- Technical Paper -

EXPERIMENTAL METHODS TO EVALUATE DIMENSIONAL CHANGE INDUCED BY ACCELERATED CARBONATION IN SEVERAL HARDENED CEMENTITIOUS MATERIALS

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ABSTRACT

In this preliminary study, dimensional changes induced by C-S-H decalcification, supposed to occur when high degree of carbonation is achieved, was investigated in parallel to the drying shrinkage, using different shape and size's Ordinary Portland Cement and slag blended cement hardened specimens. Simple experimental methods to measure the dimensional change were evaluated and it was possible to verify the complexity of the shrinkage induced by carbonation and to identify that internal humidity is a key parameter to be considered, as important as the chemical composition of the cementitious material.
Keywords: accelerated carbonation, C-H-S decalcification shrinkage, carbonation shrinkage, drying shrinkage, GGBS.

1. INTRODUCTION

To achieve net zero emissions in the cement and concrete industry, carbon capture and utilization is considered the action with the highest potential. In this context, the accelerated carbonation and CO_2 uptake of cementitious materials has been investigated widely, and the influencing factors can be summarized in material chemical composition, microstructure properties and carbonation conditions.

Achieving a high degree of carbonation is beneficial to the CO_2 uptake. In the case of powder samples, the aqueous carbonation method showed high efficiency, extracting Ca ions from different hydrates and transforming them into Calcium Carbonate (CC). In the case of hardened cementitious samples, the difference is the existence of the microstructure, which is a barrier to the CO_2 diffusion. Also, when Ca ions are extracted from hardened samples, relevant structural changes occur due to C-S-H decalcification at Ca/Si ratio <1.2 and subsequent decomposition of C-S-H into silica gel. This leads to significant shrinkage in pastes and greater decalcification shrinkage was observed in silica fume blended cement, caused by its lower initial Ca/Si [1]. The measurement of decalcification shrinkage using displacement transducer measurement in cement pastes containing ground granulated blast furnace slag has already been reported [2]. However, there is still no standardized methodology to evaluate the dimensional change caused by accelerated carbonation, a recently discovered phenomenon which requires investigation when this technology is applied, for example, in concrete structures produced by the innovative CO_2 curing methods or in the treatment of recycled concrete aggregate. Therefore, in this preliminary study, different experimental methods to measure decalcification shrinkage (dimensional change) induced by accelerated carbonation in several hardened cementitious materials were evaluated in parallel to the drying shrinkage, considering factors that could affect this phenomenon, such as binder type and specimen's shape and size.

2. MATERIALS

2.1 Paste cylinder samples

Ordinary Portland Cement (OPC), in accordance with Japanese Industrial Standard JIS R 5210, and OPC with 50% ground granulated blast furnace slag (GGBS) replacement were used as binders. Considering the significance of introducing powder wastes from concrete recycling into the life-cycle of concrete, recycled concrete aggregate powder (RCAP), obtained as a by-product of the crushing process of demolished concrete; and returned fresh concrete sludge waste after removing the aggregates by a washing process (CSW) were used replacing 15% of the binder in mass, as well as the accelerated carbonated RCAP (CRCAP) and carbonated CSW (CCSW) and limestone powder (LSP), composed by $CaCO_3$ 99% purity. RCAP and CSW powders were carbonated in an accelerated carbonation chamber 5% CO_2 concentration, 20ºC temperature, 60% relative humidity (RH), for 7 days. Previous studies reported that the carbonation of powders samples is more efficient in high water content samples than in dry conditions, as Ca ions extraction and CO_2 dissolution may be suppressed in absence of water. So, during the carbonation period, water was added and mixed to the powders to keep the water/solid ratio in mass higher than 0.50. At the end of the carbonation period, CCSW was hydrated forming partially hardened blocks, so a mechanical grinding and sieving was applied to reduce the particle size to 150 μm under. CRCAP was only sieved to obtain 150 μm under particles. All powders wastes were dried at 40°C to remove the excess of adsorbed water. The particle size

