Effect of Selected Process Parameters During Carbonation Hardening on the CO_2-Binding Potential of Cementitious Materials

Elena Woydich(✉), Anne Heisig, Harald Hilbig, and Alisa Machner

Department of Materials Engineering, Professorship for Mineral Construction Materials,
Technical University of Munich, TUM School of Engineering and Design, Franz-Langinger-Str.
10, 81245 Munich, Germany
e.woydich@tum.de

Abstract. The cement industry faces an urgent challenge to reduce CO_2-emissions. A promising technology to bind CO_2 permanently in cementitious systems is Carbon Capture and Utilization (CCU). Carbonation hardening represents one approach of CCU technologies, and consists of the following steps: pre-curing, carbonation curing and post-curing. The process parameters at each step affect the carbonation degree and rate.

During carbonation curing, combined hydration and carbonation reactions take place. This includes the formation of hydrates as well as carbonates of anhydrous clinker minerals. These reactions proceed simultaneously and are difficult to separate. Therefore, to get a deeper insight into these reactions and to control them, the process parameters that affect the carbonation reaction need to be investigated. Particular interest is ascribed to the relative humidity (RH) in the system as this considerably affects the carbonation degree, since CO_2 needs to dissolve in water to react with the calcium from the cementitious phases.

This study investigates the effect of selected process parameters during the pre- and carbonation curing on the CO_2-binding potential of cementitious systems. For this, cement pastes were prepared and pre-cured for 6 h or 12 h at 30–80% RH. The carbonation curing was performed in a CO_2 chamber at a CO_2 concentration of 50% for different durations at 50% RH. The carbonate and bound water content in the samples were quantified with thermogravimetric analysis (TGA).

The results of this study will help elucidating the carbonation hardening mechanism and act as a basis for applying CCU on cementitious materials.

Keywords: CCU · carbonation curing · relative humidity · pre-curing

1 Introduction

Carbonation hardening of cement pastes is the chemical reaction of Ca^{2+} with CO_2 to form $CaCO_3$. Consequently, the limestone calcination during cement production is reversed by this reaction. Due to the formation of $CaCO_3$ in the cementitious microstructure, the cement paste also hardens. Carbonation hardening consists of the following steps: pre-curing, carbonation curing and post-curing. Pre-curing describes the period

A. Jędrzejewska et al. (Eds.): SynerCrete 2023, RILEM Bookseries 44, pp. 616–627, 2023.
https://doi.org/10.1007/978-3-031-33187-9_57

between the casting and the CO_2 exposure of the samples. This step entails the transformation of free water into bound water, due to the ongoing hydration. The following carbonation reaction can be controlled by several process parameters such as relative humidity (RH), pre-curing duration, carbonation curing duration and temperature [1]. The present study investigates the effect of selected parameters on the total amount of calcium carbonate formed and the degree of carbonation (DoC), i.e. pre-curing at various RH, the pre-curing duration and the carbonation curing duration.

Pre-curing is important, because the pre-curing duration and the RH affect the initial phase assemblage and moisture content in the sample at the beginning of the carbonation, i.e. the moment they are exposed to CO_2 [2]. Thus, this considerably affects the $CaCO_3$ formation during carbonation [1]. Depending on the hydration state of the system prior to carbonation, there are two pathways how the carbonation reaction occurs: i) in the case of an advanced hydration, Ca-containing hydrates, such as portlandite (CH) or C-S-H phases are present. Then, these hydrates dissolve and deliver Ca^{2+} to the pore solution, which reacts with the $CO_3{}^{2-}$ in the pore solution. ii) at very early times of hydration, the anhydrous clinker phases did not form considerable amounts of hydrates yet [3]. Then, the Ca^{2+} from the anhydrous silicates dissolves into the pore solution and react directly with the $CO_3{}^{2-}$ [1, 4].

The goal of this study was to investigate the effect of RH and duration of the pre-curing and carbonation curing duration on the amount of calcium carbonate formed in cement paste samples. Therefore, samples were cast and pre-cured for either 6 h or 12 h at 30%, 50%, 80% RH. The carbonation curing was performed at 50% CO_2 concentration for 12 h, 18 h and 24 h at 50% RH. To obtain information on the carbonation degree, the bound water and the calcium carbonate content in the samples are determined by thermogravimetric analysis (TGA).

