify whether the carbonation resistance of mortars produced with a selection of alternative cements can be assessed by an accelerated test. PC is used as a reference binder. Calcium sulfoaluminate cement (CSA), a PC-cement blended with 65 mass% of slag (CEM III/B according EN 197-1, named SC in the following), a super-sulfated slag (SSC) and an alkali activated slag (ASC) represent the alternative cements. Carbonation coefficients are determined in a carbonation chamber with 1%  $\text{CO}_2$  and in sheltered and unsheltered outdoor exposure. Moreover, porosity and  $\text{O}_2$  diffusivity are determined in the carbonated and non-carbonated state to assess how strongly they affect carbonation resistance. Additionally,  $\text{CO}_2$  diffusion in the carbonated material is measured, enabling a comparison to  $\text{O}_2$  diffusion and providing quantitative input for modelling of  $\text{CO}_2$  transport in the carbonated material.

## 2 Materials and methods

### 2.1 Materials

Five different binders were used for mortar production. PC (CEM I 52.5 R) was used as reference (mortar PC) and a PC with slag (CEM III/B 42.5 N; mortar SC). According to EN 197-1 the latter has a slag content of 66–80 mass%. The third binder was CSA cement with an addition of anhydrite (AH; mortar CSA). In the super-sulfated slag, anhydrite and a minor addition of PC (mortar SSC) were used for activation. The third slag system was activated using commercially-available water glass (WG;  $\text{Na}_2\text{SiO}_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ; mortar ASC). Table 1 shows the composition of the different materials.

The mortars were produced with two different water-to-binder ratios ( $w/b$ ) (Table 2). The volume of the cement paste was kept constant for all mortars. The water present in the WG was accounted for in the calculation of the  $w/b$ . Seven prisms ( $40 \times 40 \times 160 \text{ mm}^3$ ) and one cube ( $150 \times 150 \times 150 \text{ mm}^3$ ) were produced per mix design. Mortars PC, SC and CSA were demolded 24 h after production and mortars SSC and ASC after 48 h. Mortars PC, CSA, SC and SSC were water-cured at 20 °C until testing. Mortar ASC was stored in a climate chamber at a temperature of  $20 \pm 0.5$  °C and relative humidity (RH) > 95% until testing. Three prisms were used for the strength measurements at 2, 28 and 91 days, one for accelerated carbonation and two for natural carbonation.

From the parts split-off from mortar prisms to analyze carbonation depth, samples from the non-carbonated and carbonated zones of the mortars produced with a  $w/b$  of 0.60 were separated for mercury intrusion porosimetry (MIP) analysis. The samples were immersed in isopropanol for 7 days and dried in an oven at 50 °C for another 7 days before being analyzed.

After a 2-year exposure in sheltered outdoor conditions, the carbonated layer of a split-off part of a mortar prism was separated by cutting, ground and analyzed by TGA to determine the amount of bound  $\text{CO}_2$ .

Two cores used for  $\text{O}_2$  diffusion measurement were taken from the cube 26 days after production. After 28 days, they were stored at  $20 \pm 0.5$  °C and

**Table 1** Composition of the used materials

Components	CEM I	CEM III/B	CSA	Anhydrite	Slag
CaO	62.81	50.30	40.14	39.86	44.04
SiO <sub>2</sub>	19.35	30.65	9.52	57.41	35.36
Al <sub>2</sub> O <sub>3</sub>	5.04	10.20	31.51	0.67	10.59
Fe <sub>2</sub> O <sub>3</sub>	3.08	1.25	1.31	0.27	0.46
MgO	1.87	5.00	4.17	0.10	7.33
Na <sub>2</sub> O	0.15	0.19	0.49	0.02	0.16
K <sub>2</sub> O	0.95	0.56	0.47	0.05	0.42
P <sub>2</sub> O <sub>5</sub>	0.17	0.07	0.121	0.05	0.02
TiO <sub>2</sub>	0.28	0.780	0.413	< 0.01	0.47
MnO	0.052	0.19	0.17	< 0.01	0.35
Cr <sub>2</sub> O <sub>3</sub>	0.012	0.01	0.17	n.b.	0.01
SO <sub>3</sub>	2.98	0.09	10.07	57.41	0.30
LOI	2.98	0.48	0.61	0.53	0.26
Total	99.72	99.76	99.05	100.22	99.76
CO <sub>2</sub> <sup>a</sup>	2.60	1.98	0.37	0.37	1.14
C <sup>b</sup>	n.a.	n.a.	n.a.	n.a.	n.a.
Free CaO <sup>c</sup>	0.68	0.08	0.07	n.a.	n.a.

n.a., not analyzed

<sup>a</sup>By combustion analysis<sup>b</sup>Organic carbon, determined by combustion analysis<sup>c</sup>Free CaO + Ca(OH)<sub>2</sub> (according to Franke [27])**Table 2** Mortar mix design

