

EXPERIMENTAL INSIGHTS INTO ACCELERATED CARBONATION OF GGBS-BLENDED HARDENED CEMENTITIOUS MATERIALS

Karen Midori MASUNAGA^{*1} and Takeshi IYODA^{*2}

ABSTRACT

In this study, the effects of combined GGBS replacement and accelerated carbonation on hydrated hardened cementitious materials were evaluated, with particular emphasis on the often overlooked decalcification of C-S-H and water behavior during carbonation. Greater shrinkage and mass loss, accompanied by microcracking, were observed at higher GGBS replacement levels, highlighting the need for a comprehensive understanding of carbonation mechanisms to determine optimal materials and conditions for accelerated carbonation and thereby fully realize the potential of CCUS technologies.

Keywords: Carbonation, Accelerated carbonation, GGBS, C-S-H, Decalcification, Shrinkage, SCM

1. INTRODUCTION

Carbonation has long been studied as a deterioration mechanism in reinforced concrete, with accelerated carbonation used to predict long-term effects of natural carbonation. However, growing interest in Net-Zero emissions and sustainability has led to increased use of supplementary cementitious materials (SCMs) in association with Carbon Capture Utilization & Storage (CCUS) strategies, creating a new scenario for the investigation of carbonation mechanisms.

The combination of accelerated carbonation and SCMs, such as ground granulated blast furnace slag (GGBS) has been presented as a promising approach to achieve a carbon-neutral concrete and help drive the cement and concrete industry toward Net-Zero emissions. Despite extensive research in recent years on accelerated carbonation, much of the focus has been on maximizing and quantifying CO₂ uptake, mainly assessing the several polymorphs of calcium carbonate (CC) formation. In carbonation reactions, Ca ions must react with CO₂ to form CC. However, in hardened cementitious materials, these reactions also involve the gradual decomposition of the hydrated phases, including the decalcification of C-S-H, a phenomenon that has often been neglected. Moreover, along hydrates decomposition, water is generated as an additional carbonation product, which has also received limited attention in recent studies of carbonation.

Therefore, this research explores accelerated

carbonation from a new perspective, discussing the combination of these overlooked mechanisms involved in the microstructural changes induced by accelerated carbonation of hardened cementitious materials. The microstructural changes discussed here were evaluated by mass and dimensional changes measurements, microcracking investigation and phase assemblage characterization.

2. EXPERIMENTAL PROGRAM

2.1 Materials

Ordinary Portland Cement (OPC), in accordance with Japanese Industrial Standard JIS R 5210, and GGBS were used as binders (Table 1). Paste specimens with 0%, 50% and 70% GGBS replacement and a water-to-binder ratio (W/B) of 0.50 were mixed at high speed for 3 minutes using a mortar mixer and subsequently mixed periodically until bleeding was considered negligible. Specimens were cast, compacted with a vibration table, demolded after 2 days and sealed-cured until 91 days to ensure hydration. The mix design, curing conditions and specimen size are shown in Table 2.

2.2 Accelerated Carbonation

After curing, specimens were allocated in three different conditions – direct carbonation without preconditioning (CO₂), drying (DRY), carbonation with preconditioning (PREC) – as shown in Fig.1. Accelerated carbonation was conducted in a controlled

Table 1 Characteristics of materials

Type	Density (g/cm ³)	Fineness (cm ² /g)	Chemical Composition														
			lg.loss	SiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	CaO	MgO	TiO ₂	MnO	SO ₃	Na ₂ O	K ₂ O	P ₂ O ₃	Cl	
OPC	3.14	3530	2.20	20.19	5.18	-	2.78	65.01	1.18	0.25	0.15	2.10	0.31	0.36	0.16	0.008	
GGBS	2.92	4120	-0.08	33.83	12.94	0.31	-	44.44	5.52	0.53	0.16	2.05	0.21	0.23	0.02	-	