2 Materials and Methods

2.1 Materials and Cement Pastes Preparation

For preparing the cement paste samples, a CEM I 52.5 N supplied by Heidelberg Materials was used. Table 1 shows the chemical composition of the cement determined by ICP-OES (Avio 500 ICP-OES from PerkinElmer).

Table 1. Chemical composition of the CEM I 52.5 N determined with ICP-OES [wt.%/g cement, $_{\text{ignited}}$] and Blaine specific surface area [cm^2/g].

Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SO_3	SiO_2	TiO_2	Blaine
5.3	63.7	3.4	1.1	1.7	0.3	3.1	18.7	0.3	4070

The pastes were prepared in batches of 500 g cement with a water to cement (w/c) ratio of 0.4 according to DIN EN 196-1. After mixing, the pastes were filled into a Teflon formwork (1.5 cm × 1.5 cm × 6 cm) and were compacted for 60 s on a vibrating table at 50 Hz. Then, the samples were left in the formwork for approx. 20 – 30 min until the surface has stiffened and the specimens remain true to shape. The sides of the formwork were removed, so that the CO_2 can penetrate from three sides into the sample. The samples pastes were firstly pre-cured for 6 h or 12 h at 30%, 50%, 80% RH and afterwards placed in the carbonation chamber (Mytron Bio- und Solartechnik GmbH). The carbonation curing duration at 50% RH and 50% CO_2 concentration was set to either 12 h, 18 h or 24 h. Table 2 gives an overview of the samples and the pre-curing and carbonation curing conditions investigated within this study. The nomenclature consists of the duration and conditions of pre-curing and the carbonation curing. As an example: A sample that was pre-cured for 6 h at 30% RH and then carbonated for 18 h (at 50% RH) is labelled $6H_{30}18C$. In addition, reference samples were prepared, which were cured at similar conditions as the carbonated samples but at atmospheric CO_2 concentration (approx. 0.04%), allowing for the differentiation of both reactions. The sample preparation and curing were performed at 20 °C for all samples.

2.2 Methods

The phase assemblage, the bound water and the carbonate content were analysed in all samples after carbonation curing using TGA. Prior to the analyses, the hydration of the samples was stopped by applying a double solvent exchange [5]. For this, the samples were crushed into smaller pieces and homogenised using a horizontal ball mill for 5 min at 30 Hz. This treatment grinds the samples to a fine powder ($< 63\ \mu m$). Then, the powder samples were immersed for 5 min in 100 mL isopropanol and subsequently for 5 min in 40 mL diethylether. After filtration, the samples were dried in a desiccator overnight at -0.02 bar relative pressure. TGA analyses were carried out using a Netzsch STA F3 Jupiter. The corundum crucibles were filled with 25 mg ± 4 mg sample powder and the analyses were performed over the range of 30 °C – 900 °C at a heating rate of 10 K/min. The measurement cell was purged with N_2 gas (20 mL/min) during the measurement. For evaluation of the TGA data, the first derivative (DTG) of the weight loss (WL) graphs was calculated to determine phase changes in the samples. Based on the peaks in the DTG graphs, the WL graphs were divided into several sections, according to the description in [6]. The WL was determined by the horizontal stepwise method according to [6]. The calcium carbonate (CC) content was determined by using Eq. (1) and the bound water content (BW) analysed by using Eq. (2), where w refers to the sample weight at a specific temperature.

$$CC = \frac{w_{(400^\circ C/500^\circ C*)} - w_{900^\circ C}}{w_{900^\circ C}} \times \frac{100}{44} \tag{1}$$

$$BW = \frac{w_{30^\circ C} - w_{400^\circ C/500^\circ C*}}{w_{900^\circ C}} \tag{2}$$

**Temperature range adapted depending on the WL graphs of the carbonated and the hydrated samples as described in* Sect. 3.2.

The degree of carbonation (DoC, see Eq. (5)) was determined by dividing the CO_2 content of the samples obtained experimentally with TGA after carbonation (Eq. (4)) by the theoretical maximum CO_2 content (Eq. (3)) [7] that the anhydrous cement could take up according to the CO_2 reactants.

$$CO_2content, max = 0.785(CaO - 0.7SO_3) + 1.420Na_2O + 0.935K_2O \tag{3}$$

$$CO_2content, exp. = \left(\frac{w_{400^\circ C-900^\circ C}}{w_{900^\circ C}}\right) * 100 \tag{4}$$

$$Degree\ of\ carbonation\ (DoC)\ [\%] = (\frac{CO_2content, exp.}{CO_2content, max}) * 100 \tag{5}$$

where CaO, SO_3, Na_2O, K_2O are the content [wt.%] of these oxides in the ignited cement (see Table 1).