Mortar	Binder (kg/m <sup>3</sup> )	Water (kg/m <sup>3</sup> )	w/b	Sand 0–2 mm (kg/m <sup>3</sup> )
PC-48	PC: 518	249	0.48	1488
PC-60	PC: 450	270	0.60	1488
CSA-48	CSA: 446	240	0.48	1488
	AH: 51			
CSA-60	CSA: 390	262	0.60	1488
	AH: 45			
SC-48	CEM III/B: 509	244	0.48	1487
SC-60	CEM III/B: 443	266	0.60	1488
SSC-48	SL: 427	241	0.48	1489
	AH: 50			
	PC: 25			
SSC-60	SL: 372	263	0.60	1489
	AH: 44			
	PC: 22			
ASC-48	AAS: 543	230	0.38	1488
	WG: 68			
ASC-60	AAS: 472	262	0.48	1488

35 ± 2% RH for 7 days before being dried in an oven at 50 °C for another 7 days.

One of the samples used for O<sub>2</sub> diffusion measurement was placed into the carbonation chamber at 4% CO<sub>2</sub> after analysis and kept there for 2 years. A concentration of 4% CO<sub>2</sub> was chosen as it agrees with the Swiss standard on carbonation resistance [26]. The

diffusion coefficient  $D_{\text{CO}_2,c}$  was determined at 4% CO<sub>2</sub> as well. Pre-carbonation before the diffusion test at an identical or higher concentration prevents CO<sub>2</sub> capture during the measurement, because the degree of carbonation of the cement hydrates increases with increasing CO<sub>2</sub> partial pressure [23, 24]. Any CO<sub>2</sub> binding during the test would lead to measuring an

erroneously lower  $D_{\text{CO}_2}$ . After 2 years, the cores were preconditioned for the diffusion measurement following the same procedure as described above for  $\text{O}_2$  diffusion.

Discs (diameter = 100 mm, height = 5 mm) were produced from cement pastes ( $w/b = 0.48$ ) for XRD analysis. They were cured at 20 °C and > 95% RH for 28 days. One half of the disc was removed and immersed in isopropanol for 7 days. Afterwards it was ground for XRD analysis. The other part of the disc was exposed to accelerated carbonation until it was fully carbonated according the phenolphthalein test. Then it was prepared for XRD in the same way as the non-carbonated pastes.

## 2.2 Methods

Compressive and flexural strength of the mortar prisms were determined according to DIN EN 1015-11 [28].

XRD was measured with a Panalytical X'Pert Pro in a  $\theta$ – $\theta$  configuration using  $\text{CoK}\alpha$ -radiation. The samples were scanned for 45 min between 5° and 90°  $2\theta$  using the X'Celerator detector.

Thermal gravimetry analysis (NETZSCH STA) was conducted in steps of 0.2 °C from 30 to 980 °C. Amorphous forms of  $\text{CaCO}_3$  as formed during carbonation of calcium-silicate-hydrates already starts to decompose at 400 °C [29]. But due to the peak of the remaining portlandite at 450 °C, the mass decrease in the temperature range of 500–800 °C was used to determine the loss of  $\text{CO}_2$ .

Porosity by MIP was determined with a Pascal 140/440 instrument (Thermo Fisher Scientific Inc.) applying a maximum pressure of up to  $p_{\text{max}} = 395$  MPa. The pore characteristics derived from the first intrusion were used for the analysis [30]. Pore size distributions as determined by MIP generally show a method-specific artifact in a shift towards smaller pores as a result of the ink bottle effect [30]. In spite of this limitation the method is well suited to compare the pore size distribution of different cementitious materials.

The measurement of  $\text{O}_2$  diffusion of the non-carbonated cores was conducted as described in [31–33]. A  $\text{N}_2$  flow was applied on one side of the cores and an  $\text{O}_2$  flow on the other side. On both sides of the cores the total gas pressure was identical. The  $\text{O}_2$  content in the nitrogen flow was determined until

steady-state was reached, which usually took about 1 h.

The carbonated cores were measured in the same setup with a gas mixture containing 96%  $\text{O}_2$  and 4%  $\text{CO}_2$  instead of pure  $\text{O}_2$  [33]. The analysis of  $\text{O}_2$  and  $\text{CO}_2$  was conducted simultaneously and continuously in the  $\text{N}_2$  flow until steady state was reached. In the case of  $\text{O}_2$ , this was usually achieved in less than 1 h, while 30–40 h were required using  $\text{CO}_2$ .

