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# Modification of cementitious building materials by treatment with $CO_2$

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The aim of this study was to determine the effect of $CO_2$ treatment conditions and cement composition (i.e. alkali and $C_3A$ content, cement fineness) on the microstructure, phases and the strength of hardened cement paste and mortar. The results show that $CO_2$ treatment at elevated pressures produces significant changes in the microstructure of hardened cement paste. The decomposition of the hydrates and, to some extent, non-hydrated clinker minerals to form $CaCO_3$ phases (mainly calcite) produces a dense microstructure and increases strength significantly. The strength increased with $CO_2$ pressure and the duration of treatment. A further increase in strength occurred during the subsequent storage of carbonated specimens in water or in air at 20 °C and 65 %RH owing to the ongoing hydration of residual clinker minerals. Specimens treated with supercritical $CO_2$ and then stored at 20 °C and 65 %RH reached a 28 d compressive strength which almost doubled the standard 28 d standard strength. The use of cements with a higher fineness (strength class) reduced the carbonation rate and therefore the gain in strength, owing to the lower porosity of the initial material made with these cements. The higher alkali contents of the cement led to a slower carbonation. The largest depth of carbonation and the highest increase in strength were obtained for cements with low $C_3A$ and alkali contents.

**Key words**: Portland cement, supercritical carbonation

## Introduction

The carbonation of concrete by atmospheric $CO_2$ is usually a slow process which lowers the pH value of the pore solution in the near-surface layer of concrete, thus contributing to the corrosion of steel reinforcement. However, it is also known that carbonation can increase the strength of cementitious construction components under certain conditions [1–5]. Shi et al. [2] have noted that carbonation can be an alternative to heat treatment for increasing the strength of lightweight concrete at an early age [2]. Shao et al. [3] significantly increased the early strength of cement-bonded fibre boards by treatment with exhaust gas from a rotary kiln. Moreover, the use of $CO_2$ gas during the production of cement-bonded wood fibre board has a positive effect on strength development [4, 5].

In the recent years, efforts have been made to develop new efficient binder systems with respect to increasing $CO_2$ capture during material production. Magnesia binders (Novacem) [6] have been developed for mineral $CO_2$ sequestration where carbonation contributes to hardening. De Silva et al. [7] have shown that the artificial carbonation of lime-magnesia binder specimens at 20 bar results in a significant increase in strength. Moreover, hydraulically inactive calcium silicates, such as $\gamma$-$Ca_2SiO_4$ and wollastonite ($CaSiO_3$), can be activated by carbonation [8]. Recent publications [9, 10] report the development of a novel binder with hydraulically inert calcium silicates – rankinite ($3CaO{\cdot}2SiO_2$) with wollastonite or pseudowollastonite ($CaO{\cdot}SiO_2$). Carbonation in $CO_2$-rich gas at atmospheric pressure and temperatures between 20 and 60 °C leads to a setting and hardening of this binder. Strength is produced by the formation of calcite and amorphous $SiO_2$. This binder is suitable for the production of precast concrete components. According to some authors, the hardened concrete can reach compressive strengths up to 70 MPa and flexural strengths up to 8 MPa.

In the 1990s, American patents were filed on the treatment of materials with cement or lime binders with supercritical $CO_2$ ($scCO_2$) to enhance strength [11]. Later scientific publications on the effect of $scCO_2$ considered mainly the phases and structural changes in hardened cement pastes [12–14]. It has been found that $scCO_2$ treatment of hardened cement paste leads to a complete degradation of portlandite, C-S-H phases and ettringite while forming calcium carbonate. Out of the three $CaCO_3$ modifications, calcite forms preferentially. Carbonation of the C-S-H phases leads to the formation of a highly polymerized silica gel [13–16]. The porosity of the hardened cement paste deceases during treatment [12, 14, 15] while the compressive strength increases significantly [15]. Short et al. [14] have noted that the relative humidity during the preliminary storage of hardened cement paste specimens affects the treatment process with $scCO_2$, the most favourable relative humidity for storage before $scCO_2$ treatment being about 35 % for maximum phase changes. In addition, positive effects of $scCO_2$ treatment on strength are reported for cement-bonded glass fibres [16], wood fibreboard [17] and specimens with a cement-lime binder produced by pressing [18].

