Steady-state O₂ and CO₂ diffusion in carbonated mortars produced with blended cements

Andreas Leemann · Roman Loser · Beat Münch · Pietro Lura

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Abstract The diffusion coefficient D_{O_2} , the porosity and the pore structure of mortars produced with a Portland cement and a range of blended cements containing limestone powder, microsilica, portlandite or slag were measured in the non-carbonated and the carbonated state. Additionally, the setup for measuring O₂ diffusion was adapted to measure also the CO₂ diffusion of the carbonated mortars. The diffusion coefficient D_{O_2} and the total porosity were increased in the mortars containing microsilica and slag, while they were decreased in the other mortars due to carbonation. Invariably, the pore structure became coarser in all samples. The relationship between diffusion coefficients D_{O_2} and D_{CO_2} in the carbonated mortars was always linear, with D_{O_2} systematically higher by factor of 1.37. As this factor broadly agrees with what was found in the scant literature about CO₂ diffusion, it could be used for estimating D_{CO_2} of carbonated mortar and concrete based on measurements of O₂ diffusion.

Keywords Mortar · Carbonation · Gas diffusion · Porosity

A. Leemann (✉) · R. Loser · B. Münch · P. Lura
Empa - Swiss Federal Laboratories for Materials Science
and Technology, Dübendorf, Switzerland
e-mail: andreas.leemann@empa.ch

P. Lura
Institute for Building Materials, ETH-Zurich, Zurich,
Switzerland

1 Introduction

With the aim of reducing the overall CO₂ emissions of the cement and concrete industry, the production and use of blended cements is steadily increasing. However, as concrete produced with blended cements usually displays a reduced carbonation resistance compared to concrete based on Portland cement [1–6], the process of concrete carbonation has moved into the focus of research. Conditions for accelerated testing in the laboratory, ranking of different cementitious systems and changes to the hydrate assemblages upon contact with CO₂ have been assessed in a multitude of studies [1, 3, 5, 7–19]. In comparison, little information has been published on gas diffusion in the carbonated material. This issue is of primary importance, because CO₂ needs to diffuse through the carbonated layer to reach the non-carbonated material and a precise knowledge of the CO₂ diffusion coefficients is essential for numerical models of carbonation [20–24]. In addition, since the presence of oxygen is necessary for steel corrosion, also measurements of the diffusion coefficient of O₂ in carbonated concrete are of interest [25].

Houst and Wittmann [25] determined O₂ and CO₂ diffusion coefficients in pre-carbonated ordinary Portland cement (OPC) pastes in a non-steady-state setup. In their experiments, the carbonation of 1–3 mm thick cement paste discs was conducted at a CO₂ concentration of 80–90%, while the CO₂ concentration in the

gas used for the measurements was 2%. The higher CO_2 concentration during pre-carbonation compared to the CO_2 concentration during the actual measurements has the advantage that active CO_2 binding during the measurement is prevented. However, there is recent evidence [10, 24] that a high CO_2 concentration during pre-carbonation may induce significantly higher degree of carbonation of the cement hydrates, accompanied by a larger impact on porosity, than carbonation at lower CO_2 concentrations.

The CO_2 diffusion coefficients of cement paste, mortar and concrete samples produced with OPC were determined in a steady-state setup by Jung et al. [26]. Both non-carbonated and carbonated discs with a thickness of 10 mm were measured at different relative humidity levels using 100% CO_2 as measuring gas. Unfortunately, Jung et al. [26] do not report the conditions at which the samples were carbonated. Part of the CO_2 diffusing through the non-carbonated samples becomes bound in the hydrated products of the cement. However, as carbonation is a relatively slow process, part of the CO_2 was nevertheless able to diffuse through the samples. The effect of CO_2 binding during the measurement is evident in the comparison between the concrete samples produced with a w/c of 0.58, 0.50 and 0.42. As the time required to reach steady-state conditions is increasing with decreasing w/c, the difference of the CO_2 diffusion coefficient between non-carbonated and carbonated samples is increasing with decreasing w/c.