The procedure for the determination of the carbonation coefficient is based on SN 505 262/1 [26], but a  $\text{CO}_2$  concentration of  $1 \pm 0.1\%$  was used instead of  $4 \pm 0.1\%$ . The temperature was  $20 \pm 1$  °C and relative humidity (RH)  $57 \pm 3\%$ . One mortar prism was used for natural carbonation in sheltered exposure and another one for unsheltered exposure. Before transferring the mortar prisms to the carbonation chamber and the outdoor exposure, the initial carbonation depth was determined. An approximately 2.5 cm thick slice was split of the prisms. The freshly broken surface was sprayed with phenolphthalein and photographed. Carbonation depth was measured on 20 points. After the initial measurement, the carbonation depth of the samples in the carbonation chamber was measured after an exposure of 7, 28 and 63 days. The carbonation depth of the samples in the outdoor exposure was determined after 2 years. The carbonation coefficient  $K_{\text{ACC}}$  was determined by calculating the regression of the carbonation depth as a function of the square root of time (Eq. 1):

$$K_{\text{ACC}} = (d_K - A)/\sqrt{t} \quad (1)$$

where  $K$  is the carbonation coefficient,  $d_K$  the carbonation depth in mm,  $A$  the initial carbonation depth after curing in mm and  $t$  the time in years.

## 3 Results

### 3.1 Overview

The results on strength, diffusion and carbonation of the mortars are summarized in Table 3. The XRD results of the cement pastes and MIP results of the mortars, both in non-carbonated and carbonated state, are only presented in their respective paragraphs.



**Table 3** Summary of the results

Mortar	Compressive strength			Flexural strength			Diffusion coefficient			Carbonation coefficient			TGA	
	2 days (MPa)	28 days (MPa)	91 days (MPa)	2 days (MPa)	28 days (MPa)	91 days (MPa)	$D_{O_2,nc}$ ( $10^{-8}$ m <sup>2</sup> /s)	$D_{O_2,c}$ ( $10^{-8}$ m <sup>2</sup> /s)	$D_{CO_2,c}$ ( $10^{-8}$ m <sup>2</sup> /s)	$K_{ACC}$ (mm/year <sup>1/2</sup> )	$K_{N,S}$ (mm/year <sup>1/2</sup> )	$K_{N,US}$ (mm/year <sup>1/2</sup> )	CO <sub>2</sub> <sup>bou</sup> (m-%)	CaO <sup>carb</sup> (m-%)
PC-48	27.5	53.6	61.8	5.8	9.2	9.1	1.5	0.29	–	5.1	0.7	1.4	5.8	52
PC-60	16.2	36.8	45.6	4.0	7.3	7.9	2.60	1.6	1.2	11.8	1.4	2.8	6.4	65
CSA-48	52.4	66.5	73.6	7.6	7.1	7.2	0.35	0.94	–	5.9	0.8	2.5	2.6	44
CSA-60	40.6	50.7	49.3	6.7	6.1	5.2	2.6	4.1	3.0	15.4	1.1	4.0	2.5	46
SC-48	6.2	50.7	60.3	1.4	9.5	9.4	0.14	3.4	–	17.6	1.4	3.1	4.0	37
SC-60	2.3	37.0	45.7	0.7	7.8	8.2	0.33	5.4	4.0	25.7	2.5	6.0	3.8	39
SSC-48	3.4	19.4	22.5	0.9	5.9	7.5	1.5	9.6	–	41.3	3.4	7.4	2.8	38
SSC-60	1.0	12.4	14.4	0.6	4.5	5.7	3.8	13.5	9.1	55.5	4.7	12.9	2.7	41
ASC-48	23.6	46.5	61.4	6.0	8.0	7.2	0.22	1.8	–	23.3	1.7	3.3	4.1	55
ASC-60	8.9	26.9	31.3	2.0	5.2	4.6	0.13	2.5	1.5	32.3	2.5	6.6	4.6	70

$CO_{2,bou}$ :  $CO_2$  bound in the carbonated layer of the mortars as mass% of the mortar

$CaO_{carb}$ : carbonated amount of reactive  $CaO$  in the carbonated layer of the mortars calculated from  $CO_{2,ads}$  and cement composition

### 3.2 Compressive and flexural strength

Mortars CSA shows by far the highest strength after 2 days, with only a moderate increase in compressive strength until 28 days and even a decrease in the case of flexural strength (Table 3). Even after 28 days, their compressive strength is higher than the one of mortars PC. However, the flexural strength of mortar CSA is lower than mortar PC. The strength development is much slower for the slag systems. However, mortar SC and ASC reach similar compressive strength as mortar PC after 28 days. Only mortar SSC displays considerably lower values than the other mortars, even after 28 days. The flexural strength is similar for all slag systems. It is in the range of mortars CSA but lower than the one of mortars PC.