Earlier publications have paid little attention to the effect of the cement composition and fineness on the carbonation process and strength development of cementitious materials in $scCO_2$. It is expected that the alkali content of the cement affects the carbonation process due to the change in pore solution composition. The present work focuses on the effect of cement alkalinity, the amounts of $C_3A$ or $C_4AF$ in Portland cement and cement fineness (strength class) on changes in the microstructure, phase composition and strength of the hardened cement paste and mortar produced by treatment with $CO_2$.

## Methods and materials

The chemical compositions of the cements were determined by digestion in lithium metaborate and analysis using ICP-OES. The amounts of crystalline mineral phases were quantified by X-ray diffraction (theta-theta goniometer 3003 TT Agfa NDT Pantak Seifert). The addition of 10 % ZnO served as an internal standard for the determination of the amorphous fraction using the Rietveld refinement. Scanning electron microscopy studies were carried out on fragments and thin sections of hardened cement paste specimens

(SEM Jeol JSM5900LV). Quantitative analysis at selected points was performed with an EDX system (company Röntec). The porosity and pore size distribution of hardened cement paste specimens were determined by mercury intrusion porosimetry (Micromeritics AutoPore III). The specific surface area of cement specimens was determined according to Blaine, EN 196-6. The depth of carbonation was measured by spraying fractured specimen surfaces with an alcoholic phenolphthalein solution. The strength of the specimens was determined according to EN 196-1.

Tables 1 and 2 present the mineralogical and chemical composition as well as the Blaine specific surface area of the cements used. The alkali-rich cements C1, C1A and C1B are produced from clinker manufactured at the same cement plant and differ mainly in fineness. Cement C2 is a low-alkali cement. Cements C3 and C4 differ mainly in their contents of $C_3A$ and $C_4AF$.

**Table 1.** Mineralogical composition and Blaine specific surface area of the cements

| Cement | $C_3S$ | $C_2S$ | $C_3A$ | $C_4AF$ | Blaine area |
|---|---|---|---|---|---|
| | wt.% | | | | $cm^2/g$ |
| C1 | 56.6 | 11.3 | 6.6 | 12.6 | 3200 |
| C1A | 57.5 | 13.7 | 8.8 | 11.8 | 4000 |
| C1B | 57.0 | 13.7 | 8.7 | 9.2 | 5000 |
| C2 | 45.7 | 23.7 | 8.7 | 8.7 | 3250 |
| C3 | 56.0 | 15.6 | 9.1 | 7.1 | 2650 |
| C4 | 48.3 | 22.1 | 1.3 | 18.7 | 3600 |

**Table 2.** Chemical composition of the Portland cements

| Name | Cement | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | $Na_2O_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | wt.% | | | | | | | | |
| C1 | CEM I 32.5 R | 18.70 | 5.01 | 3.53 | 61.34 | 1.64 | 2.81 | 1.20 | 0.24 | 1.02 |
| C1A | CEM I 42.5 R | 18.56 | 5.86 | 3.52 | 63.74 | 1.76 | 3.17 | 1.24 | 0.25 | 1.06 |
| C1B | CEM I 52.5 R | 18.07 | 5.45 | 3.36 | 63.79 | 1.74 | 3.52 | 1.23 | 0.25 | 1.06 |
| C2 | CEM I 32.5 R | 22.09 | 4.95 | 2.80 | 62.55 | 0.99 | 2.70 | 0.46 | 0.26 | 0.56 |
| C3 | CEM I 32.5 R | 20.04 | 5.06 | 2.29 | 65.44 | 1.49 | 2.45 | 0.97 | 0.19 | 0.83 |
| C4 | CEM I 32.5 N SR | 20.00 | 3.71 | 5.60 | 63.67 | 1.88 | 2.35 | 0.84 | 0.12 | 0.67 |

Mortar specimens with dimensions 4×4×16 cm were produced according to the EN 196-1 with w/c ratios of 0.5. Crushed limestone sand with the particle size distribution of standard sand was used for the production of selected specimens. To investigate the effect of $Na_2O_{eq}$ on carbonation in detail, the alkali content of Portland cement C2 with an $Na_2O$ eq. of 56 wt.% was increased by adding NaOH to obtain the $Na_2O_{eq}$ of cement C1 (1.02 wt.%).

Parallel to the mortar specimens, cement pastes were prepared with a w/c ratio of 0.5. To prevent sedimentation of the flowable binder pastes, the pastes were poured into wide-mouth bottles and rotated until a mini slump of 7 ± 1 cm was reached before pouring into the moulds (160×40×40 mm).