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distribution is shown in the Fig. 1 and the amount of bond water (considering the temperature range between 40°C-550°C), Calcium Hydroxide (CH) content and CC content, obtained from thermogravimetric analyses (TGA) are presented in the Fig. 2. Cement pastes were prepared with a water-binder ratio (W/B) of 0.40 and cast in cylinder forms 35mm diameter per 10mm height (thick) and 38mm diameter per 5mm height (thin). The water curing period was settled to more than 91 days. The pastes mixtures are identified in the Table 1.

2.2 Mortar rectangular bar samples

To evaluate another measuring methodology, mortar specimens of two sizes, (40x40x160mm) and (20x40x160mm), were cast with pins. OPC and OPC with 70% GGBS were used as binders, the W/B was set to 0.60 and the sand-binder ratio was reduced from the usual value of 3.0 to 1.0. As carbonation occurs in the paste phase, the aim was to achieve high carbonation degree by preventing/compensating the paste content's reduction in mortar. Different from the pastes, no powder additions were used, and mortar was sealed cured for 7 days. The mortar mixtures are identified in the Table 2.
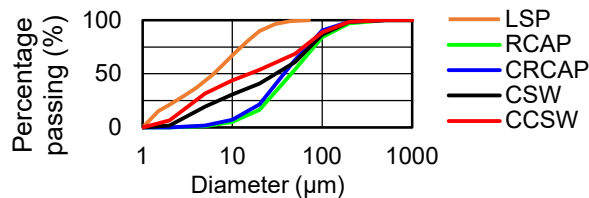

Fig. 1 Particle size distribution of powders used in pastes samples mixes
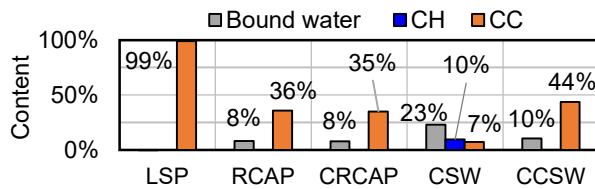

Fig. 2 Chemical composition of powders used in pastes samples mixes, from TGA

Table 1 Pastes mixtures identification

Mix	Binder	Powder
N	OPC	-
B	50% OPC + 50% GGBS	-
N-LSP	OPC	LSP
B-LSP	50% OPC + 50% GGBS	LSP
N-RCAP	OPC	RCAP
B-RCAP	50% OPC + 50% GGBS	RCAP
N-CRCAP	OPC	CRCAP
B-CRCAP	50% OPC + 50% GGBS	CRCAP
N-CSW	OPC	CSW
B-CSW	50% OPC + 50% GGBS	CSW
N-CCSW	OPC	CCSW
B-CCSW	50% OPC + 50% GGBS	CCSW

Table 2 Mortar mixtures identification

Mix	Binder	Powder
OPC	OPC	-
BC	30% OPC + 70% GGBS	-

3. EXPERIMENTAL TESTS PROCEDURES

3.1 Accelerated carbonation

Cylinder pastes and rectangular mortar bar samples were placed inside the carbonation chamber 20% CO_2 concentration, 20ºC, 60% RH after the curing period, without any additional drying time. Therefore, pastes were in saturated surface dry (SSD) conditions and mortars were between SSD and air-dry conditions, and drying shrinkage was allowed to occur in parallel to the accelerated carbonation. The CO_2 concentration was set higher for carbonating the hardened specimens, compared to the powders used in the section 2.1, to achieve higher carbonation degree in less time, and also considering the fact that most accelerated carbonation technologies propose concentrations around 14%, which is the CO_2 concentration in the exhaustion systems of cement industries. To facilitate water evaporation and CO_2 diffusion, all specimens' surfaces were exposed, without sealing. The comparative no CO_2 condition was a controlled chamber 20ºC, 60% RH with environmental CO_2 concentration.