### 3.3 XRD

After carbonation, C–S–H, ettringite and monocarbonate are not detected any more in paste PC and only a minor amount of the originally-abundant portlandite is still present (Table 4). Due to the  $CO_2$  uptake,  $CaCO_3$  is formed with calcite as the dominant polymorph. As C–S–H is X-ray amorphous, its change due to carbonation cannot be followed with XRD. In [34] it has been shown by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) that C–S–H of identical cement pastes as used in this project de-calcifies, resulting in the formation of a low Ca/Si-ratio C–S–H and  $CaCO_3$ . In paste SC, the initial hydrates C–S–H, portlandite, ettringite, monocarbonate and hemihydrate are not detected anymore after carbonation and only the three  $CaCO_3$  polymorphs can be identified. The ettringite of paste CSA is converted into bassanite, aragonite and vaterite by carbonation, with minor amount of ettringite still present. Additionally, amorphous  $Al(OH)_3$  is formed, as identified in [34] by SEM/EDX, but cannot be detected here by XRD. In paste SSC, the initial hydrates C–S–H and ettringite are converted to the three  $CaCO_3$  polymorphs, gypsum and bassanite. After carbonation of paste AAS, C–S–H and hydro-talcite disappear and only the three  $CaCO_3$  polymorphs are detected by XRD.

**Table 4** Phases and their relative amounts as identified in cement pastes with a  $w/b$  of 0.48 in the non-carbonated (ncarb) and the carbonated (carb) state

Phase	Paste PC		Paste CSA		Paste SC		Paste SSC		Paste ASC	
	ncarb	carb	ncarb	carb	ncarb	carb	ncarb	carb	ncarb	carb
C-S-H	+				+		++		++	
Portlandite	+++	+			+					
Ettringite	+		+++	+	+		++			
Monocarbonate	+				+					
Hemicarbonate					+					
Hydrotalcite									+	
Calcite	+	+++				+++	++		+++	
Aragonite		+		+		+	+		+	
Vaterite		+		+		+	+		+	
Gypsum							++			
Bassanite				++			+			

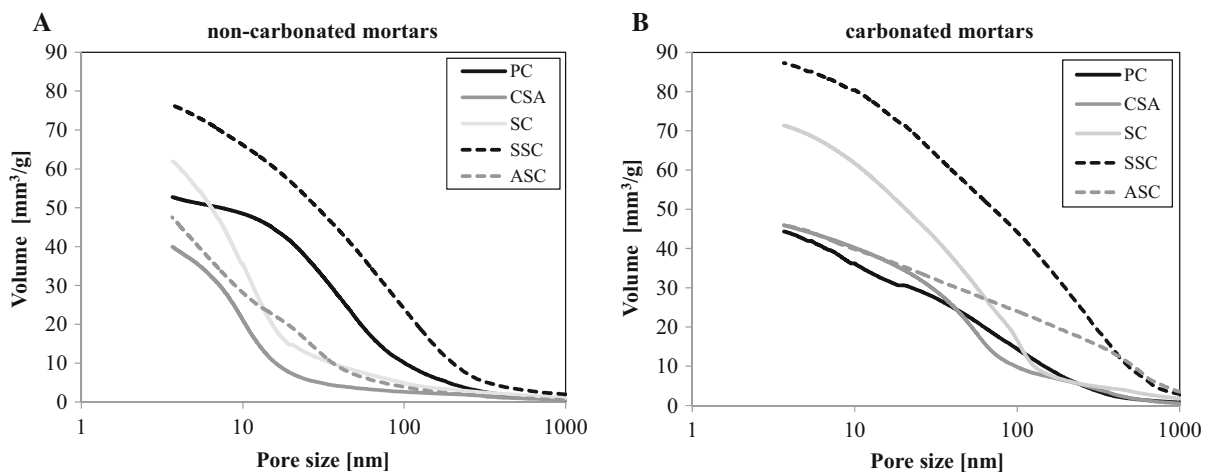
### 3.4 TGA

The bound  $\text{CO}_2$  in the carbonated layer of the mortars exposed to sheltered outdoor conditions varies between 2.5 and 6.4 mass% (Table 3). Mortar PC displays the highest amount of bound  $\text{CO}_2$  in the carbonated layer, while  $\text{CO}_2$  binding is the lowest for mortars CSA and SSC. These mortars rely on ettringite as a main hydration product, which is transformed into the non- $\text{CO}_2$  containing phases bassanite and gypsum by carbonation, explaining the low amount of bound  $\text{CO}_2$  (Table 4). The chemical composition of the cements gives information on the reactive CaO in the different cements. As anhydrous cement clinker and slag are still present in the mortars [34] not all of the CaO is available for carbonation. Still, the total

amount of CaO can be used to give an indication about the degree of carbonation in the carbonated layers of the different mortars. The adsorbed amount of  $\text{CO}_2$  translates into a degree of carbonation between 37% (mortar CSA-48) and 70% (mortar ASC-60) in the carbonated layer (Table 3). In the case of mortar PC and SC, the  $\text{CO}_2$  binding is higher for the samples with higher  $w/b$ , as already observed in PC pastes [24].

### 3.5 MIP

In the non-carbonated state, total porosity increases in the order of mortar CSA, ASC, PC, SC and SSC (Fig. 1a). Mortars SC and ASC and especially mortar CSA show a higher amount of small pores < 20 nm than mortar PC and SSC. After carbonation, only

**Fig. 1** Porosity of the mortars in the non-carbonated (a) and the carbonated state (b)

mortar PC exhibits a lower total porosity than in the non-carbonated state (Fig. 1b). However, the size of the pores has increased. In all other mortars, total porosity and pores size have both increased due to carbonation.