After a 1 day storage in the moulds at 20 °C and >95 %RH, the mortar or paste bars was demoulded. Afterwards, the specimens were stored for 1 day at 20 °C and 65 %RH and then at 20°C and 35 %RH in a climatic chamber until $CO_2$ treatment. The $CO_2$ treatment was performed at specimen ages of 1, 7 and 14 days.

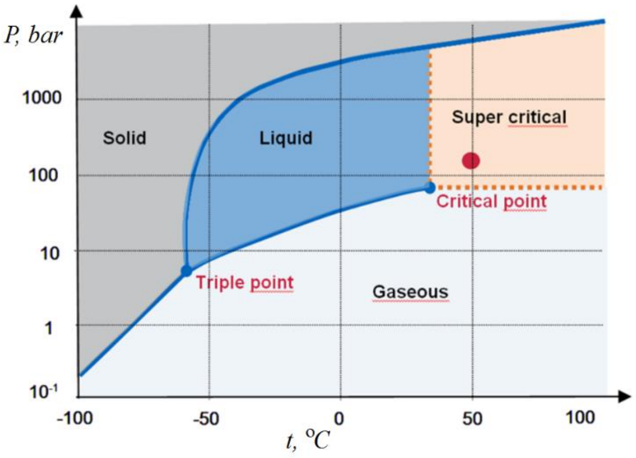

**Fig. 1.** Phase diagram of carbon dioxide [19]

The critical point in the Pt phase diagram of carbon dioxide (Fig. 1) is at 72.8 bar and 31.2 °C. The specimens were treated for 4 or 24 h in a reactor (Fig. 2) in $scCO_2$ at a pressure of 150 bar and a thermostatically controlled temperature of 50 °C (red dot, Fig. 1). The relatively high pressure of 150 bar was chosen to accelerate $scCO_2$ penetration into the hardened cement paste matrix. This pressure was reached within one hour. During the pressure build-up, the temperature of the mortar specimens increased up to about 60 °C due to the exothermic carbonation reaction in the pressure reactor; in the case of hardened cement paste specimens, the temperature increased up to about 75 °C.

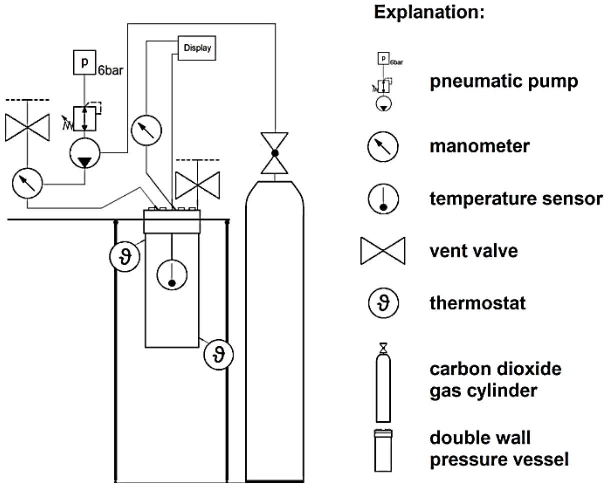

**Fig. 2.** Scheme for $scCO_2$ treatment

After treatment, the pressure was usually reduced over an hour. In some cases this period was extended to three hours, because the mortar specimens with C1A and C1B containing higher strength class cements disintegrated when depressurizing over one hour. In addition, 4 or 24 hour treatments with gaseous $CO_2$ were performed at 20 °C and 50 bar. After $scCO_2$ treatment, the specimens were covered with a damp cloth and, if necessary, cooled to 20 °C before measuring the depth of carbonation, length, weight and strength. Parallel tests were performed with non-carbonated reference specimens. Porosity, pore size distribution and microstructure were investigated using fragments of the specimens. The specimens were dried at 40 °C and ground to <32 µm for the XRD analysis of mineralogical composition.

## Results and discussion

### Carbonation depth

The rate of carbonation of hardened cement paste or mortar specimens depends primarily on the porosity and moisture content of the hardened paste [15]. The rate of carbonation decreases significantly with increasing moisture content and decreasing porosity. Thus the carbonation depth mortar bars after $scCO_2$ treatment increased with the duration of preliminary storage, i.e. with decreasing the moisture content (Fig. 3). A higher cement fineness (higher strength class) resulted in a higher degree of hydration of the cement and therefore in a lower porosity of the hardened cement paste which reduced the rate of carbonation.