3.2 Mass change measurement

Mass of pastes and mortar samples were recorded using digital scales with 0.001g and 0.01g precision, respectively.

3.3 Dimensional change measurement
(1) Pastes cylinder specimens

The diameter change of pastes samples, prepared according section 2.1, was measured periodically using digital measuring caliper 0.01mm resolution (Fig. 3 left). The diameter was measured in two perpendicular directions and the average was used in the dimensional change ratio calculation.
(2) Mortar rectangular bar specimens

The dimensional change of mortars bar samples, prepared according section 2.2, was measured using digital length comparator (Fig. 3 right). The average of three measurements, using two specimens, was used in the dimensional change ratio calculation.

3.4 Flexural and compressive strength

Flexural and compressive strength were obtained according to the test procedures of JIS R5201 Physical Testing Methods for Cement, for the mortar bars after finishing the curing period, from an average of two and four measurements, respectively.

Fig. 3 Dimensional change measuring methods

3.5 Carbonation depth

Carbonation depth of mortar samples were obtained using phenolphthalein solution indicator for additional (40x40x160mm) specimens, with only 2 opposite faces exposed to the same carbonation conditions of the dimensional and mass change measurements' specimens, without pre-drying and adapting the method proposed by JIS A 1152. The average of six measurements was recorded as a result.

3.6 Porosity

Pastes specimens' Archimedes porosity was obtained from additional cubic specimens (16x16x16mm).

4. RESULTS AND DISCUSSION

4.1 Pastes cylinder samples

Mass change of the cylinder pastes samples, for no CO_2 and CO_2 20% conditions, is presented in the Fig. 4. For thin cylinder specimens in no CO_2 condition (Fig. 4(a)), the mass loss caused by the drying of saturated samples occurred continuously during all test period of 56 days. The long water curing period of 91 days created a dense microstructure, which difficulted the evaporation of the capillary water even for small thin samples. About the powder addition and differences in binder type, there was no clear trend, as the mass variation caused by the loss of capillary water was similar and in the last measurement the difference was less than 0.5%.

On the other hand, for thin cylinder specimens in CO_2 20% condition (Fig. 4(b)), the mass change showed a different pattern. There was an initial rapid mass increase, especially for slag blended specimens, a second phase of small mass decrease and a final phase of mass increase, reaching maximum stabilization at 3%. The initial and final mass increase in carbonation conditions can be explained by the CO_2 uptake by pastes hydrates, such as CH, followed by CC precipitation (Eq. 1).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$
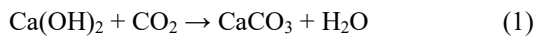
This indicates that initial water loss from the saturated pastes occurred rapidly for the cylinder thin samples, even before the first mass measurement, allowing the CO_2 diffusion inside the pores. An exception was for the N sample, which showed mass loss for all measurements, but the reason is not clear. The intermediary mass loss may be caused by loss of internal capillary or adsorbed water from the specimens. It is not clear if it was caused by some relative humidity change inside the chamber or some microstructural change in the specimens after some carbonation.

For thick cylinder specimens carbonated at CO_2 20% (Fig. 4(c)), only mass change was measured to be compared to the thin samples' results, and a similar three phase mass change pattern was observed. However, the magnitude of mass increase was amplified and maximum value reached 5%, being observed for OPC binders. In this case, thickness influenced the drying of capillary water from saturated samples and OPC is known for having more simple porosity microstructure

than slag blended cement and the water loss of may have occurred earlier than slag blended samples, allowing the CO_2 diffusion and CC precipitation, leading to the mass increase.