Namouniara et al. [27] determined the CO_2 diffusion coefficient of non-carbonated OPC pastes and OPC pastes blended with ground-granulated blast furnace slag ("slag"). In order to minimize active CO_2 binding of the cement hydrates during the measurements in a non-steady-state setup with a gas containing 80% CO_2 , the samples were pre-conditioned at a temperature of 105 °C. One main disadvantage of this approach is that ettringite loses its crystalline water [28] and that the chemically bound water in calcium-silicate-hydrate is partly lost as well [29, 30]. Therefore, a substantial change in porosity and with it an artificial increase in the diffusion coefficient is to be expected when drying at 105 °C.

The goal of the present study is to determine diffusion coefficient D_{O_2} in non-carbonated mortars and both diffusion coefficients D_{O_2} and D_{CO_2} in carbonated mortars produced with a range of blended

cements. The ratio between diffusion coefficients D_{O_2} and D_{CO_2} in the carbonated mortars should ideally allow to assess diffusion coefficient D_{CO_2} also in the non-carbonated mortars based on the results obtained by O_2 diffusion. Additionally, the changes in porosity caused by carbonation are studied and correlated with the changes in diffusion coefficient. One of the mortars is produced with an ordinary Portland cement (OPC), while three other mortars are blended with limestone powder (LS), microsilica (MS) and slag (S). Additionally, portlandite is used for blending, since it does not decrease the CO_2 binding capacity of the mortar like the other three additions [16].

2 Materials and methods

2.1 Materials

For mortar production OPC (CEM I 52.5 R according to EN 197) was used. One mortar was produced with OPC (mortar OPC). In three mortars, 15 mass% of the OPC were replaced with limestone powder (mortar L-15), microsilica (mortar MS-15) and portlandite powder (mortar P-15). The fifth mortar (mortar SL-66) was produced with a blended cement containing 66 mass% of slag (CEM III/B 32.5 R). The total content of cement and mineral additions (i.e., the total binder content) varied between 507 and 518 kg/m³. The slight variation is a result of keeping the volume of paste constant at 413 l/m³. The water-to-binder ratio was 0.48. As aggregate, standard quartz sand (0–2 mm) was used. The same cement, mineral additions and mix design as in [16] were applied.

For the diffusion measurements one mortar cube (150 × 150 × 150 mm³) and one mortar prism (40 × 40 × 160 mm³) were produced per mortar. They were demolded after 24 h and subsequently moist cured [in a room at 20 ± 0.5 °C and > 95% relative humidity (RH)] until the age of 28 days. Afterwards, one core (diameter of 100 mm, height of 50 mm) was extracted per cube to measure O_2 diffusion. The cores were conditioned at 20 ± 0.5 °C and 35 ± 2% RH for 7 days and then dried in an oven at 50 °C for another 7 days before the measurement started. After the O_2 diffusion measurements, the height of the core was reduced from 50 to 16 mm to allow faster carbonation. The samples were

stored for 2 years in a carbonation chamber at 20 °C and 57% relative humidity using a CO₂ concentration of 4%. The degree of carbonation of the cement hydrates is dependent on CO₂ concentration [10, 24], but at the used level it can be expected that about 50% of the reactive CaO in the binder of the mortars has carbonated [24]. Afterwards, the same sample conditioning was applied as for the O₂ diffusion measurements of the non-carbonated samples. The experimentally-determined RH in mortar OPC at this stage is $17.2 \pm 0.8\%$, which indicates the RH range achieved with the chosen conditioning. This value is lower than the threshold of 70% RH below which the permeability and the diffusivity of mortar and concrete show little change with decreasing RH [25, 31].

For the carbonation measurements the mortar prisms were moist-cured until 28 days after demoulding, stored at 20 °C and 57% RH before being moved into the carbonation chamber (4% CO₂, 20 ± 1 °C, $57 \pm 2\%$ RH). Samples for MIP were extracted from carbonated and non-carbonated areas of the mortars using pincers after 28 or 63 days in the carbonation chamber. Afterwards, the extracted pieces were first stored in isopropanol for 7 days and then oven-dried at 50 °C for 7 days.

2.2 Methods

The O₂ diffusion coefficient D_{O_2} of the non-carbonated cores was measured as described in [32–34]. A N₂ flow was applied on one side of the cores and an O₂ flow on the other side. The total gas pressure on both sides of the cores was identical. The O₂ content in the nitrogen flow was measured until steady-state was reached, which usually took about 1 h.