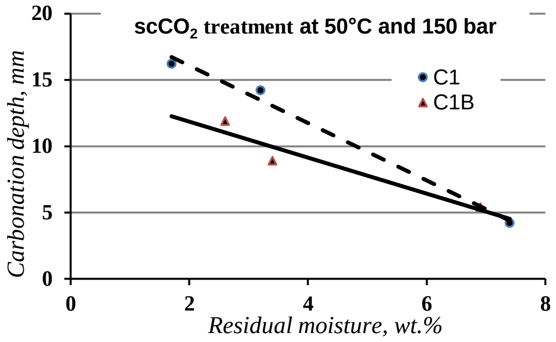

**Fig. 3.** Carbonation depths of mortar specimens with CEM 32.5 R (C1) and CEM 52.5 R (C1B) after $scCO_2$ treatment at 50 °C and 150 bar. Effect of moisture content of the specimens before carbonation. The moisture content was determined by drying the specimens at 50 °C to equilibrium.

At constant porosity, the alkali content of the hardened cement paste had a significant effect. The carbonation depths of the mortar specimens C1 and C2 depended on the alkali content of the cement. Specimens made with the higher alkali content cement C1 exhibited on the whole lower carbonation depths (Fig. 4). Cement C1 contains more alite and therefore more portlandite in the hardened paste than does the low-alkali cement C2. The porosities of the reference specimens C1 and C2 were almost identical. In order to clarify whether the alkali content of the cement or the alite content mainly affects the rate of carbonation, NaOH was, as already mentioned, added to the low-alkali cement to produce the same alkali content as cement C1. The alkali addition resulted in a lower carbonation rate as observed for the specimens with cement C1 (Fig. 4), i.e. the rate of carbonation decreases with the alkali content of the cement. The mortar specimens with the low-$C_3A$ and low-alkali cement SR-C4 were almost completely carbonated.

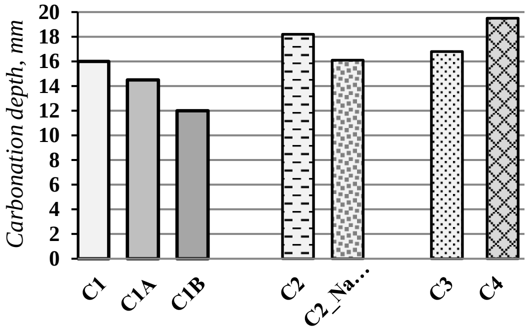

**Fig. 4.** Carbonation depths of mortar specimens after treatment in $scCO_2$ at 50 °C and 150 bar in dependence of cement. C2_NaOH: cement C2 with added NaOH for 1.02 wt.% $Na_2Oeq$.

### Compressive and flexural strengths

The $scCO_2$ treatment at 150 bar resulted in a significant increase in the compressive strength of the mortar specimens (Fig. 5). After 4 h treatment, relative strengths (based on the strengths of the reference specimens) of about 120 to about 270 % were measured depending on the carbonation depth (Fig. 5). The absolute compressive strengths of the specimens with Portland cement of strength class 32.5 R (N) were at 64 to 68 MPa significantly higher than the 28 d standard strengths of these cements (Fig. 6). The highest compressive strength 71 MPa was measured for mortar specimens with crushed limestone sand. However, these specimens contained a higher volume fraction of the binder paste owing to the replacement of standard sand by weight. The use of Portland cements with higher strength classes resulted in a lower increase in strength. The compressive strengths of the specimens with alkali low-cements C2 and C4 were higher than that of the alkali-rich cement C1.

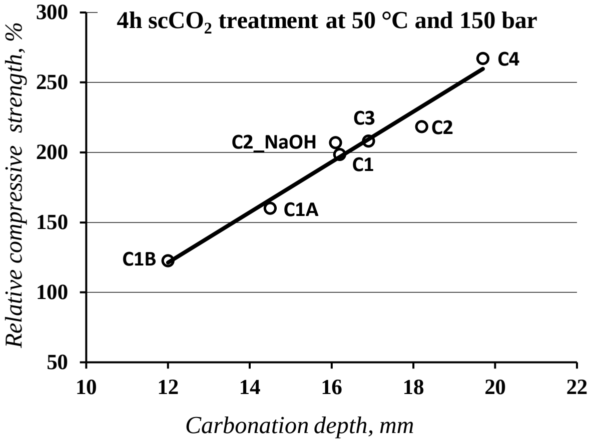

**Fig. 5.** Relative compressive strength in dependence of carbonation depth. Reference: the compressive strength of the reference specimens (identical preliminary storage) at the same age