Table 2 Experimental settings

	OPC	GGBS	W/B	Curing	Specimen size
OPC	100%	0%		Sealed 91 days	(20x40x160) mm bars with pins
B50	50%	50%	0.50	20°C, 100% RH	Cubes cut to 2 mm
B70	30%	70%			

*1 Postdoctoral Researcher, College of Engineering, Shibaura Institute of Technology, Dr.E., JCI Member

*2 Professor, College of Engineering, Shibaura Institute of Technology, Dr.E., JCI Member

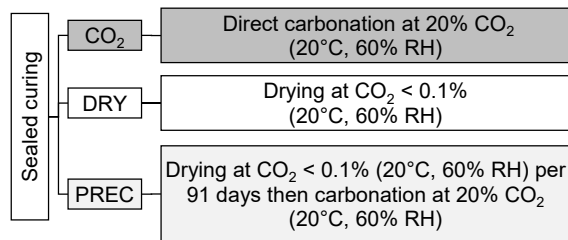


Fig.1 Diagram of the experimental conditions.

chamber 20% CO₂ concentration, 20°C, 60% relative humidity (RH). The drying condition was also a controlled chamber with same temperature and RH.

2.3 Dimensional and Mass Changes Measurement

The test was performed adapting the instructions of JIS A 1129-3 (Methods of measurement for length change of mortar and concrete – Part 3: Method with dial gauge), using prismatic paste specimens of (20x40x160) mm cast with pins. Dimensional change was measured using a digital length comparator instrument, with 0.001 mm resolution (Fig.2). The average of three measurements, obtained from two specimens, was used in the calculations. The mass of the same specimens was recorded using digital scales with a resolution of 0.01 g, and all calculations of mass change ratio, including those for the preconditioned samples, were performed using the post-curing mass as reference.

2.4 Ultrasonic Pulse Velocity (UPV) Test

The UPV test was used to quantitatively investigate microcracking in the hardened paste specimens, with measurements conducted at the same ages as the dimensional and mass changes measurements. The device (Fig.2) has two built-in transducers with dry-point-contact with fixed base (150 mm), which are insensitive to the surface condition. UPV test is applied to assess concrete durability by correlating the propagation time of ultrasonic waves and near-surface condition of concrete. Measurements are performed by surface scanning, searching for flaws by abnormal decreasing of the velocity (or increasing of the propagation time). To measure UPV, the same surface of each specimen was tested five times, and the median value was used.

2.5 Calcium Carbonate Content

Whole 2 mm cubic paste specimens exposed to CO₂ and DRY conditions were crushed to obtain powder samples. This specimen size enabled assessment of carbonation degree of each mix over time, without considering CO₂ diffusion effects. Thermogravimetric analysis (TGA) was conducted using a Netzsch equipment on approximately 20 mg of ground powder samples (<150 µm), in an open vessel. Recordings were performed continuously over a temperature range from 25°C to 1000°C, at a heating rate of 20°C/min, in a nitrogen (N₂) atmosphere with flow rate of 150 ml/min. Differential thermal analysis (DTA), using Al₂O₃ as a reference material, was also conducted to identify initial and final temperatures of CC decarbonation, defined as 680-860°C. The results were compared with the



Fig.2 Equipment for dimensional change measurement (left) and UPV test (right).

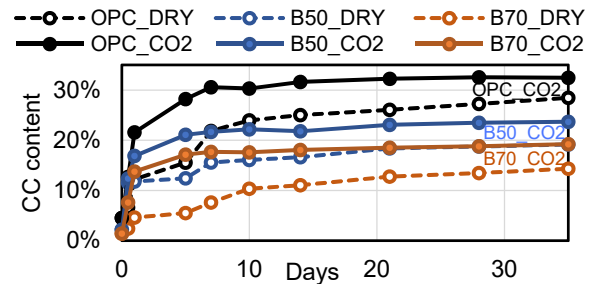


Fig.3 CC content of 2 mm cubic pastes.

corresponding mass loss profiles from differential thermogravimetry (DTG). By combining TGA with DTA and DTG, the decomposition mass changes derived from thermal data and the molecular masses of CC and CO₂ were used to quantitatively determinate the CC content, with normalization based on the sample mass at 40 °C.