The carbonated cores were measured the same way, with the difference that a gas mixture containing 96% O₂ and 4% CO₂ was used instead of pure O₂. O₂ and CO₂ were analyzed simultaneously and continuously in the N₂ flow. While the O₂ reached steady-state conditions in less than an hour, it took between 30 and 40 h for the CO₂ to reach steady-state. A CO₂ concentration of 4% was chosen for the diffusion measurements, as this was the same concentration at which the sample had been carbonated for 2 years. A CO₂ concentration higher than the one used for the carbonation of the mortars would have caused CO₂ binding during the test, as the degree of carbonation of the cement hydrates increases with increasing CO₂

partial pressure [10, 24]. Using 4% CO₂ eliminated the influence of CO₂ binding in the samples during the measurement.

Additionally, preliminary tests have shown that it is not possible to determine a CO₂ diffusion coefficient of the non-carbonated samples with the setup employed in this study. CO₂ binding was so significant that no measurable amount of CO₂ was able to diffuse through the samples within 60 h of testing. As the effect of CO₂ binding on CO₂ diffusion cannot be quantified in non-carbonated samples, it seems impossible to determine a CO₂ diffusion coefficient in non-carbonated cementitious materials with the experimental approach employed in this study.

The diffusion coefficients D_{O_2} and D_{CO_2} were calculated in the following way. Suppose a stream of CO₂ gas with a volume fraction of s_1 on the upper side of the sample core of thickness ∂x (m) and area A (m²). The lower side of the disc is flushed by a stream of nitrogen gas at a flow of f in (m³/s).

Assuming Fick's law, the diffusion coefficient D (m²/s) through the core is

$$D = - \frac{J \cdot \partial x}{\partial c} \quad (1)$$

The concentration gradient ∂c from top to down of the observed gas in mol per volume (mol/m³) is

$$\partial c = - \frac{s_1 - s_2}{V_m} \quad (2)$$

with the detected volume fraction s_2 of the diffused gas in parts per million, and its molar volume V_m .

Simultaneously, from the nitrogen gas flow f , the molar diffusion flux J (mol/m²s) from top to down is

$$J = \frac{s_2 \cdot f}{A \cdot V_m} \quad (3)$$

Combining together, the diffusion coefficient can be estimated by

$$D = \frac{s_2 \cdot f \cdot \partial x}{A \cdot (s_1 - s_2)} \quad (4)$$

MIP was performed using a Pascal 140/440 (Thermo Fisher Scientific Inc.) instrument. The maximum pressure used was $p_{\max} = 395$ MPa. The pore characteristics derived from the first intrusion were used for the analysis [35]. It is noticed that, due to limitations of the maximum applied pressure, MIP is able to measure the capillary pores and only the largest

gel pores [36]. In addition, the main drawback of MIP is the systematic shift to smaller pores due to the ink bottle effect (e.g., [35]). On the other hand, at 70% RH, most of the gel pores that are inaccessible to MIP are expected to be saturated in the mortars on which O_2 and CO_2 diffusion was measured. For this reason, the MIP porosity is expected to give a reasonable estimation of the porosity that is accessible to gas diffusion.

3 Results

Compressive strength and carbonation coefficients in accelerated conditions and natural exposure of mortars with identical mix design are given in [16]. An overview of the diffusion results is given in Table 1. As only one sample per mortar was used for this study, no standard deviation can be given. However, other projects on mortars conducted with the same setup have shown that the standard deviation increases with decreasing O_2 diffusion coefficient [16, 33, 34]. In the range of the values given below, the standard deviation typically varies within the range 1–14%.

The diffusion coefficient D_{O_2} in mortars OPC, L-15 and P-15 is decreased due to carbonation by a factor of about 2 (Fig. 1). An opposite trend is observed in the mortars containing siliceous additions: the diffusion coefficient D_{O_2} of mortars MS-15 and SL-66 is considerably increased upon carbonation.

The diffusion coefficients $D_{O_2,c}$ and $D_{CO_2,c}$ show a linear relationship in the carbonated mortars, with values for diffusion coefficient $D_{CO_2,c}$ being lower by a factor of 1.37 (Fig. 2).