3 Results

3.1 Variation of Pre-curing Duration

Figure 1 shows the CC content after carbonation of samples with the same sample ages (24 h) that were pre-cured for 6 h or 12 h at various relative humidities (30–80% RH). On the second y-axis, the CC content was corrected by subtracting the initial CC content present in the cement (5.4 wt.%). According to Fig. 1, the samples $6H_{50}18C$ und $6H_{80}18C$ show a similar amount of CC (~42 wt.%). Lowering the pre-curing humidity to 30% RH ($6H_{30}18C$) results in a reduction in CC content (to ~31 wt.%). The effect of the RH during pre-curing is more obvious with an expanding pre-curing duration.

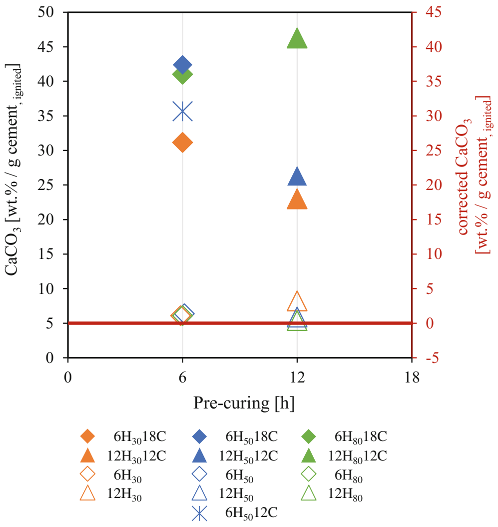

Fig. 1. $CaCO_3$ content of samples with sample ages (24 h) that were pre-cured for 6 h or 12 h at various RH (30, 50, 80%). In addition, the sample pre-cured for 6 h at 50% RH and 12 h carbonation cured and the reference samples ages (6 h and 12 h, hollow symbols) are shown as well. The error of all results is approx. 2 wt.%.

For the samples pre-cured for 12 h at 30 and 50% RH, a similar amount of CC and DoC could be determined after carbonation (see Fig. 1 and Table 2). Interestingly, the samples, which are pre-cured at 30% and 50% RH for 12 h and carbonated for 12 h, show a lower amount of CC compared to the samples that are pre-cured for 6 h. This could be caused by a shorter carbonation curing duration (12 h to 18 h). However, the results of the samples $6H_{50}12C$ compared to $12H_{50}12C$ confirm that longer pre-curing results in a decreased CC content and DoC after carbonation. The amount of CC in the hydrated reference samples results from the cement and from the uptake of the atmospheric CO_2 during curing.

3.2 Variation of the Carbonation Curing Duration

Figure 2 shows the WL and DTG curves of samples with same sample age (various pre-curing and carbonation curing duration) and samples with same carbonation curing duration (24 h). The samples $6H_{50}18C$, $6H_{50}24C$ exhibit a higher weight loss in the temperature range of bound water (up to 400 °C) compared to the samples with expanded pre-curing durations ($12H_{50}12C$ and $12H_{50}24C$), although more hydration products are supposed to be formed during the expanded pre-curing time [8–10]. In addition, the WL graph of the reference sample ($24H_{50}$) shows a lower weight loss due to bound water (up to 400 °C) compared to the carbonated samples (see Fig. 2 and Table 2).

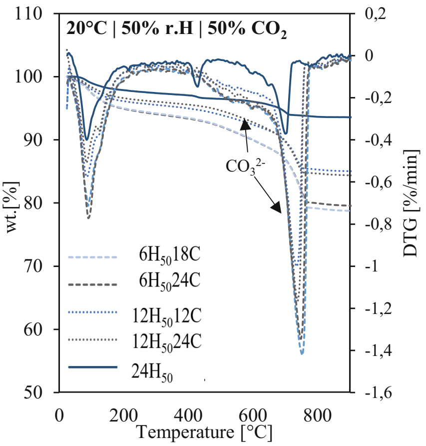

Fig. 2. TG and DTG curves from 30 – 900 °C of samples pre-cured at 50% RH for 6 h or 12 h and carbonated for 18 h, 12 h or 24 h respectively. In addition, the curves for the reference sample hydrated for 24 h are shown.