3. RESULTS AND DISCUSSIONS

3.1 Drying (DRY) x Carbonation (CO₂)

The CC content for each mix under DRY and CO₂ conditions was calculated to evaluate its influence on dimensional and mass changes (Fig.3). For small (thin) sample sizes, the carbonation rate impact can be neglected, and CC formation becomes directly proportional to the CaO content of the mixes, following the order OPC > B50 > B70. Furthermore, CC precipitation was faster and more pronounced under accelerated carbonation condition (CO₂), than under natural carbonation condition (DRY), as expected.

Fig.4 shows the dimensional and mass changes of OPC, B50 and B70 pastes, in CO₂, DRY and PREC conditions. A negative dimensional change (shrinkage) was observed under all three conditions, with its magnitude increasing with higher GGBS replacement levels. The influence of the binder composition was more pronounced under both carbonation conditions than under DRY condition, as evidenced by the significant increase in shrinkage with increasing GGBS replacement. This behavior can be associated with the initial reduced calcium hydroxide (CH) content and lower Ca/Si ratio of C-S-H in GGBS-blended systems, which promote the decalcification shrinkage of C-S-H [1][2][3]. The polymerization of silica chains has been reported to cause structural changes in the C-S-H gel phase, which can lead to macroscopic shrinkage. In addition, although GGBS incorporation results in higher carbonation rates (i.e., faster full cross section carbonation), the carbonation degree is limited by the

reduced CaO content, leading to a lower total amount of CC (Fig.3). This reduced CC content, which may be partly amorphous in SCM-blended pastes, provides less physical confinement for C-S-H structural reorganization, thereby resulting in greater shrinkage [1].

Regarding mass change, in CO₂ conditions, B70 initially exhibited almost no variation, reflecting the balance between mass gain from CC formation and mass loss due to evaporation of free water, retained in the pores after sealed curing. With prolonged carbonation, however, a progressive mass decrease was observed instead of the mass increase expected from further CC precipitation. This mass decrease seems to be caused by the hydrates decomposition upon prolonged accelerated carbonation, resulting in microstructural changes and additional free or bond water evaporation. Oppositely, the balance between CC formation and water evaporation outcomes in continuous positive mass change for OPC_CO₂, which shows an increasing trend even after 200 days of accelerated carbonation.

Interestingly, the GGBS content was not directly correlated with the mass increase during the initial days of accelerated carbonation without preconditioning (CO₂ condition). The intermediate GGBS mixture (B50) exhibited the largest initial mass increase among the mixes and did not follow an intermediate trend between

B70 and OPC, as observed for dimensional change (Fig.4). B50's largest initial mass increase suggests that CC precipitation is occurring intensely than B70, considering that it has higher CaO content (Fig.3), but water formation and/or evaporation from the specimens is not occurring in the same magnitude, because of differences in the porosity and maybe in the hydrated phase that is being decomposed. This initial phase assemblage and microstructure seems to have determined the mass change trend, keeping it positive for B50, but negative for B70. In addition, even though carbonation is continuing to occur in both GGBS-blended samples, as seen by the crescent shrinkage (from low Ca/Si C-S-H decalcification); water release/evaporation seems to be dominant than CC formation, not leading to a posterior increase in mass.