Dimensional change of the diameter in thin cylinder pastes samples is presented in the Fig. 5. For no carbonation conditions (Fig. 5(a)), there was no stable dimensional change and shrinkage of the samples could not be measured. From the detected mass change, drying shrinkage occurred to some extent, but the caliper resolution was not sufficient to determine its magnitude.
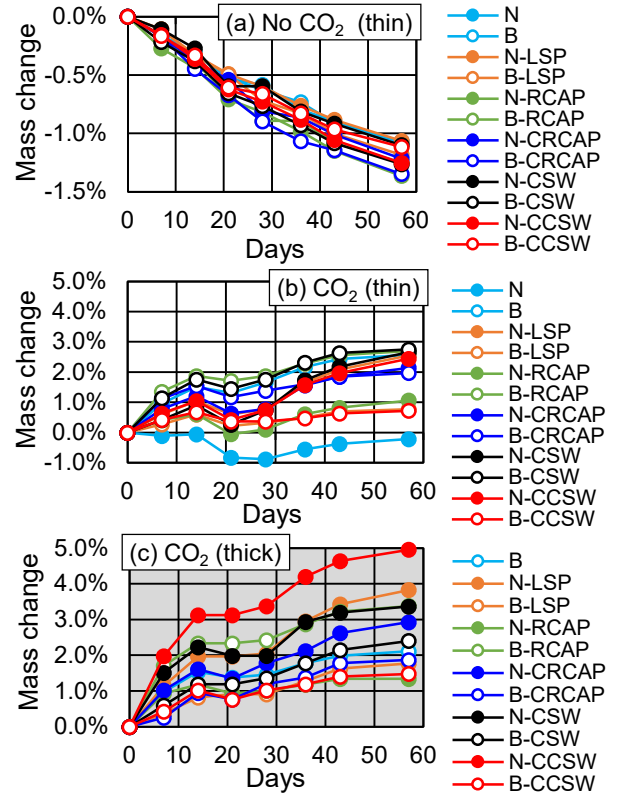
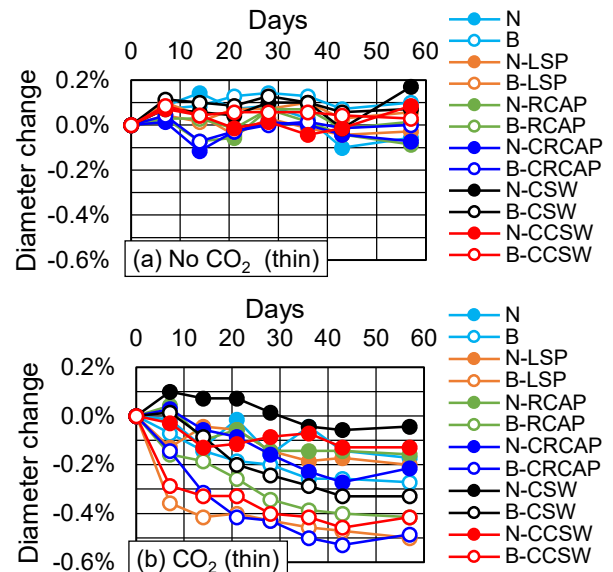Fig. 4 Mass change of pastes samples, in no CO_2 and CO_2 conditions

Fig. 5 Diameter change of pastes samples, in no CO_2 and CO_2 conditions

Differently, for carbonation conditions (Fig. 5(b)), there was a trend of shrinkage of the pastes, notably for slag blended specimens, indicating that differences in chemical composition and microstructure before carbonation affected the dimensional change and the simple measurement method using a caliper could somehow point out it in the results. Therefore, carbonation shrinkage measurement showed to have an order of magnitude greater than drying shrinkage and could be measured with certain accuracy using this method, while drying shrinkage could not be measured, as seen in the Fig. 5(a).