Between 400 °C and 500 °C the hydrated sample shows a WL, which represents the decomposition of CH [6]. The carbonated samples do not show the presence of CH but instead an continuous WL starting at 400 °C and ending at a peak at 600 – 900 °C, which is known to represent the decomposition of carbonates [6]. The shoulder on the carbonate peak at lower temperatures represents the decomposition of amorphous calcium carbonate (ACC) [10, 14, 15]. Consequently, the temperature ranges for carbonates and bound water in Eqs. (1) and (2) needed to be adapted for carbonated samples compared to the hydrated references. In addition, amorphous calcium carbonate was reported to accommodate a certain amount of so-called structural water, which can dehydrate below 400 °C [10, 11]. Water released from hydrates during carbonation consequently could be bound either in ACC or in hydrated silica gel [10, 12, 13]. The section between 600–900 °C indicates higher content of CC when the samples are pre-cured for a shorter duration (6 h compared to 12 h) regardless the carbonation curing duration of 18 h or 24 h. This will be further described in the following.

Figure 3 a) and b) show the CC content of all samples investigated within this study. In Fig. 3 a) the results for the samples with the same sample age (24 h) and different pre-curing and carbonation durations are shown. The samples pre-cured at 30% and 50% RH show higher CC precipitation after 6 h compared to 12 h of pre-curing. In addition, the sample pre-cured for 6 h at 50% RH shows a significant increase in the CC content compared to the sample pre-cured at 30% RH for the same duration.

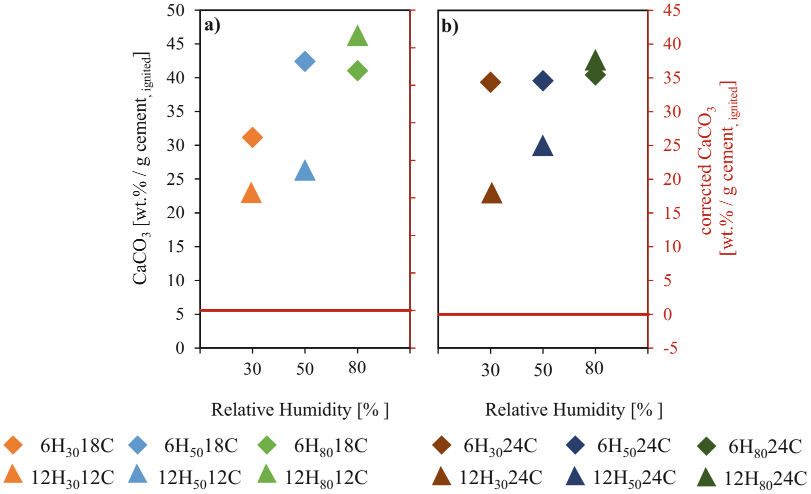

Fig. 3. CaCO$_3$ content after carbonation of samples pre-cured at 30, 50 or 80% RH for a) samples with sample age of 24 h and b) samples with carbonation curing duration of 24 h investigated within this study. The error of all results is approx. 2 wt.%.

This is less obvious after 12 h of pre-curing, where the samples pre-cured at 30 and 50% RH show a similar amount of CC. In contrast to this, the effect of pre-curing duration is less significant when samples are pre-cured at 80% RH. Here, the difference in CC content across all pre-curing durations is about 5 wt.%. When comparing the samples regarding their RH pre-curing conditions, the samples pre-cured at 80% RH show the highest amount of CC. In Fig. 3 b) the results for the samples that were carbonated for 24 h are shown. Expanding the carbonation curing duration leads to no significant increase in the CC precipitation for the samples pre-cured for 12 h at 30% and 80% RH. This is also true for the 6 h pre-cured samples at 80% RH. There is a significant increase in the CC content with carbonation curing time for the 6 h pre-cured samples at 30% RH and to a lesser extent for the 12 h pre-cured samples at 50% RH. It should be noted that the sample $6H_{50}18C$ (Fig. 3a) shows a higher amount of CC than the sample $6H_{50}24C$ (Fig. 3b). While the CC content is not necessarily increased by prolonged carbonation, it is not supposed to be decreased. We have no explanation for this at the moment, but additional measurements are being carried out.