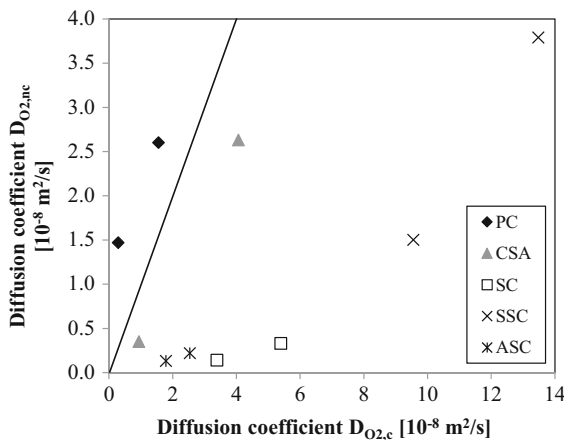
### 3.6 O<sub>2</sub> diffusion

The diffusion coefficient  $D_{O_2,nc}$  is the lowest for mortar SC and ASC with mortar CSA at the lower  $w/b$  being in the same range. The values for mortar PC are higher and only surpassed by mortar SSC. A clear relation of the diffusion coefficient to the compressive strength is not evident (Fig. 2), as it is typical in the case of PC-based systems with different mineral additions [4, 5, 35].

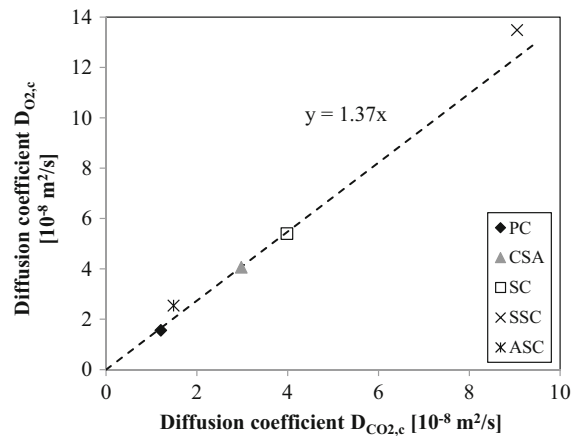
After carbonation, only mortar PC shows a decreased diffusion coefficient  $D_{O_2,c}$  (Fig. 2). At the same time, it displays the lowest value in the carbonated state of all mortars, since the mortars containing slag exhibit a marked increase of the diffusion coefficient.

### 3.7 CO<sub>2</sub> diffusion

In regard to the diffusion coefficient  $D_{CO_2,c}$  the mortars are ranked the same order as with the diffusion coefficient  $D_{O_2,c}$  (Fig. 3). Mortar PC exhibits the lowest value and mortar SSC the highest. Mortars PC, CSA and SC show exactly the same ratio between diffusion coefficient  $D_{CO_2,c}$  and  $D_{O_2,c}$  as previously found for blended Portland cement mortars containing



**Fig. 2** Diffusion coefficient  $D_{O_2,nc}$  of the mortars as a function of diffusion coefficient  $D_{O_2,c}$ . The line indicates a ratio of 1:1

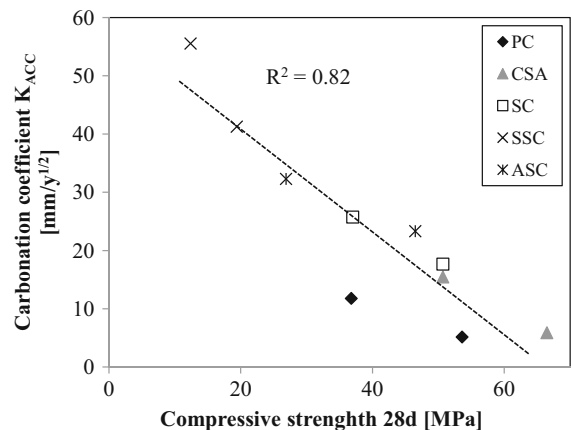


**Fig. 3** Diffusion coefficient  $D_{O_2,c}$  as a function of diffusion coefficient  $D_{CO_2,c}$  of the carbonated mortars. The line indicates the relation between diffusion coefficients  $D_{CO_2,c}$  and  $D_{O_2,c}$  as established for blended Portland cement mortars in [33]

different mineral additions in [33]. Mortars ASC and SSC show a slightly higher diffusion coefficient  $D_{O_2,c}$  for a given diffusion coefficient  $D_{CO_2,c}$ .

### 3.8 Accelerated carbonation

The carbonation coefficients  $K_{ACC}$  of the different mortars differ significantly (Table 3 and Fig. 4). Mortars PC and CSA display comparable low values. The systems with slag show higher carbonation coefficients  $K_{ACC}$  increasing in the order of mortars SC, ASC and SSC. The carbonation coefficient  $K_{ACC}$  shows a relatively good correlation with compressive strength (Fig. 4). However, mortar PC exhibits a



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



clearly lower carbonation coefficient  $K_{ACC}$  than the other mortars for a given compressive strength.