The maximum shrinkage for CO_2 condition measured during all the experimental test period is presented in the Fig. 6. It indicates that slag blended cement pastes showed larger total shrinkage, which includes the dimensional change caused by the carbonation and drying together. This is an interesting result considering that usually OPC samples shows higher drying shrinkage compared to slag blended cement samples. Therefore, the accelerated carbonation impacted directly in the total shrinkage behavior, suggesting that it may have led to significant microstructural changes in the samples. It has been reported that carbonation shrinkage is associated with the decalcification of C-S-H and polymerization of silica chains. Also, the presence of CH helps in limiting C-S-H decalcification and then reducing carbonation shrinkage and cracking [3]. Consideration of the differences in the hydrates phase can explain why slag binder samples showed higher shrinkage than OPC ones.

Also, from Fig. 6, about the powders' addition, samples with high CC content (see Fig. 2) showed larger carbonation shrinkage. To identify which parameters may have influenced the shrinkage results obtained for the pastes samples containing these powders, correlation between Archimedes porosity of the same pastes samples, carbonation coefficient K (of mortars prepared for a parallel study, but using the same powder's addition) and the CC content in the pastes (obtained from TGA) are presented in the Fig. 7. As pastes specimens used were thin, the shrinkage caused by carbonation in these specimens was not so dependent on the porosity itself or on the carbonation coefficient K of the similar mortars, as shown in Fig. 7 (a) and Fig. 7 (b). In contrast, Fig. 7 (c) suggests that chemical composition of the paste may be one key factor influencing this dimensional change (shrinkage), and in this case it was represented by CC content. Some amount of CC from the powder's addition may have affected the hydration and its excess (CC remained inside pastes) also might have influenced the microstructural changes during carbonation.

4.2 Mortar rectangular bar samples

Mortar's flexural and compressive strength results before carbonation are shown in the Fig. 8.There was no discrepancy in mechanical properties between BC and OPC. The carbonation depth measured in parallel to the shrinkage is shown in the Fig. 9, and the results shows that BC 20 mm thickness samples had the full section carbonated in less than 7 days and 40mm ones, at 21 days. In contrast, OPC 20mm were fully
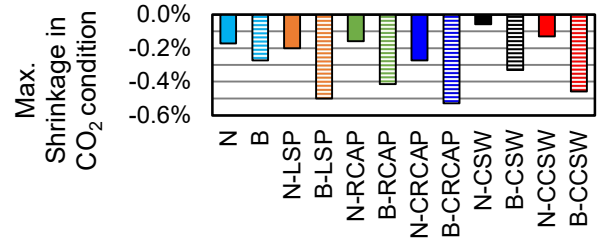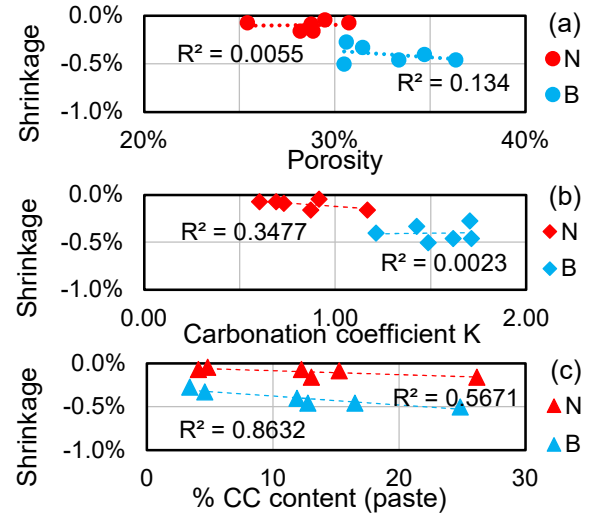
Fig. 6 Max. shrinkage of pastes in CO_2 conditions

Fig. 7 Correlation between max. shrinkage of and (a) porosity, (b) carbonation coefficient K and (c) CC content of OPC and slag blended pastes

carbonated only after 42 days and 40mm ones were still not completely carbonated during the test period of 42 days, set for this experimental study.