Table 2. List of pre- and carbonation curing conditions of all samples investigated within this study. In addition, the bound water (BW) and the calcium carbonate (CC) content determined by TGA as [wt.%/g cement, $_{\text{ignited}}$] and the DoC [%] determined by Eq. (5) are given.

	pre-curing conditions		carbonation curing conditions			Results		
name	time	RH	time	RH	CO_2	BW	CC	DoC
	[h]	[%]	[h]	[%]	[%]	[wt.%]	[wt.%]	[%]
$6H_{30}18C$	6	30	18	50	50	5.7^a	31.2	27.5
$6H_{50}18C$	6	50	18	50	50	8.1^a	42.4	37.5
$6H_{80}18C$	6	80	18	50	50	8.6^a	41.1	36.3
$6H_{30}24C$	6	30	24	50	50	8.3^a	39.4	34.8
$6H_{50}24C$	6	50	24	50	50	6.7^a	31.4	35.0
$6H_{80}24C$	6	80	24	50	50	9.9^a	40.2	35.8
$6H_{50}12C$	6	50	12	50	50	7.0^a	35.7	31.5
$6H_{30}{}^*$	6	30	0	–	–	4.7^b	6.1	5.4
$6H_{50}{}^*$	6	50	0	–	–	4.5^b	6.4	5.7
$6H_{80}{}^*$	6	80	0	–	–	4.1^b	6.4	6.1
$12H_{30}12C$	12	30	12	50	50	5.6^a	24.0	21.2
$12H_{50}12C$	12	50	12	50	50	5.4^a	24.4	23.3
$12H_{80}12C$	12	80	12	50	50	7.3^a	46.3	40.9
$12H_{30}24C$	12	30	24	50	50	3.2^a	23.0	20.4
$12H_{50}24C$	12	50	24	50	50	5.2^a	30.0	26.5
$12H_{80}24C$	12	80	24	50	50	9.5^a	42.7	37.7
$12H_{30}{}^*$	12	30	0	–	–	6.1^b	8.2	7.3
$12H_{50}{}^*$	12	50	0	–	–	6.8^b	5.9	6.0
$12H_{80}{}^*$	12	80	0	–	–	7.6^b	6.4	6.2
$24H_{30}{}^*$	24	30	0	–	–	6.8^b	7.1	6.3
$24H_{50}{}^*$	24	50	0	–	–	7.3^b	7.5	7.0
$24H_{80}{}^*$	24	80	0	–	–	8.8^b	7.7	8.3

* *Reference samples* ^{a} *= The BW was determined up to 400 °C and CC from 400 °C*
^{b} *= The BW was determined up to 500 °C and CC from 500 °C*

4 Discussion

4.1 Effect of Pre-curing Conditions on the Calcium Carbonate Content

Samples of the same age (24 h) that were pre-cured for either 6 h or 12 h at various RH and carbonated for 18 h or 12 h, respectively, are compared ($6H_{30/50/80}18C$ and $12H_{30/50/80}12C$) in order to discuss the effect of the RH and the pre-curing duration on the CC content. The effect of the pre-curing duration differs depending on the RH. At 30% and 50% RH, the samples pre-cured for 12 h ($12H_{30}12C$ and $12H_{50}12C$) contain less CC and show a lower DoC after carbonation compared to samples pre-cured for 6 h ($6H_{30}18C$ and $6H_{50}18C$, see Fig. 1 and Table 2). The pre-curing duration has a lower impact on the CC precipitation when the samples are stored at 80% RH (see Fig. 1 and Table 2). While we mostly compare samples that were carbonated for different carbonation curing durations (12 h vs 18 h), this is also visible for samples carbonated for the same duration ($12H_{50}12C$ vs $6H_{50}12C$). Therefore, the amount of CC and the DoC in the samples decreases with increasing pre-curing duration at 30% and 50% RH. This is in agreement with the pre-curing study in [4], as they saw a decrease in the CO_2 uptake with increase pre-curing durations.

