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Nano $CaCO_3$ seeding for improving properties of limestone calcined clay cement through in-situ carbonation

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Abstract:

This study proposes an effective strategy to simultaneously enhance the mechanical performance and CO_2 sequestration capacity of limestone calcined clay cement (LC^3) incorporating low-grade calcined clay through aqueous carbonation. 25% of the cement fraction in LC^3 was subjected to aqueous carbonation for 10 to 40 mins with a water-to-solid ratio of 2.0, leading to the in-situ precipitation of nano-sized $CaCO_3$. A maximum CO_2 uptake of 15.78% was achieved after 40 min of carbonation. After mixing with the remaining materials of the LC3 formulation, the synergistic dilution and nucleation effects of in-situ nano $CaCO_3$ promoted the hydration of silicate and aluminate phases, thereby refining the pore structure of LC^3. At 3 days, the fraction of fine capillary pores (10-50 nm) increased remarkably, reaching 54% and 60% after 30 and 40 min of carbonation, respectively, and this refinement was largely preserved at 28 days. Consequently, the 28-day compressive strength of LC^3 mortars increased by 34.93% and 32.07% at carbonation durations of 30 and 40 min, respectively, compared with the control group. However, substantial consumption of portlandite during pre-carbonation constrained the later development of carboaluminate phases, which highlights a trade-off between enhanced early hydration and limited availability of secondary hydration products. These findings offer new insights into the role of in-situ $CaCO_3$ precipitation in modifying hydration and pore structure, demonstrating that

aqueous carbonation is an effective route to enhance LC^3 performance while facilitating CO_2 sequestration.

Keywords: Aqueous carbonation; CO_2 sequestration; In-situ carbonation; Limestone calcined clay cement; Nano $CaCO_3$

1. Introduction

The cement industry is one of the major contributors to global energy consumption and CO_2 emissions, accounting for approximately 6-8% of total anthropogenic CO_2 emissions worldwide [1,2]. With the urgent challenges of global climate change, the development of low-carbon and high-performance cementitious materials has become a research priority. Since most CO_2 emissions arise from clinker calcination, reducing clinker content is a widely recognised promising strategy to mitigate the environmental impact of cement production [3].

Limestone Calcined Clay Cement (LC^3) has attracted increasing attention in recent years due to its reduced clinker factor and favourable mechanical performance [4,5]. By partially replacing clinker with calcined clay and limestone, LC^3 reduces clinker consumption of approximately 40-50%, resulting in a reduction of CO_2 emissions by about 30-40% per ton of cement, compared with Portland cement [6]. Moreover, the pozzolanic reactivity of calcined clay, combined with the synergistic effect of limestone, promotes the formation of dense hydration products, such as hemicarboaluminate (Hc) and monocarboaluminate (Mc) [7–9], thereby enhancing the mechanical properties and durability of the cementitious matrix. Nevertheless, LC^3 suffers from relatively slow early-age hydration and insufficient strength development, which restricts its broader application [10,11].

In recent years, various nanoparticles have been explored as hydration accelerators in cement-based materials. Among them, nano-SiO_2 not only provides abundant nucleation sites but also reacts pozzolanically with $Ca(OH)_2$ to generate additional C-S-H, thereby enhancing later-age strength and structural homogeneity [12–14]. Nano C-S-H seeds serve as precursors or templates for the epitaxial growth of C-S-H, thereby

providing the most direct and efficient contribution to hydration kinetics [15,16]. In contrast, nano $CaCO_3$ promotes hydration through a combined physical-chemical mechanism, since it not only provides filler and nucleation effects but also interacts chemically with reactive aluminates. Moreover, the polymorphs of $CaCO_3$ (calcite, aragonite, and vaterite) influence the fluidity and compressive strength of cement-based materials due to their differences in solubility and reactivity [17–19].

In LC^3, calcium carbonate plays a crucial role as a major constituent, actively participating in hydration by interacting with alumina phases and stabilising carboaluminate hydrates. While reducing the particle size to the nanoscale can promote these effects by providing additional nucleation sites, the external incorporation of nano $CaCO_3$ is often limited by agglomeration and poor dispersion, which can limit its efficiency [20,21]. This highlights the necessity for a method that ensures both high intrinsic reactivity and optimal dispersion.

To address these dispersion challenges, in-situ aqueous carbonation is proposed. Compared to dry carbonation and semi-dry carbonation, aqueous carbonation exhibits significantly faster reaction kinetics [22], a more uniform carbonation product distribution [23] and relatively simpler process control [24]. Distinct from traditional gas-solid carbonation, the process is primarily controlled by the aqueous diffusion of carbonate species (CO_3^{2-}/HCO_3^-), generated through the dissolution of CO_2 in the solution. Specifically, calcium-bearing phases (e.g., $Ca(OH)_2$ and C-S-H) release calcium ions, which then react in situ through a "dissolution-precipitation" process to form nanoscale $CaCO_3$ and alumina-silica gel, thereby densifying the microstructure [19,25,26]. Notably, the high-water demand of LC^3 is highly compatible with the liquid-rich environment required for aqueous carbonation, ensuring efficient transport. Within the favourable environment, the in-situ generated nanoscale $CaCO_3$ serves as nucleation sites to promote cement clinker hydration [27]. The carbonated cement slurry, consisting of residues and filtrate obtained after varying carbonation durations, was blended with the other materials of the LC^3 binder. Subsequently, the effects of carbonation duration on fresh properties, mechanical strength, and microstructural development (hydration and pore structure) were analysed. Specifically, the hydration

process of LC^3 incorporating carbonated cement slurry was investigated using X-ray diffraction (XRD), thermogravimetric analysis (TG), low-field nuclear magnetic resonance (LF-NMR), and scanning electron microscopy (SEM).