Similarly, this balance between hydrates decomposition, CC precipitation and water formation/evaporation can also be discussed in the case appear to be limited during the early days of carbonation without precondition, due to the formation of a CC layer. of OPC. Despite its highest CaO content, the initial carbonation rate and degree advance (CO₂ diffusion) This layer can also partially entrap water produced during the carbonation reactions, which may in turn also hinder the CO₂ diffusion. However, after approximately

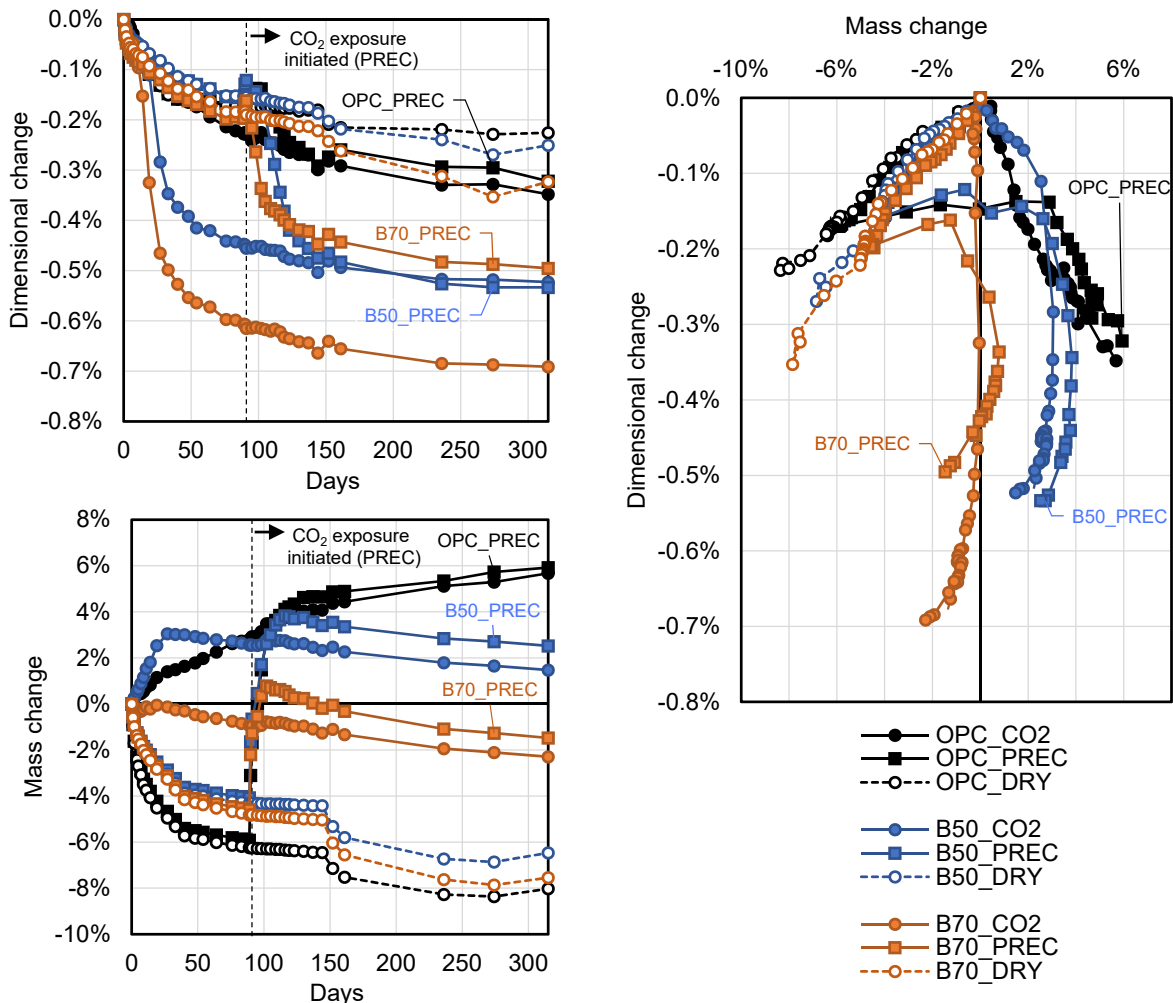


Fig.4 Dimensional and mass changes of pastes in direct carbonation (CO₂), carbonation after preconditioning (PREC) and drying (DRY) conditions.