This can be explained by the fact, that carbonation is a diffusion-controlled process. Upon hydration, the formation of hydrates leads to a refinement of the microstructure and could hinder the penetration of CO_2 into the sample and decelerate the carbonation reaction. After 12 h of pre-curing, the hydration has progressed considerably more than after 6 h. This can be seen in the increase of the bound water content due to the ongoing formation of hydrates (see Table 2, comparing $6H_{30/50/80}$ and $12H_{30/50/80}$). Additionally, there is a chemical difference: The carbonation reaction occurs with the present hydrates and/or the anhydrous clinker. When the hydration is less advanced (e.g., after 6 h), the hydration of the clinker phases did not yet form considerable amounts of hydration phases, but instead the dissolved Ca^{2+} ions potentially react with the CO_2 directly. This reaction is assumed to proceed quite fast [4]. However, hydrates such as portlandite also have a high carbonation affinity and carbonate fast [17, 18]. The carbonation affinity of hydrates as well as anhydrous silicate phases can strongly vary depending on the carbonation curing conditions [4, 19]. Further investigations to the reaction process at the applied conditions are needed.

The results in Fig. 3b) confirm that a shorter pre-curing duration (6 h) at 30% RH leads to an increased CC precipitation in the cement paste samples compared to pre-curing for 12 h also for a carbonation curing duration of 24 h. However, it seems at 50% and 80% RH, the pre-curing duration does not have a significant effect on the amount of CC formed. This is visible in Fig. 3b) where the samples pre-cured for 6 h ($6H_{50}24C$ and $6H_{80}24C$) show similar CC contents as the samples pre-cured for 12 h ($12H_{50}24C$ and $12H_{80}24C$) after carbonation curing for 24 h.

The results in Fig. 3a) and b) show a general trend of increased CC content after carbonation curing with increasing RH during pre-curing. The only exception from this is the sample $6H_{50}24C$. This is not expected at first, as the hydration is assumed to proceed faster, or at least not slower, at 80% RH than at lower RH. This would lead to a similar or even denser microstructure after pre-curing at 80% RH compared to 30% RH and should potentially limit the carbonation reaction as described above.

However, the water content in the pores is an important aspect for an efficient carbonation reaction at the time the CO_2 penetrates the sample. The moisture content in the pores is, amongst others, affected by the degree of hydration and the RH during curing. During hydration, water is bound in the hydrates and the water content in the pores is reduced. After 6 h of pre-curing at an RH of 50% or 80%, the available moisture in the pores seem to be sufficient to accelerate the carbonation compared to 30%, see Fig. 1 and Fig. 3.

After 12 h of pre-curing, the effect of pre-curing in high humidity becomes more noticeable. At 80% RH, it appears to be enough moisture available in the pores, while at 30% and 50% RH there may not be enough moisture to accelerate the reaction. Yet, the higher CC content for samples pre-cured at 80% RH compared to 30% or 50% RH ($12H_{30/50/80}12C$ and $12H_{30/50/80}24C$), can be explained by the fact that the carbonation of solid phases is not only diffusion-controlled but also requires a dissolution and precipitation reaction [18]. At 30% and 50% RH there is potentially not enough water present in the pores to dissolve sufficient Ca^{2+} ions to form considerable amounts of CC.

Unless the pore system is clogged, higher moisture content in the system can adsorb a larger amount of CO_2 and dissolve a larger amount of Ca^{2+}. Therefore, a higher RH could promote the carbonation reaction. It should be noted that the amount of Ca^{2+} in the liquid phase depends on the solubility of Ca^{2+}, e.g., depending on the pH and the stability of the dissolving phases that deliver Ca^{2+} into the pore solution, e.g., a clinker phase or a hydrate. However, the important factor is the amount of CO_2 that is adsorbed for initiating the reaction [20, 21]. The Ca^{2+} ions eventually also precipitate as calcium carbonate. The amount as well as the spatial distribution of the $CaCO_3$ formed, depend on the amount of the liquid phase in the system. The precipitation of $CaCO_3$ can be observed in the pore space filled with solution and around the cement particles, depending on the reaction conditions [4, 19, 22]. The investigation of the pore solution composition and the microstructure was not part of this study but will be performed in a further study to explain this in more detail.

4.2 Effect of Carbonation Curing Duration on Calcium Carbonate Content

In this chapter, we discuss the effect of the carbonation curing duration comparing samples with the same pre-curing duration (6 h or 12 h) but different total sample ages (18 h, 24 h or 36 h).