### 3.9 Natural carbonation

Mortar PC displays the lowest carbonation coefficients  $K_N$  followed by mortar CSA in both sheltered and unsheltered exposure (Fig. 5). While the coefficients of mortar SC and ASC are similar, the values of mortar SSC are considerably higher. In relation to the other mortars, the carbonation coefficient  $K_{N,US}$  of mortar CSA is relatively low for a given carbonation coefficient  $K_{N,S}$ . There is a good correlation between carbonation coefficients  $K_{N,S}$  and  $K_{N,US}$  ( $R^2 = 0.93$ ), which differ by a factor of 2.5.

## 4 Discussion

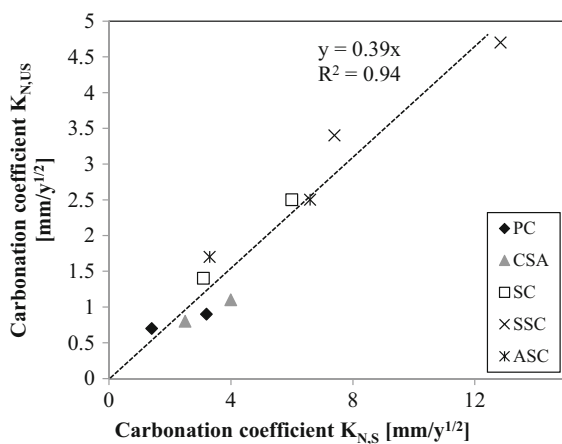
Strength development depends on cement type. However, the ratio between compressive and flexural strength varies between the different mortars. While the ratio is similar for mortars PC, SC and ASC, between 5.0 and 5.8 in average for the different ages, mortar CSA displays a higher ratio (8.4) due to a relatively low flexural strength. Mortar SSC shows the opposite trend with a relatively high flexural strength (ratio of 2.8). In the case of SSC, the ratio seems dependent on the fineness of the slag [9]. This example illustrates that the mechanical properties of mortar and

concrete produced with alternative cements may differ from PC-systems.

The low values of the diffusion coefficient  $D_{O_2,nc}$  for the slag systems and their high amount of fine pores compared to mortar PC is typical for these cements [4, 5, 8, 36, 37]. An exception is mortar SSC, which exhibits a high diffusion coefficient  $D_{O_2,nc}$  and high porosity. The chosen binder proportions of slag, anhydrite and PC seem not have been ideal resulting in a relatively low degree of reaction as indicated by the low strength values as well. The very low diffusion coefficient  $D_{O_2,nc}$  of mortar CSA with the lower  $w/b$  agrees with the very low amount of pores  $> 20$  nm measured by MIP.

Carbonation has a pronounced effect on both porosity and diffusion coefficient  $D_{O_2}$  of all mortars. The decrease of diffusion coefficient  $D_{O_2}$  in the case of mortar PC is clearly related to the decrease in total porosity. The total porosity decrease seems to have a stronger effect on the diffusivity than the coarsening of the pores due to carbonation. The increase of diffusion coefficient  $D_{O_2}$  of the other mortars can be attributed to both an increase in total porosity and to the coarsening of the pore system. The change of both parameters is less pronounced in mortar CSA compared to the slag systems. The correlation between diffusion coefficient  $D_{O_2,c}$  and  $D_{CO_2,c}$  confirms the relation between these two parameters previously established in [33]. Only mortars SSC and ASC show a slightly lower diffusion coefficient  $D_{CO_2,c}$  for a given diffusion coefficient  $D_{O_2,c}$ . It is not understood yet, how pore size distribution in the carbonated mortars may influence the ratio between the carbonation coefficients  $D_{O_2}/D_{CO_2}$ . It is hypothesized in [33, 38] that a certain variation might be possible. However, the experimentally-determined ratio can provide a base for diffusion models.  $O_2$  and  $CO_2$  diffusion in the mortars is expected to be dominated by Knudsen diffusion [33, 38].