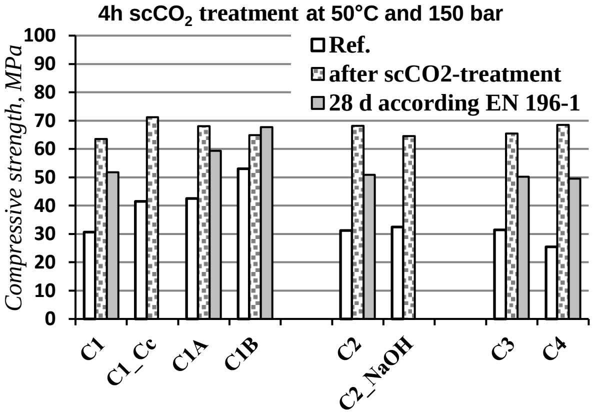

**Fig. 6.** Compressive strength of mortar specimens with different cements. C1_Cc: specimens with crushed limestone sand. C2_NaOH: cement C2 with added NaOH for 1.02 wt.% $Na_2O$eq.

Carbonation usually did not lead to an increase in the flexural strength of the mortar specimens (Fig. 7). In most cases, the flexural strength was lower than that of the reference specimens. Here, the specimens with cement C4 were an exception. The replacement of the quartz sand by crushed limestone sand with an equivalent granulometric composition significantly improved the flexural strength after carbonation. Apparently, the carbonaceous aggregate provided – as opposed to quartz sand – a surface for the crystallization of carbonate phases during treatment, thus improving the connection between the aggregate particles and the hardened cement paste matrix at the contact zone. Farahi et al. [18] also noted an increase in the flexural strength of mortar specimens with calcitic aggregate after $scCO_2$ treatment.

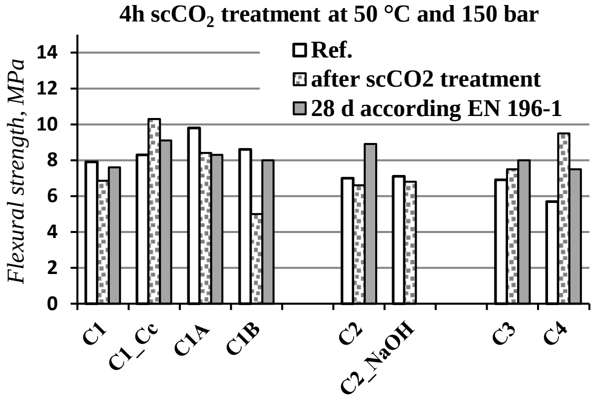

**Fig. 7.** Flexural strength of mortar specimens with different cements. C1_Cc: specimens with crushed limestone sand. C2_NaOH: cement C2 with added NaOH for 1.02 wt.% $Na_2O$eq

In earlier investigations [20], it has been found that an increase in the strength of hardened cement paste specimens with *w/c* = 0.6 can be produced after a 48 hour treatment at only 3 bar and 20 °C. Consequently, the mortar specimens with C1 were also exposed to gaseous $CO_2$ for 4 h or 24 h at 20 °C and 50 bar. In other tests, the treatment regime with supercritical $CO_2$ was extended to 24 h. Some of the treated specimens were stored in water at 20 °C or in the air at 20 °C / 65 %RH up to an age of 28 days.

As expected, the compressive strength increased with treatment pressure and time (Fig. 8). After 4 hours of carbonation at 50 bar, the increase in strength was significant. However, even after the subsequent storage until the age of 28 d in water, the strength was below the standard 28 d strength. The 24 hour treatment in gaseous $CO_2$ produced almost the same increase in strength as did the 4 hour treatment in supercritical $CO_2$. The subsequent storage of $CO_2$-treated specimens in water or in a climatic chamber at 20 ° C and 65 % RH led to a further increase in compressive strength. The highest 28 d compressive strengths were achieved after the subsequent storage at 20 °C and 65 %RH and were, in the case of 98 MPa for specimens treated with $scCO_2$ for 24 h, almost twice as high as the 28 d standard strength. The flexural strength also increased significantly and exceeded that of specimens stored for 28 d in accordance with DIN EN 196-1. After carbonation, a small proportion of clinker minerals did not react. After depressurizing, the calcium silicates react with water to form C-S-H phases and portlandite. During the subsequent storage, a pozzolanic reaction between portlandite and the silica gel formed during the carbonation is possible. The formation of C-S-H phases resulted in the further increase in compressive and flexural strength.