The results in, Table 2, Fig. 2 and Fig. 3a) and b) show that for samples pre-cured for 12 h at 50% RH an increase in the carbonation curing duration from 12 h ($12H_{50}12C$) to 24 h ($12H_{50}24C$) results in an increase in the amount of CC formed. This indicates that after 12 h of carbonation, the reaction is not fully completed. Due to the denser microstructure after 12 h of pre-curing, the diffusion of CO_2 and consequently the formation of CC proceeds slower than in samples pre-cured for 6 h. However, this effect could not be seen for samples pre-cured at 30% and 80% RH, where an increase in the carbonation curing duration did not result in an increase CC content. The reason for this is unknown and requires further investigation.

When looking at samples that were pre-cured for 6 h, the carbonation curing duration has different effects on the CC content and DoC depending on the RH during pre-curing. When the samples were pre-cured for 6 h at 80% RH, an increase in the carbonation curing duration from 18 h to 24 h does not yield an increase in the CC content, see Table 2. This indicates that for these conditions the maximum CC content and DoC is already reached after 18 h of carbonation. However, when the samples were pre-cured for 6 h at 30% RH, an increase in the carbonation curing duration from 18 h to 24 h results in an increased CC content. This indicates that at 30% RH the carbonation reaction is not fully completed after 18 h of carbonation curing and confirms the impact of the moisture content in the samples on the carbonation reaction rate, as already discussed in Sect. 4.1.

It should be noted, after the samples were pre-cured for 6 h at 50% RH, an increase in the carbonation curing duration from 18 h to 24 h results in an apparent decrease in CC content. This is supposed to be an artefact, as described in Sect. 3.2.

5 Conclusion

This study focuses on the effect of the relative humidity (RH) during pre-curing, the pre-curing duration and carbonation curing duration on the calcium carbonate content (CC) and the Degree of Carbonation (DoC). For this, cement pastes were prepared, pre-cured for 6 h or 12 h at 30–80% RH, and consequently carbonated at a CO_2 concentration of 50% for different durations at 50% RH. The carbonate and bound water content were quantified with TGA in all samples after carbonation.

For the samples pre-cured at 80% RH, no significant effect of elongating the pre-curing duration on the CC content could be observed. In contrast to this, it seems that at lower RH the effect of expanding the pre-curing duration has a higher impact on the CC content. There, the amount of CC is reduced in samples pre-cured for 12 h compared to 6 h. Due to the prolongation of the pre-curing duration, the hydrates can form a denser microstructure, which could hinder the CO_2 penetration into the sample. The samples with the same carbonation curing duration (24 h) and various pre-curing durations confirm this observation.

Generally, at higher RH and with shorter pre-curing durations the samples show an increase in the CC content and the DoC after carbonation curing. The key factors to receive a high carbonation precipitation is the initial phase assemblage and moisture content in the sample at the beginning of the carbonation curing. This is confirmed by the fact that the effect of carbonation curing duration is depended on the RH during pre-curing. Our results indicate that the carbonation of hydrates is slower compared to the carbonation of anhydrous or freshly reacted clinker phases, as the latter seem to dissolve Ca^{2+} more quickly. According to the results and the applied conditions in this study an overall degree of carbonation (DoC) of approx. 30% could be reached.

Overall, our results indicate that the RH at pre-curing has a higher impact on the final CC content than the pre-curing and carbonation curing duration.

This paper presents a part of an extensive study, in order to understand the mechanism of carbonation hardening in more detail and to investigate the effect of various process parameters. Further studies on process parameters, microstructure, and pore solution compositions are currently being carried out.