80 days of carbonation, the mass gain of OPC surpassed that of B50 and continued to increase, even with concurrent evaporation of free water. This suggests that in high CaO systems, prolonged carbonation can still lead to an increase in sample mass despite a simultaneous decrease in pore saturation. In contrast, the GGBS-blended mixes exhibited a mass decrease under prolonged carbonation, as discussed previously.

From the right part of Fig.4, it is possible to confirm the linear relationship between dimensional and mass change for DRY condition. Although the addition of GGBS to the system can reduce the mass loss from free capillary water evaporation, due to the more finely distributed porosity [4], in the GGBS-blended mixes, natural carbonation appears to influence the results after prolonged exposure. This is evidenced by an increase in shrinkage in B50_DRY and B70_DRY despite lower mass loss, deviating from the trend observed in OPC_DRY. Under CO₂ condition, the relationship is initially linear but opposite to drying (positive mass change due to CO₂ uptake). With prolonged carbonation, GGBS addition causes this trend to curve, as mass loss from water evaporation upon accelerated carbonation becomes dominant.

The results presented here are influenced not only by the phase assemblage and microstructure of each binder type, but also by the specimens' size and shape (exposed surface area and volume). However, they highlight the limitations of estimating the CO₂ uptake in hardened cementitious materials with different binders solely by measuring the sample weight. Since carbonation releases water and maintaining a perfectly closed system is challenging, this phenomenon cannot be neglected and requires careful evaluation, particularly under accelerated carbonation conditions, where hydrates decomposition occurs to a greater extent than

under natural carbonation.

3.2 Preconditioning Impact on Carbonation Kinetics

In Fig.4, CO₂ exposure of the PREC samples was initiated after 91 days of pre-drying. All PREC samples exhibited a rapid and abrupt mass increase, reaching a higher maximum mass gain than the directly carbonated samples (CO₂). The prior removal of free water enhanced CO₂ diffusion into the pores, leading to a faster carbonation rate, a greater degree of carbonation, and supposedly a higher CO₂ uptake. Regarding the dimensional change of PREC samples, an expansion was observed in the first days of carbonation (more clearly visible in the shifted results in Fig.5). This suggests that the rapid and abrupt CC precipitation within the pores not only filled the voids but may also have contributed to the overall volume increase. Another hypothesis is that hygroscopic expansion occurred due to the uptake of water released during these rapid carbonation reactions, but this requires further investigation.

Also from Fig. 4, after prolonged carbonation, final mass and dimensional changes of CO₂ and PREC carbonated samples are similar for OPC and B50. This indicates that simultaneous drying and carbonation (CO₂) led to similar dimensional and mass changes compared to drying and subsequent carbonation (PREC), for OPC and B50. In contrast, for B70, shrinkage under CO₂ condition exceeds that under PREC, despite similar mass changes. This will be discussed in Section 3.3.

To better assess the effect of preconditioning, the pre-drying period was excluded, by adjusting the origin of the PREC results, presented in Fig.4. The resulting shifted values (PREC(shifted)) were then compared with the calculated dimensional and mass changes, obtained as the difference between measurements under CO₂ and DRY conditions at each age, as follows:

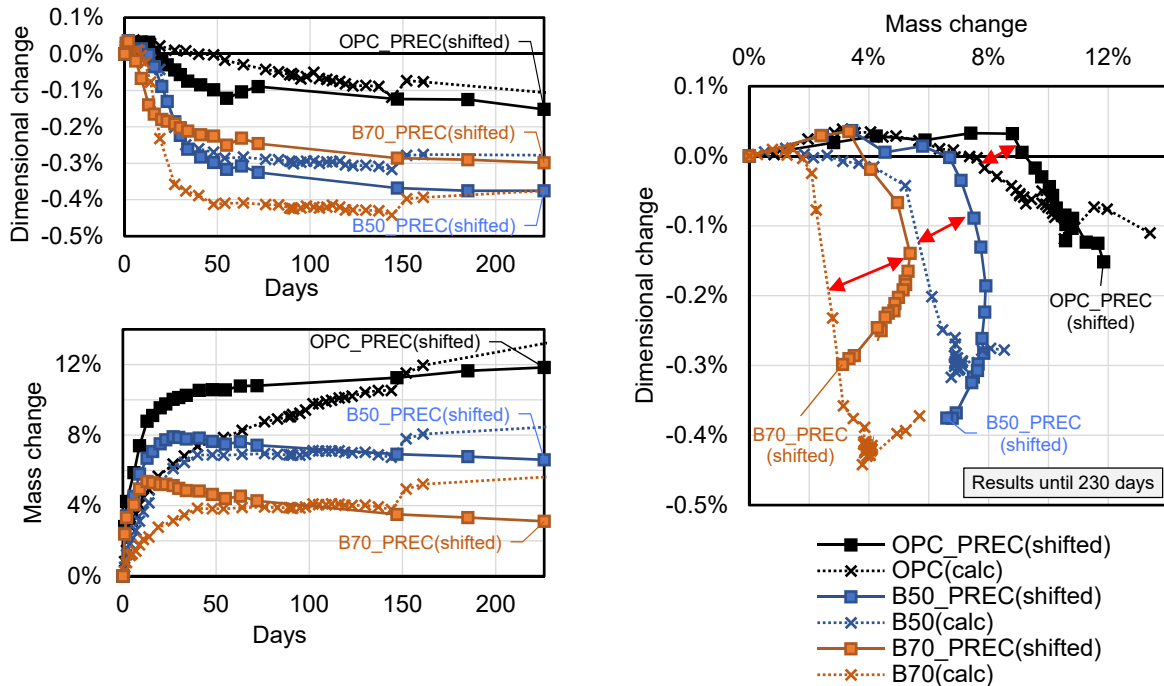


Fig.5 Shifted dimensional and mass changes of pastes carbonated after preconditioning (PREC(shifted)), compared to calculated values (calc) from the measurement results of CO₂ and DRY conditions.

$$X_{(calc)} = X_{(CO_2)} - X_{(DRY)} \quad (1)$$

where,

$X_{(calc)}$: Calculated dimensional (or mass) change

$X_{(CO_2)}$: Dimensional (or mass) change in CO₂ condition

$X_{(DRY)}$: Dimensional (or mass) change in DRY condition

These results are shown in Fig.5. The calculated values do not match the shifted results for each mixture because carbonation occurring simultaneously with drying (PREC condition) induces microstructural changes that affect mass and dimensional changes differently than when carbonation follows preconditioning. In other words, although specimens were measured at the same age, the mass and dimensional changes due to drying alone differ from those caused by drying when it occurs simultaneously with accelerated carbonation.

In the right part of Fig.5, it can be seen that GGBS addition increased the discrepancy between the calculated values and shifted measurements of PREC samples. The larger mass increase suggests that preconditioning promoted carbonation progress by allowing CO₂ to access more hydrates earlier, facilitating CC precipitation. This discrepancy between measurements and calculations, with overall larger difference between the results as GGBS replacement increases, may also indicate that microstructural changes induced by accelerated carbonation are more pronounced – and potentially more detrimental – with increasing GGBS content in the system. The lower Ca/Si of C-S-H and the reduced pH, cause C-S-H – the main hydrate in GGBS-blended systems – to undergo decalcification and subsequent decomposition more easily/rapidly. This results demonstrate the significant impact of SCMs in the kinetics of the carbonation reactions as well as the preconditioning influence on the final carbonation degree of hardened cementitious materials.