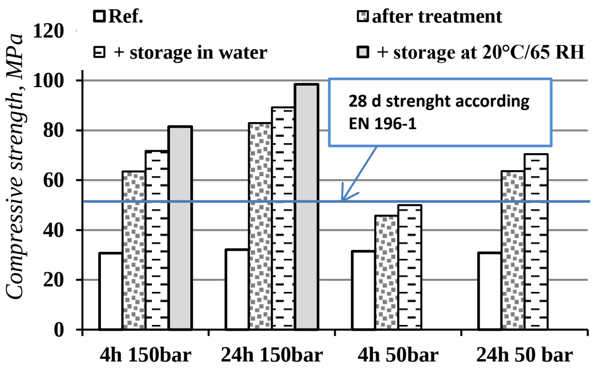

**Fig. 8.** Compressive strength of mortar specimens with cement C1 after various treatments

## Volume change

Immediately after carbonation, the mortar specimens exhibited an increase in length up to about 0.33 mm/m regardless of cement composition. The elongation increased with the intensity of treatment (pressure and time). The increase in length may result from (a) the volume increase of the solid phases when $CaCO_3$ forms from portlandite and (b) swelling due to the uptake of reaction water by the silica gel structure or the carbonated C-S-H phases. During the carbonation of portlandite, the volume of solid phases increases by about 2 % to 13 %, depending on the $CaCO_3$ modification formed. However, it is well-known that the carbonation of the C-S-H phases leads to a shrinkage process in the hardened cement paste. According to [21] and [22], this shrinkage is mainly due to the formation of highly polymerized silica gels and a corresponding reduction in volume. Whether the hardened cement paste shrinks or swells during carbonation in $scCO_2$ depends on the porosity of the initial hardened cement paste. In earlier studies [23] with hardened cement paste specimens having a high w/c ratio of 0.6, the pore space was found to be sufficient to accommodate an additional volume of solid phases without producing an expansive stress. In this case, the carbonation of the C-S-H phases causes the contraction of the specimens.

## Porosity and pore size distribution

The reference specimens with cement of strength class 32.5 possessed a relatively high porosity of about 40 vol.% for the hardened cement paste specimens and about 18 vol.% for the mortar. Cement composition and alkali addition only slightly affected the total porosity of the reference specimens. As expected, the porosity of the reference specimens decreased with increasing the strength class. Treatment with supercritical or gaseous $CO_2$ resulted in a significant reduction in porosity and an increase in the proportion of gel pores (<20 nm). The subsequent storage of the carbonated specimens in water led to an increase in the proportion of gel pores. Figure 9 shows, for example, the pore size distribution of the mortar specimens with cement C1.

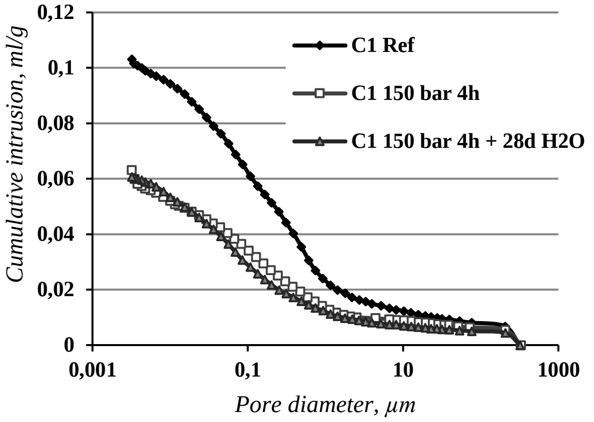

**Fig. 9.** Pore size distribution of mortar specimens with cement C1 before and after 4 h of treatment in $scCO_2$ at 50 °C and 150 bar and after the subsequent storage in water at 20 °C up to the age of 28 days

## Mineralogical investigations

The carbonation of the hardened cement paste affected the phase assemblage decisively. XRD revealed the usual hydrates of Portland cement, portlandite and ettringite in the reference specimens (Fig. 10) and, as the main constituent, X-ray amorphous phases attributable to C-S-H. In addition, calcite and the residual clinker minerals alite, belite ($\beta$-$C_2S$), brownmillerite ($C_4AF$) and small amounts of $C_3A$ were present. Treatment with $scCO_2$ reduced the amount of C-S-H phases (X-ray amorphous), and the hydrate phase ettringite was no longer identifiable. The amounts of residual calcium silicates $\beta$-$C_2S$ and $C_3S$ also decreased significantly. The small amounts of portlandite in the figure are due to the hydration of non-carbonated alite or belite directly after carbonation. Calcite was the dominant carbonate modification out of calcite, aragonite and vaterite. The alkalinity and the $C_3A$ content of the cements did not significantly affect the quantitative distribution of the carbonate modifications. The contents of carbonate phases in all the specimens treated with $scCO_2$ were in the order of size calcite > vaterite > aragonite. Phases with aluminium and sulphate were not identified by XRD in the carbonated specimens.