According to the MIP measurements, mortar MS-15 and SL-66 containing siliceous additions have a considerably higher amount of fine pores (below about 20 nm) than the other mortars (Fig. 3). Additionally,

Fig. 1 Diffusion coefficient $D_{O_2,c}$ of the carbonated mortars as a function of the diffusion coefficient $D_{O_2,nc}$ of the non-carbonated mortars. The line indicates equality

Fig. 2 Diffusion coefficient $D_{O_2,c}$ as a function of diffusion coefficient $D_{CO_2,c}$ of the carbonated mortars

their total porosity is lower. Mortar P-15 exhibits the highest total porosity.

A coarsening of the pores due to carbonation is indicated in all mortars by MIP (Fig. 3). However,

Table 1 Overview of the O_2 and CO_2 diffusion results

Mortar		OPC-48	L-15	MS-15	P-15	SL-66
$D_{O_2,nc}$	($10^{-8} \text{ m}^2/\text{s}$)	1.49	2.35	0.38	1.84	0.13
$D_{O_2,c}$	($10^{-8} \text{ m}^2/\text{s}$)	0.77	1.36	1.35	1.16	1.97
$D_{CO_2,c}$	($10^{-8} \text{ m}^2/\text{s}$)	0.53	1.02	0.92	0.86	1.46

$D_{O_2,nc}$ = O_2 diffusion coefficient in non-carbonated mortar

$D_{O_2,c}$ = O_2 diffusion coefficient in carbonated mortar

$D_{CO_2,c}$ = CO_2 diffusion coefficient in carbonated mortar

Fig. 3 Pore volume as a function of the pore radius of all mortars in the non-carbonated (a) and the carbonated state (b)

while the total porosity is decreased in mortars OPC, L-15, MS-15 and P-15, the carbonation of mortar SL-66 results in increased total porosity.

4 Discussion

The decrease of the diffusion coefficient D_{O_2} in the mortars OPC, L-15 and P-15 with carbonation can be attributed to the substantial decrease of total porosity, although MIP also shows some degree of coarsening of the pores. The substantial increase of diffusion coefficient D_{O_2} in the case of mortar SL-66 is a consequence of the increase in total porosity and of the coarsening of the pores. In the case of mortar MS-15, the total porosity is decreased but the coarsening of the pores is more pronounced than for all other mortars, resulting in an increase of diffusion coefficient D_{O_2} upon carbonation.

When the results of this study are compared with the literature, it can be noticed that the ratio between diffusion coefficients D_{O_2} and D_{CO_2} determined by Houst and Wittmann [25] for Portland cement pastes with w/c 0.50 (a w/c comparable to that of the mortars examined in our study) varies from 1.27 to 1.46 with increasing RH (see Table 3 and Eq. 11 in [25]).

Moreover, the mix design of one mortar used in Jung et al. [26] was similar to the one of mortar OPC. The reported diffusion coefficients D_{CO_2} of 3.5 and $0.8 \times 10^{-8} \text{ m}^2/\text{s}$ at 10 and 45% RH respectively are higher than $0.53 \times 10^{-8} \text{ m}^2/\text{s}$ measured in this study for mortar OPC. However, they are in a similar range, also considering that there are differences in the w/c (0.48 vs. 0.50 in [26]), in the measuring gas (4 vs. 100% CO_2 in [26]) and in RH (17 vs. 10 and 45% in [26]).

The linear relationship between diffusion coefficients $D_{O_{2,c}}$ and $D_{CO_{2,c}}$ found both in this study and in [25] indicates that the diffusion of the two gases is not influenced differently by the cement-specific pore systems. This linear relationship is an important observation. If it applies for all types of pore systems in cementitious materials, it would be sufficient to determine the oxygen diffusion coefficients D_{O_2} in order to calculate the CO_2 diffusion coefficients D_{CO_2} . This approach has two main advantages. First, steady-state conditions are reached much faster with O_2 compared to CO_2 , reducing the measurement time and the amount of gas consumed. Secondly, based on this observation the previously-mentioned impossibility of measuring the diffusion coefficient D_{CO_2} in non-carbonated samples could be bypassed.