While the faster carbonation of the slag systems in comparison to mortar PC was expected [4, 5, 9, 25, 39, 40], the low carbonation coefficient  $K$  of mortar CSA was not anticipated. On the one hand, the low carbonation coefficient of mortar CSA seems to confirm the findings of [13], where it was shown that CSA-based concrete in service has a carbonation resistance comparable to PC-based concrete. On the other hand, mortar produced with the same CSA-



**Fig. 5** Carbonation coefficient  $K_{N,US}$  of the mortars in unsheltered exposure as a function of carbonation coefficient  $K_{N,S}$  in sheltered exposure

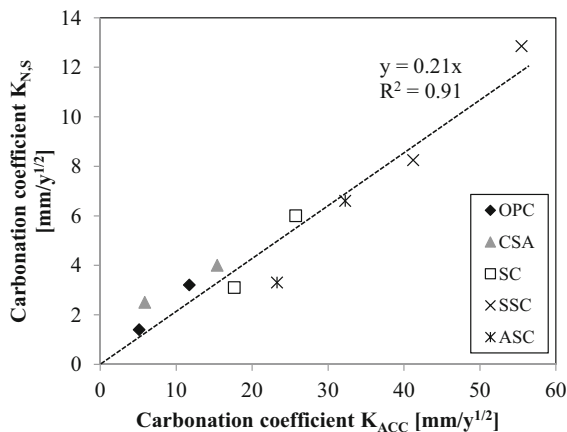




cement as in this project but cured only for 3 days compared to 28 days of curing in this project showed a considerably lower carbonation resistance than PC-based mortar cured for the same time [10]. In [13], the high carbonation resistance of CSA-concrete with low  $w/b$  is attributed to the low porosity and to self-desiccation, making it difficult for water and  $\text{CO}_2$  to penetrate and cause carbonation. Another possible reason goes in the opposite direction, although it is as well linked to the high amount of very fine pores in mortar CSA (Fig. 1a). Due to capillary condensation, the amount of pores filled with water at a given RH and therefore not accessible to  $\text{CO}_2$  might be higher compared to the other mortars with coarser pores. As such, carbonation could be slowed down. The low carbonation coefficient  $K_{N,US}$  at a given carbonation coefficient  $K_{N,S}$  compared to the other mortars points in this direction.

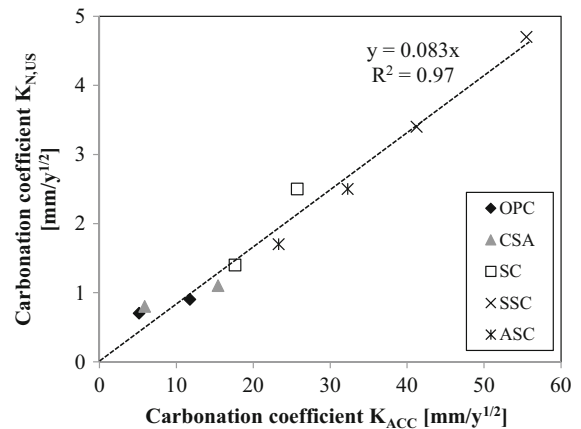
The carbonation coefficient  $K_{ACC}$  shows a very good correlation to the carbonation coefficients  $K_{N,S}$  and  $K_{N,US}$  (Figs. 6, 7). This clearly shows that accelerated carbonation with a  $\text{CO}_2$  concentration of 1% is able to assess the carbonation resistance in natural conditions of the studied systems. This applies as well to mortar ASC, where the transferability of results obtained with accelerated carbonation to natural exposure has been questioned [11].

In PC-based systems, the carbonation coefficient  $K$  shows an excellent correlation to the  $\text{CO}_2$  buffer or binding capacity per volume of cement paste, expressed as the water-to-reactive-CaO-ratio ( $w/\text{CaO}_{\text{reactive}}$ ), [4, 5]. However, this approach is less