In earlier work [15], changes in the C-S-H and aluminous phases in the hardened cement paste during $scCO_2$ treatment were investigated using solid state NMR. $^{29}$Si NMR spectroscopy revealed that the quantity of sites $Q^0$, $Q^1$ and $Q^2$, associated with unhydrated silicates and C-S-H phases, decreased considerably during carbonation while forming $Q^3$ and $Q^4$ sites indicating a high degree of network formation (cross-linking). Studies with $^{27}$Al NMR showed the presence of aluminium in bridging tetrahedra $q^2$(2Si) as well as a large proportion of aluminium in ettringite in the hardened cement paste specimens before carbonation. During supercritical carbonation, ettringite disappeared and the aluminium incorporated in the silica gel structure containing predominantly $q^4$(4Si) sites.

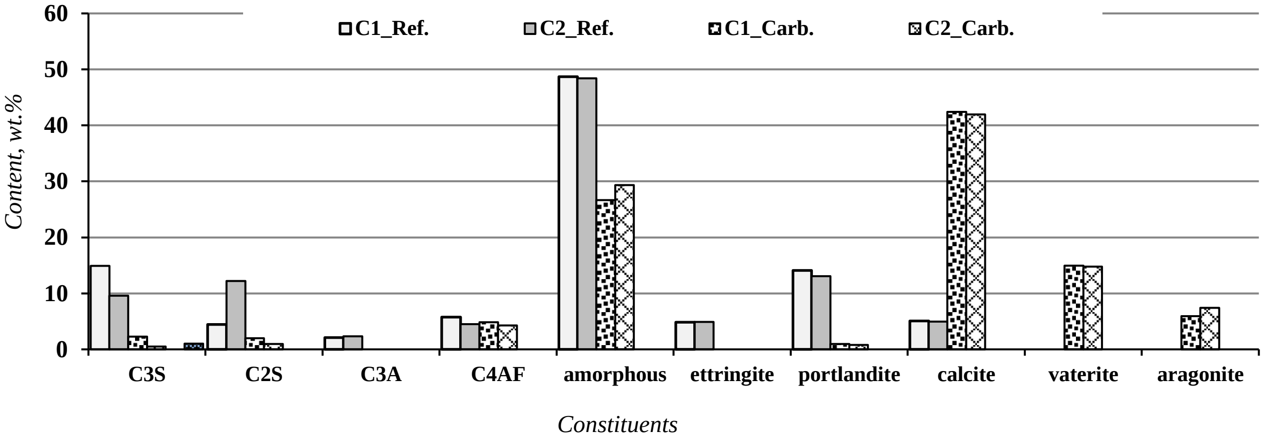

**Fig. 10.** Change in the mineralogical composition of hardened cement paste specimens with cements C1 and C2 after 4 h of carbonation at 50 °C and 150 bar

By means of scanning electron microscopy, residual clinker minerals $C_3S$, $C_2S$ and $C_4AF$ as well as the hydration products C-S-H and portlandite were observed in the microstructure of the hydrated cement paste (not shown). The $scCO_2$ carbonation led to a pronounced change in the hardened cement paste microstructure which became denser containing mainly irregularly shaped compact particles (Fig. 11).