Mass change of OPC and BC mortar samples in CO_2 20% carbonation and no CO_2 (only drying) conditions is presented in the Fig. 10. For both conditions, an initial mass decrease was observed for all OPC and BC, both 40mm and 20mm thickness specimens. For the drying condition, 20mm samples showed rapid mass loss, considering the large surficial area/volume ratio, which facilitates the evaporation of the capillary water. At the last measurement, the final mass loss was similar for all OPC regardless of thickness, but BC still kept having a stable gap between the curves of different thickness specimens.

Now, for CO_2 20% carbonation condition (Fig. 10), a unique behavior could be observed, where OPC specimens showed pronounced mass increase and similar for 40mm and 20mm specimens after 21 days of carbonation. This coincides with the time when mass loss from water evaporation in the no CO_2 condition stabilized. This suggests that the pronounced mass gain may be attributed to the CC precipitation inside the pores (see Eq. 1) after water evaporation, which allowed the CO_2 diffusion. However, it is important to note that 40mm and 20mm OPC samples have not the full cross section carbonated at this point. Therefore, this measured mass gain in OPC samples in CO_2 condition, contrasted to the constant mass loss in only drying condition samples, indicates that carbonation can occur in parallel to the drying. Differently, BC specimens in CO_2
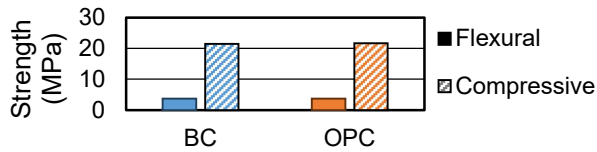
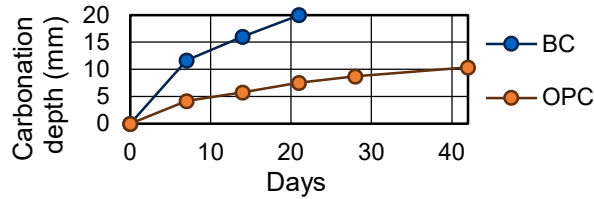Fig. 8 Mortar's flexural and compressive strength
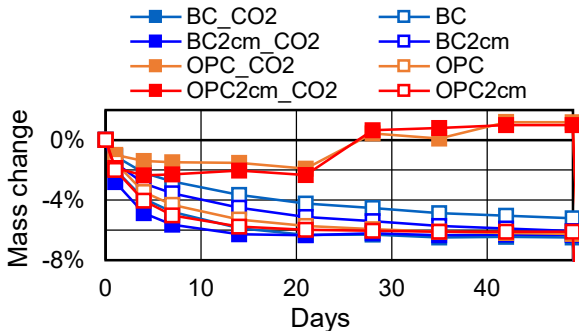

Fig. 9 Mortar's carbonation depth

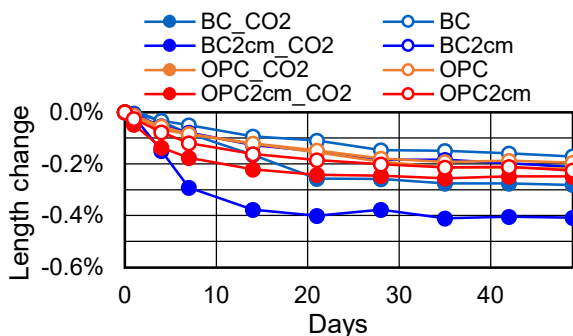Fig. 10 Mass change of mortar samples in CO_2 and no CO_2 conditions

Fig. 11 Length change of mortar samples in CO_2 and no CO_2 conditions
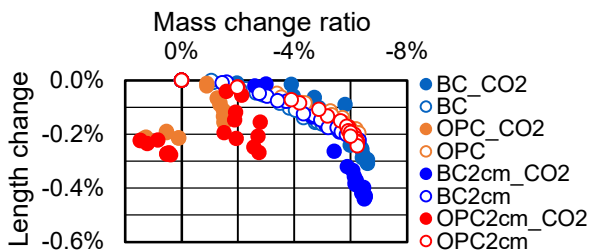