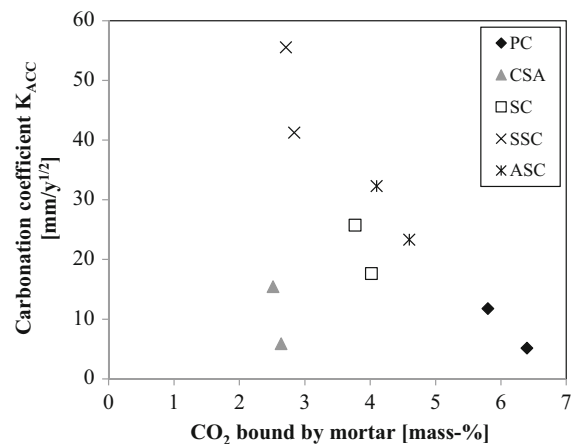


**Fig. 6** Carbonation coefficient  $K_{N,S}$  as a function of carbonation coefficient  $K_{ACC}$

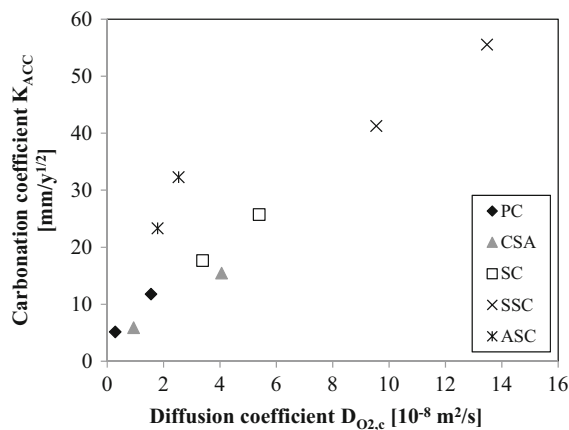
suitable in systems where a substantial part of the  $\text{CaO}$  is present in ettringite that is transformed into non- $\text{CO}_2$  binding gypsum and bassanite by carbonation, like in the case of mortars CSA and SSC. Therefore, the effectively bound  $\text{CO}_2$  in the carbonated zone of the mortars exposed to sheltered outdoor exposure (Table 3) is used to compare it to the carbonation coefficient  $K_{ACC}$ . A trend is evident, according to which the more  $\text{CO}_2$  is bound in the carbonated zones, the lower is the carbonation coefficient  $K_{ACC}$  (Fig. 8). This confirms the importance of the buffer capacity for the carbonation resistance. However, mortar CSA shows a different behavior, i.e. it adsorbs a relatively low amount of  $\text{CO}_2$  for is low carbonation coefficient  $K_{ACC}$ . As discussed above, not chemical but physical



**Fig. 7** Carbonation coefficient  $K_{N,US}$  as a function of carbonation coefficient  $K_{ACC}$



**Fig. 8** Carbonation coefficient  $K_{ACC}$  as a function of the amount of chemically bound  $\text{CO}_2$  in the carbonated zone of the mortars



**Fig. 9** Carbonation coefficient  $K_{ACC}$  as a function of diffusion coefficient  $D_{O_2,c}$

reasons linked to the high amount of fine pores seem to be responsible for the high carbonation resistance of mortar CSA.

The diffusion coefficient  $D_{O_2,nc}$  shows no correlation at all with the carbonation resistance of the mortars (Table 3). However, when the carbonation coefficient  $K$  is compared with the diffusion coefficients in the carbonated material, a relation seems to be obvious: the carbonation coefficient  $K_{ACC}$  increases linearly with the increasing diffusion coefficient  $D_{O_2,c}$  (Fig. 9) and likely  $D_{CO_2,c}$ , as shown by the correlation of both diffusion coefficients in Fig. 3. Only mortar ASC exhibits a different relation between the carbonation coefficient  $K_{ACC}$  and the oxygen diffusion coefficient  $D_{O_2,c}$ . This relation between carbonation coefficient  $K_{ACC}$  and the diffusion coefficients  $D_{CO_2,c}$  and  $D_{O_2,c}$  indicates that the supply of  $CO_2$  through the carbonated layer to the non-carbonated material of the mortars is an important parameter for the progress of carbonation.

As discussed above, the buffer capacity relates as well to the carbonation resistance. Because a decrease of diffusion coefficients  $D_{CO_2,c}$  and  $D_{O_2,c}$  goes together with an increase of bound  $CO_2$ , the influence of the individual parameters on the carbonation resistance cannot be assessed.

## 5 Conclusions

The carbonation resistance of mortar PC, CSA, SC, SSC and ASC produced with alternative cements was

studied in accelerated and natural conditions. The changes of hydrate assemblage and of porosity due to carbonation were investigated.  $O_2$  diffusion was determined in the non-carbonated and carbonated mortars, while  $CO_2$  diffusion was measured in the carbonated mortars. The results allow to draw the following conclusions:

- The carbonation coefficient  $K_{ACC}$  of mortars determined in accelerated condition with 1%  $CO_2$  shows an excellent correlation with the carbonation coefficients  $K_{N,S}$  and  $K_{N,US}$  determined in natural conditions. These results validate the use of accelerated testing for systems produced with alternative cements.
- The carbonation coefficients  $K$  are considerably higher for the three slag-based systems (mortar SC, SSC and ASC) compared to mortar PC and CSA. The three slag-based systems exhibit lower resistance to carbonation.
- Carbonation of the mortars leads to an increase in pore size and total porosity, which goes together with an increased diffusivity. The exception is mortar PC, whose total porosity and diffusion coefficient  $D_{O_2}$  decrease in spite of the coarsened pore system.
- The diffusion coefficient  $D_{O_2,c}$  of mortar PC, CSA and SC are exactly 1.37 times higher than the diffusion coefficient  $D_{CO_2,c}$ , which confirms recent findings [33]. Mortar SSC and ASC show a slightly larger difference.
- The amount of bound  $CO_2$  correlates with the carbonation resistance, showing the importance of the  $CO_2$  buffer capacity. Mortar CSA is an exception, which might be explained by its low porosity and fine pores, combined with capillary condensation that slows down carbonation.
- The diffusion coefficient  $D_{O_2,c}$  and  $D_{CO_2,c}$  correlate to the carbonation coefficient  $K$ , indicating the importance of  $CO_2$  transport in the carbonated layer.

**Acknowledgements** The authors would like to thank J. Kaufmann for the MIP measurements and P. Lura for the critical review of the manuscript.

**Funding** This study was not funded by external sources. It was conducted with Empa means (employer of all authors).



## Compliance with ethical standards

**Conflict of interest** The authors declare that they do not have a conflict of interest.

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