In summary, preconditioning seems to accelerate and then improve the efficiency of CO₂ uptake, by reducing the CO₂ supply time required to achieve a certain carbonation degree, by the previous partial removal of free capillary water. Also, even though previous studies reported C-S-H decalcification as the main shrinkage mechanism, from the measurements under three different conditions, understanding the water behavior upon carbonation seems to be primordial in accelerated conditions, especially in SCM blended systems, where the detachment of bound water seems to

have a complicated and significant influence in the mass and dimensional changes. However, each impact could not be assessed independently and further investigation is required to clarify the mechanisms involved in the microstructural changes upon accelerated carbonation.

3.3 UPV decrease

It is important to note that cracking was visually apparent after only few days of accelerated carbonation, both for OPC and GGBS-blended mixes. Therefore, dimensional change upon carbonation resulted not only in volume contraction of the whole specimen, but also in the appearance of microcracking, from the differential stresses inside the specimen and internal restriction to the shrinkage. The microcracking was quantified using UPV measurements and to enable comparison among different binders, the results are presented as percentage decreases in UPV, instead of absolute values (m/s).

From Fig.6, it can be seen that both drying and accelerated carbonation decreased the UPV. A denser matrix is expected to exhibit higher UPV. In our study, this hypothesis appears to hold, as the magnitude of the UPV decrease (and the UPV itself) follow the sequence OPC > B50 ≈ B70 in DRY specimens. This trend is also observed under both carbonation conditions, which can be attributed to the more pronounced porosity filling effect of carbonation in OPC compared to B50 and B70 (see Fig.3). For the drying condition, UPV appears to reflect, to some extent, the pore saturation, as indicated by the initial decrease in UPV during drying, even in the absence of visible surface cracking. However, this decrease stabilized after a few days, despite continued water evaporation, as evidenced by the ongoing mass loss in Fig.4.

On the other hand, under both accelerated carbonation conditions, UPV decreased markedly over time, attributable to near-surface flaws (see Section 2.4) and may quantitatively reflect the shrinkage-induced microcracking under carbonation. The reduction in UPV was more pronounced in GGBS-blended samples, which also exhibited greater shrinkage (see Fig.4).

Comparing CO₂ and PREC samples, OPC and B50 exhibited similar final values, while B70 showed a difference around 7%. The higher UPV decrease in B70 PREC sample than the CO₂ one, can be linked to the correspondingly smaller shrinkage observed in Fig.4. As carbonation-induced dimensional changes involve both shrinkage and microcracking, preconditioning appears to have caused greater microcracking in B70, which in turn limited the overall volumetric change of B70_PREC relative to B70_CO₂.

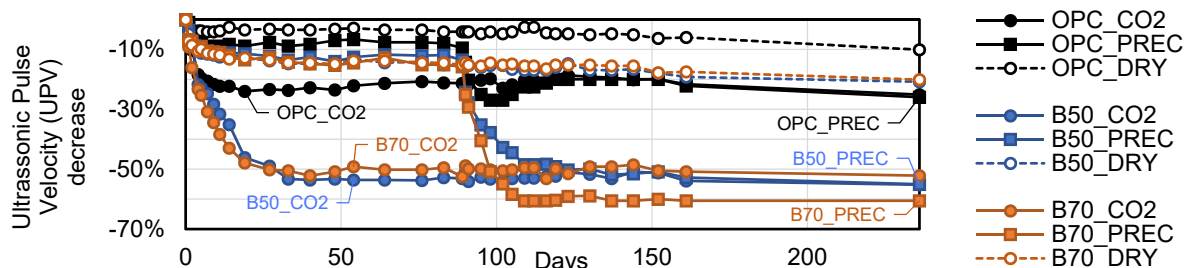


Fig.6 UPV decrease of OPC, B50 and B70 pastes in CO₂, DRY and PREC conditions.