Fig. 12 Relationship between mass change and length change of all mortar specimens

conditions showed mass reduction, even after the full cross section being carbonated, at 7 days for 20mm ones and after 21 days for 40mm specimens (see Fig. 9), and there was no abrupt alteration in the mass change pattern. In addition, comparing the mass change of BC non-carbonated and BC carbonated specimens, the mass loss was larger for the carbonated ones, contrasting with the

expected result of mass increase with carbonation, as seen in OPC samples.

The Fig. 11 presents the dimensional length change of OPC and BC mortar specimens. In only drying condition, the shrinkage was limited to a maximum value of less than 0.25%. On the other hand, in the combined carbonation and drying condition, the length change achieved a maximum value of 0.4%, for the BC 20mm thickness' specimens. It is important to highlight that this value was obtained for the carbonation conditions settled in this experiment. Also, the length change was noticeable more for the thinner specimens, indicating that the specimen size (and exposed area) is a key factor to be considered when evaluating the dimensional change induced by accelerated carbonation in hardened cementitious materials.

Comparing the differences in OPC and BC shrinkage trends in CO_2 conditions, it was expected that larger carbonation shrinkage in BC could be associated with higher degree of carbonation and, consequently, greater mass increase from CC precipitation. But, as shown in the Fig. 10, the expected mass gain in BC CO_2 condition did not occur, even for larger shrinkage. On the contrary, the mass loss in CO_2 condition surpassed the mass loss in no CO_2 conditions. The reason may be related to the humidity that was still stored inside the pores before carbonation, and the carbonation may have affected the water retention capacity of BC hardened samples microstructure.

The relationship between mass change and length change of all specimens for drying and carbonation conditions is shown in the Fig. 12. For the only drying conditions, OPC and BC specimens followed a similar curve and there is a good correlation between these two parameters, as expected. Oppositely, for carbonation conditions, there is a clear dissimilarity in mass and length change behavior between OPC and BC samples. For OPC, as the carbonation progressed the mass loss from water evaporation was limited, resulting in mass increase in the last measurements. Also, as the CC formation was occurring, the clogging of capillary pores may have limited the mass loss from evaporation and the advance of carbonation. As it has been reported that the change in microstructure and the posterior carbonation shrinkage depend mainly on the competition between the clogging of capillary pores filled with CC and the formation of additional pores induced by decalcification of C-S-H, for the carbonation conditions set in this study, carbonation reaction in OPC may have occurred mainly between CO_2 and CH, and/or C-S-H decalcification may have not reduced Ca/Si to values smaller than 1.2 [1]. In BC case, even large shrinkage occurred, the supposed mass gain from CC precipitation was counteracted by some phenomenon. Further investigation is necessary, but as discussed previously, it may be an indication of porosity coarsening in BC samples with the accelerated carbonation, which led to an extra water evaporation than OPC specimens.

The focus of this investigation was to finally verify the occurrence of dimensional change in accelerated carbonation conditions using simplified methodologies. So, to neglect the effect of drying, length
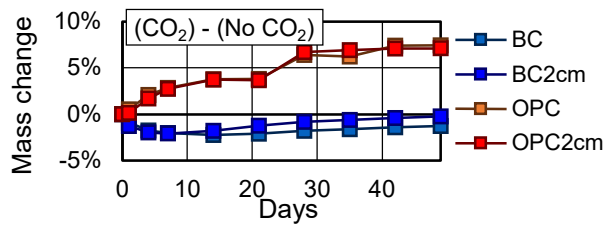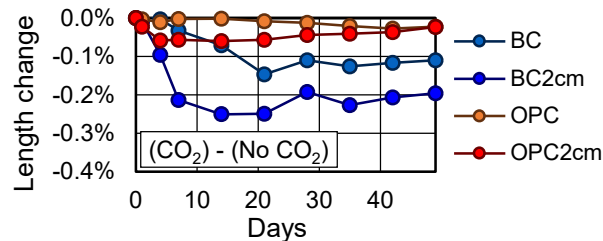
Fig. 13 Calculated mass change for mortar