References

1. Zhang, D., Ghouleh, Z., Shao, Y.: Review on carbonation curing of cement-based materials. J. CO2 Utiliz. **21**, 119–131 (2017)
2. Stoian, J., et al.: New insights into the prehydration of cement and its mitigation. Cem. Concr. Res. **70**, 94–103 (2015)
3. Young, J.F., Berger, R.L., Breese, J.: Accelerated curing of compacted calcium silicate mortars on exposure to CO2. The American Ceramic Society No. 19-T-73 (1974)
4. Zhang, D., Li, V.C., Ellis, B.R.: Optimal pre-hydration age for CO2 sequestration through portland cement carbonation. ACS Sustain. Chem. Eng. **6**, 15976–15981 (2018)
5. Winnefeld, F., Schöler, A., Lothenbach, B.: Sample preparation. In: Scrivener, K., Snellings, R., Lothenbach, B. (Eds.), A Practical Guide to Microstructural Analysis of Cementitious Materials, pp. 1–32, CRC Press
6. Lothenbach, B., Durdziński, P., De Weerdt, K.: Thermogravimetric analysis. In: Scrivener, K., Snellings, R., Lothenbach, B. (Eds.), A Practical Guide to Microstructural Analysis of Cementitious Materials, pp. 178–206, CRC Press
7. Steinour, H.H.: Some effects of carbon dioxide on mortars and concrete-discussion. J. Am. Concr. Inst. (1959)
8. Thonemann, N., Zacharopoulos, L., Fromme, F., Nühlen, J.: Environmental impacts of carbon capture and utilization by mineral carbonation: A systematic literature review and meta life cycle assessment. J. Clean. Prod. **332**, 130067 (2022)
9. Zajac, M., Skocek, J., Durdzinski, P., Bullerjahn, F., Skibsted, J., Ben Haha, M.: Effect of carbonated cement paste on composite cement hydration and performance. Cem. Concr. Res. **134**, 106090 (2020)
10. Ihli, J., et al.: Dehydration and crystallization of amorphous calcium carbonate in solution and in air. Nat. Commun. **5**, 3169 (2014)
11. Bots, P., Benning, L.G., Rodriguez-Blanco, J.-D., Roncal-Herrero, T., Shaw, S.: Mechanistic insights into the crystallization of amorphous calcium carbonate (ACC). Cryst. Growth Des. **12**, 3806–3814 (2012)
12. Skocek, J., Zajac, M., BenHaha, M.: Carbon Capture and Utilization by mineralization of cement pastes derived from recycled concrete. Sci. Rep. **10**, 5614 (2020)
13. Morandeau, A., Thiéry, M., Dangla, P.: Investigation of the carbonation mechanism of CH and C-S-H in terms of kinetics, microstructure changes and moisture properties. Cem. Concr. Res. **56**, 153–170 (2014)
14. Ashraf, W., Olek, J.: Carbonation behavior of hydraulic and non-hydraulic calcium silicates: potential of utilizing low-lime calcium silicates in cement-based materials, Journal of Material. Science **51**, 6173–6191 (2016)
15. Goto, S., Suenaga, K., Kado, T., Fukuhara, M.: Calcium silicate carbonation products. Am. Ceramic Soc. **78**(11), 2867–2872 (1995)
16. Locher, F.: Zement: Grundlagen der Herstellung und Verwendung, Verl. Bau und Technik (2000). ISBN: 9783764004002
17. Librandi, P., Nielsen, P., Costa, G., Snellings, R., Quaghebeur, M., Baciocchi, R.: Mechanical and environmental properties of carbonated steel slag compacts as a function of mineralogy and CO2 uptake. J. CO2 Utiliz. **33**:201–214 (2019)
18. Mehdipour, I., Falzone, G., La Plante, E.C., Simonetti, D., Neithalath, N., Sant, G.N.: How microstructure and pore moisture affect strength gain in portlandite-enriched composites that mineralize CO2. ACS Sustain. Chem. Eng. **7**, 13053–13061 (2019)
19. Zajac, M., Skibsted, J., Skocek, J., Durdzinski, P., Bullerjahn, F., Ben Haha, M.: Phase assemblage and microstructure of cement paste subjected to enforced, wet carbonation. Cem. Concr. Res. **130**, 105990 (2020)

20. Rothstein, D., Thomas, J.J., Christensen, B.J., Jennings, H.M.: Solubility behavior of Ca-, S-, Al-, and Si-bearing solid phases in Portland cement pore solutions as a function of hydration time. Cem. Concr. Res. **32**, 1663–1671 (2002)
21. Galan, I., Glasser, F.P., Baza, D., Andrade, C.: Assessment of the protective effect of carbonation on portlandite crystals. Cem. Concr. Res. **74**, 68–77 (2015)
22. Zajac, M., Irbe, L., Bullerjahn, F., Hilbig, H., Ben Haha, M.: Mechanisms of carbonation hydration hardening in Portland cements. Cem. Concr. Res. **152**, 106687 (2022)