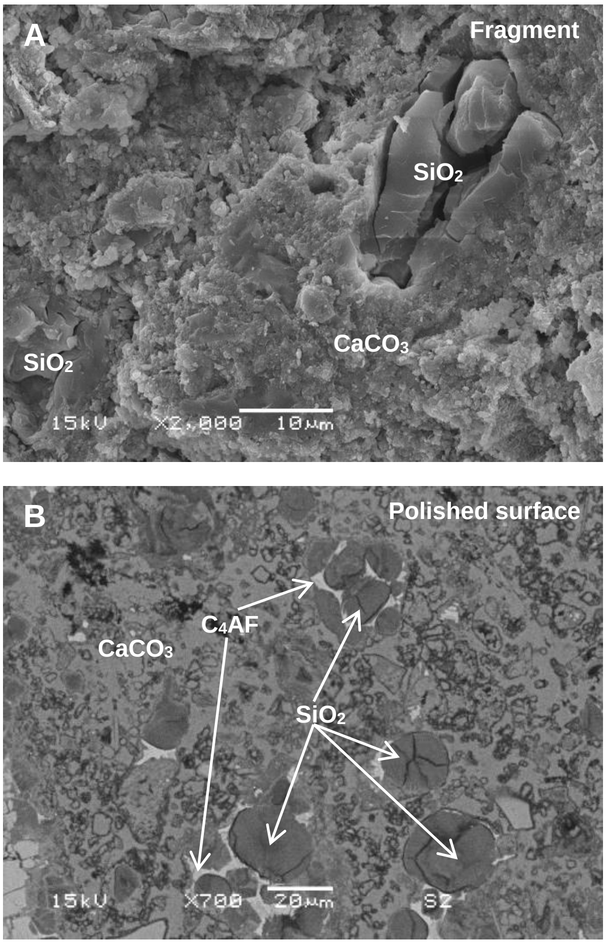

**Fig. 11.** Scanning electron micrographs of hardened cement paste after 4h of $scCO_2$ treatment. Secondary electron (A) and backscattered electron image (B), hardened cement paste with cement C1

Bright $C_4AF$ particles and dark Si-rich areas ($SiO_2 \cdot xH_2O$) embedded in a fine-grained carbonated binder matrix are apparent in the backscatter images of the polished surface of the carbonated specimens. The calcium silicates reacted during carbonation with the acidic pore solution to form silica gel particles with sizes up to about 30 µm. These directly replaced the original alite or belite particles. The C/S ratio of the silica gel particles calculated from EDX analysis was very low and ranged between 0.2 and 0.8. Residual calcium silicates $C_3S$ and $C_2S$ were only occasionally present (not shown).

## Conclusions

The test results show that the controlled carbonation treatment at higher $CO_2$ pressures results in a significant change in the hardened cement paste microstructure. The decomposition of hydration products and, to some extent, residual clinker minerals to form $CaCO_3$ phases, mainly calcite, produces a dense microstructure and increases compressive strengths significantly. The compressive strength was observed to increase with $CO_2$ pressure and the duration of treatment. An increase in flexural strength was obtained by using calcitic aggregates. A further increase in compressive and flexural strength occurred during the storage of specimens in water or air at 20 °C and 65 %RH after carbonation treatment. This was due to the hydration of residual clinker minerals. The specimens treated in $scCO_2$ and then stored at 20 °C and 65 %RH until an age of 28 almost doubled the standard 28 d compressive strength.

The initial porosity and moisture content of the hardened cement paste and mortar specimens affected the rate of carbonation decisively. The use of cements with a higher strength class affected the carbonation rate and therefore the strength gain unfavourably owing to the lower porosity before the treatment. Cements with a high alkali equivalent also reduced the rate of carbonation. The largest carbonation depth and the highest strength increase were obtained for specimens made with a cement low in $C_3A$ and alkalis.

$CO_2$ treatment could be applied in the production of, for example, cementitious, porous lightweight components (lightweight panels, wood concrete, etc.). Such materials would have no carbonation shrinkage and would be resistant to sulphate and other forms of alkaline chemical attack. Inexpensive, non-alkali-resistant glass fibres could be used to reinforce the material.

In view of the necessity to reduce the global $CO_2$ emissions, part of the $CO_2$ released during the production of Portland cement would be captured during the production of this new material.

## Acknowledgements

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## CEMENTINIO AKMENS MODIFIKAVIMAS APDOROJANT ANGLIES DIOKSIDU

### Santrauka

Darbe tirta karbonatizacijos įtaka įvairios sudėties cementinio akmens savybėms. Buvo nustatyta, kad karbonatizacija superkritinės būsenos anglies dioksidu daro didelį poveikį cementinio akmens mineraloginei sudėčiai ir mikrostruktūrai. Vykstant šiam procesui, iš dalies suardomi nehidratuoti klinkerio mineralai, kalcio hidrosilikatai ir kiti hidratai ir susidaro $CaCO_3$ fazės. Dėl to sumažėja cementinio akmens poringumas ir gerokai padidėja stipris gniuždant. Laikant apdorotus bandinius vandenyje ar ore, jų stipriai toliau didėja. Didesnė cemento stiprumo klasė ir didesnis šarmų kiekis cemente negatyviai veikia karbonatizacijos greitį ir stiprumines cementinio akmens savybes.