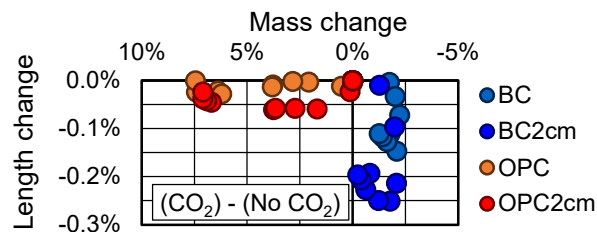Fig. 14 Calculated length change for mortar

Fig. 15 Relationship between calculated mass change and calculated length change in mortar

and mass changes from the only drying condition were subtracted from the carbonation conditions ones, and the calculated values are presented in Fig. 13 and Fig. 14. Also, the relationship between these parameters is shown in the Fig. 15. While for BC the calculated mass gain was almost zero, for OPC, the length change was insignificant. In other words, for OPC the mass gain from CO_2 uptake could be assessed during the measurement period, and the balance between water evaporation and CC precipitation inside the pores, somehow seems to have limited the shrinkage extent. In BC case, the initial Ca/Si of C-S-H is known for being lower than in OPC pastes and it was also reported that C-S-H can be completely decalcified even in OPC pastes, for $CO_2 > 10\%$ [4]. Ca/Si was not investigated in this study, but as the full cross section was carbonated, the larger dimensional change of BC compared to OPC may be associated to the decalcification shrinkage of this initially low Ca/Si C-S-H.

5. CONCLUSIONS

From the results of the experimental methods to evaluate dimensional change induced by accelerated carbonation, the following conclusions can be drawn:

(1) The initial (partially) saturated surface dry state of pastes and mortars before carbonation, adopted in this study, increased the complexity when evaluating the mass and length changes induced only by the carbonation, as drying was occurring in parallel. Nonetheless, most accelerated carbonation techniques, such as CO_2 curing, are applied in hardened cementitious materials at early curing ages, when internal humidity is different than external, and the free water inside the samples is gradually removed while CO_2 gas diffusion occurs. Therefore, the experimental methodology and results presented here can represent the accelerated carbonation phenomenon as it really occurs, i.e., when this innovative technology is applied to hardened cementitious materials.

(2) In thick and thin cylinder paste specimens, dimensional change induced by carbonation could be measured using simple caliper, but some refinements are necessary to achieve more accuracy and precision, and the validity of the measurement method needs to be verified. The use of powder wastes from concrete recycling and limestone powder, which contains large amount of CC in its composition, increased the shrinkage extent.

(3) For (40x40x160mm) and (20x40x160mm) mortar specimens, the length compactor method was shown to be sufficiently accurate and precise. But as the exposed surficial area is different and the measurements were done for specific CO_2 conditions, these parameters needs to be properly defined to propose a standardized evaluation method of the dimensional change induced by accelerated carbonation. Regarding binder type, in OPC mortar samples, as drying shrinkage occurred in parallel to the carbonation, major contribution to the length change can be attributed to the drying shrinkage. On the other hand, in the case of BC samples, decalcification shrinkage of the initially low Ca/Si C-S-H, induced by accelerated carbonation, may be associated as the main contributor to the dimensional change.

(4) Finally, the influence of the drying of water occurring in parallel to the CC precipitation with the carbonation reaction is a key factor to be evaluated in the accelerated carbonation of hardened cementitious materials, as the ongoing drying and carbonation shrinkage may cause significant microstructure changes.

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