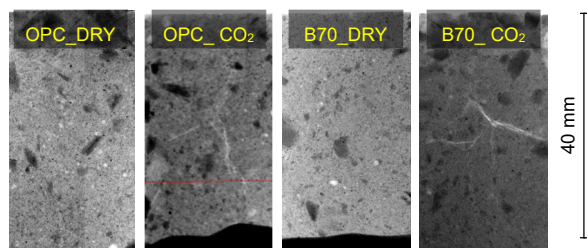


Fig.7 Internal microcracking in mortars.

3.4 Significance of the Microstructural Changes Induced by Accelerated Carbonation.

The remaining question is whether the reported mass and dimensional changes and microcracking in pastes are significant enough when discussing their occurrences in real concrete structures or real applications of CCUS technology, as long-term accelerated carbonation is not feasible. Although surficial microcracking was not visible by sight in mortar samples from previous study [5], from observations using X-Ray microscope (Matsusada Precision μ Ray8700), internal microcracking was observed only in the accelerated carbonated OPC and B70 mortars (Fig.7).

Long-term accelerated carbonation (20% CO_2) does not appear to produce the same effects as natural carbonation at much lower CO_2 concentrations in OPC concrete, even after decades of exposure. Evidence from existing structures nearing the end of service life indicate that deterioration arises from multiple factors than natural carbonation alone. However, negative effects of natural carbonation in high SCM blends have been widely reported. In addition, microcracking was also observed in thin cement pastes slices after prolonged carbonation at 3% CO_2 , particularly in high SCM samples [6]. This cracking was attributed to decalcification shrinkage of C-S-H, as ^{29}Si NMR spectra showed a marked decrease in C-S-H peaks, indicating the formation of Ca-rich silica gel with a low Ca/Si ratio, which also explains the microcracking observed in this study. The 3% CO_2 was chosen by the authors as it ensures representativeness with natural carbonation, and it is much lower than the 20% CO_2 adopted in the present study, raising the question whether similar cracking could occur under natural carbonation conditions.

Although accelerated carbonation can capture CO_2 , fill pores via CC precipitation and potentially enhance the stability of hardened materials to posterior natural carbonation [7], its negative effects over prolonged exposure cannot be ignored, especially in SCM blended systems, where accelerated carbonation can lead to the decomposition of the hydration products and may induce microcracking at a level that can affect the integrity of the cement matrix microstructure. Therefore, the results of this study highlight the risks of applying accelerated carbonation to SCM-blended hardened cementitious materials and emphasize the need to explore alternative methods to enable its safe implementation.

5. CONCLUSIONS

This study examined accelerated carbonation in

GGBS-hardened cementitious materials, by evaluating dimensional and mass changes, microcracking and phase assemblage in hydrated OPC, B50 and B70 pastes.

(1) CC formation is the main driver to mass gain during carbonation, while C-S-H decalcification (silica chain polymerization) primary governs dimensional changes. This results in macroscopic shrinkage and microcracking, particularly in GGBS-blended systems, characterized by low CH content, reduced Ca/Si ratio C-S-H and limited CC formation.

(2) However, water behavior (transformation, transport and evaporation) upon accelerated carbonation was also identified as a critical factor influencing microstructural changes and should not be disregarded.

(3) Preconditioning plays a key role in hardened cementitious materials with relatively large cross sections by enhancing the CO_2 diffusion and reducing early-stage water entrapment, especially under accelerated carbonation. In B70, preconditioning followed by carbonation, resulted in smaller shrinkage (overall volumetric change) than simultaneous drying and carbonation. Conversely, the larger decrease in UPV may indicate increased degree of microcracking.

(4) A comprehensive understanding of carbonation mechanisms is essential for assessing the suitability of accelerated carbonation under specific materials and exposure conditions. Such knowledge is critical for fully exploring the potential of CCUS technologies, particularly in SCM-blended cementitious systems.

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