While carbonation appears to coarsen the porosity of cementitious materials, it is at the moment unclear how it affects the ratio D_{O_2}/D_{CO_2} that was determined experimentally on carbonated samples in this study. It is possible that for non-carbonated materials, with a different proportion of fine and coarse pores, this ratio might vary to a certain extent (see discussion in Houst and Wittmann [25]). While this issue may be possibly solved in the future by numerical modelling of gas diffusion in the pore space, our assumption that the ratio is constant may be used as a starting point for current reactive/diffusive models.

This initial assumption may be corroborated to a certain extent by looking at the fundamentals of gas diffusion in porous materials. As observed by Houst

and Wittmann [25], one would expect a diffusivity ratio of O_2 and CO_2 of $\frac{D_{O_2}}{D_{CO_2}} = \sqrt{\frac{M_{CO_2}}{M_{O_2}}} \cong 1.17$, where M_{CO_2} and M_{O_2} are the molar masses of the two gases, if diffusion in a pore system made of straight cylindrical pores and Knudsen diffusion as the dominating diffusion mechanism are assumed.

Houst and Wittmann [25] calculated mean free paths of 73 nm for O_2 and 45 nm for CO_2 for the temperature and pressure conditions of their experiments. These values may be slightly underestimated, since they were calculated assuming pure O_2 or CO_2 gases, while in [25] a mixture of 78% N_2 , 20% O_2 and 2% CO_2 (and water vapor) was used. Also in this paper, mixtures of N_2 and O_2 or of all three gases were present in the pores of the mortars during the measurements.

Furthermore, considering the pore size distributions of the mortars studied in this paper (see Fig. 3), a substantial amount of pores have a diameter smaller than about 100 nm, even in the carbonated mortars. Moreover, in mature mortars, the main gas diffusion paths are expected to be through the gel pores and the small capillary pores due to the depercolation of the capillary pores [37, 38]. For these small pores, with sizes ranging from a few nm to tens of nm at most, the mean free path of the gases is larger than the diameter of the pore. Therefore, Knudsen diffusion is expected to dominate. This will also affect the overall diffusion through the whole pore system of the mortars, since Knudsen diffusion is substantially slower than normal diffusion occurring in the larger pores. This is also the conclusion of Houst and Wittmann [25] for their cement pastes with w/c 0.40 and 0.50.

Additional studies are needed to confirm the difference between diffusion coefficients D_{O_2} and D_{CO_2} . Furthermore, more information on the kinetics of CO_2 binding by cement hydrates is required to better understand its impact on the CO_2 diffusion and progress of the carbonation front.

5 Conclusions

In this study, the diffusion coefficient D_{O_2} was determined on non-carbonated and carbonated mortars with different binders, while the diffusion coefficient D_{CO_2} was measured only on carbonated mortars, since CO_2 binding made this measurement impossible in

non-carbonated mortars. Additionally, changes in the porosity and pore size distribution of the mortars in the non-carbonated and the carbonated state were analyzed using MIP. The results obtained from the five different mortars allow to draw the following conclusions:

- In mortars OPC, L-15 and P-15, carbonation leads to a decrease of diffusion coefficient D_{O_2} , while an increase is observed in mortars MS-15 and SL-66, both containing siliceous additions.
- The decrease of diffusion coefficient D_{O_2} is caused by a reduction of total porosity due to carbonation that dominates the simultaneous coarsening of the pore system in case of mortars OPC, L-15 and P-15.
- The increase of diffusion coefficient D_{O_2} observed in mortars MS-15 and SL-66 is the result of more pronounced coarsening of the pore system in case of mortar MS-15 and increase of total porosity with a coarsening of the pore system in case of mortar SL-66.
- Diffusion coefficients D_{O_2} and D_{CO_2} show a linear relationship with lower values for diffusion coefficients D_{CO_2} by a factor of 1.37 (compare with 1.27–1.46 found in [25] for a cement paste with w/c 0.50).
- Since the ratio between the diffusion coefficients D_{O_2} and D_{CO_2} is constant in mortars with different binders, it is hypothesized that one can calculate the diffusion coefficient D_{CO_2} of non-carbonated mortars by measuring their diffusion coefficient D_{O_2} and dividing by the ratio 1.37 found in carbonated mortars. However, CO_2 binding during diffusion in non-carbonated material has still to be taken into account.

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Compliance with ethical standards

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

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