2. Materials and Methods

2.1 Materials

In this study, commercially available P·I 42.5, produced by Shandong Cement Group, was used as the main binder. Calcined clay, with a strength activity index of 84.23% in accordance with ASTM C311 [28], was sourced from Nanjing, China. Calcium carbonate and gypsum, both supplied by Merck, were used as supplementary materials for the preparation of LC^3. The properties of these materials meet the relevant requirements specified in ASTM C618 [29].

The chemical and mineralogical compositions of the raw materials were determined using X-ray fluorescence (XRF) and quantitative X-ray powder diffraction (XRD), as presented in Table 1. The particle size distribution of each raw material is presented in Fig. 1. Polycarboxylate ether (PCE) superplasticiser was employed to maintain the comparable flowability of mortars [30,31]

Table 1. Chemical and mineralogical compositions of raw materials (*wt*.%)

Oxide	Cement	Calcined clay	Limestone	Gypsum
SiO_2	18.5	55.95	0.36	0.016
Al_2O_3	3.99	34.62	0.25	0.017
Fe_2O_3	3.40	1.79	0.06	-
CaO	59.17	0.91	54.07	49.48
MgO	3.79	1.75	0.40	0.02
SO_3	3.41	0.14	0.09	50.44
Na_2O	0.23	0.49	-	0.01
K_2O	1.18	3.86	0.01	0.01
TiO_2	0.25	0.28	0.01	-
M_nO	0.09	0.02	-	-
P_2O_5	0.08	0.05	-	-
LOI	1.87	1.07	43.04	20.91
C_3S	63.66			
C_2S	13.64			
C_3A	6.86			

C_4AF	8.93
Anhydrite	2.13

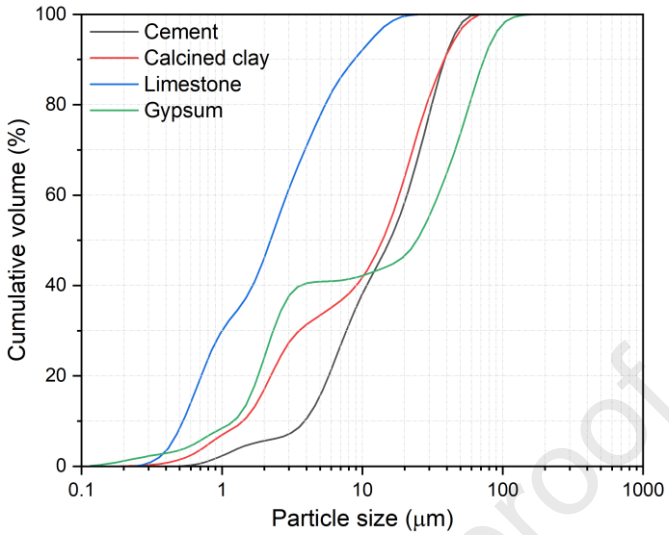

Fig. 1. Particle size distribution of raw materials.

2.2 Methodology

In this study, the LC^3 formulation employed was composed of 50% ordinary Portland cement, 30% calcined clay, and 15% limestone by mass. Additionally, 5% gypsum ($CaSO_4 \cdot 2H_2O$) was added as a regulator to control the setting behaviour of the binder, following the procedure established by Avet and Scrivener [7]. The water-to-binder ratio (w/b) was maintained at a constant value of 0.5 for all mixtures. To investigate the effect of aqueous carbonation on the hydration and microstructural development of LC^3, 25% of the cement was subjected to carbonation by immersion in an aqueous solution saturated with CO_2, at a water-to-cement ratio of 2.0.

2.2.1 Aqueous carbonation of cement suspensions

The aqueous carbonation experiments were conducted at ambient temperature and pressure in a 500 mL beaker containing a cement suspension prepared by mixing 100 g of cement with 200 g of deionised water. Before carbonation, the suspension was homogenised by magnetic stirring at 500 rpm for 3 min and maintained at the same stirring rate throughout the procedure to ensure uniform dispersion. High-purity CO_2 gas (purity > 99.9%) was bubbled into the suspension at a flow rate of 1 L/min through

an air stone positioned 1 cm below the liquid surface. The carbonated cement suspensions were designated CO_2-10, CO_2-20, CO_2-30, and CO_2-40, corresponding to carbonation durations of 10, 20, 30, and 40 minutes, respectively, with the uncarbonated suspensions used as the control group (CO_2-0). A schematic of the aqueous carbonation setup established in this study is presented in Fig. 2.

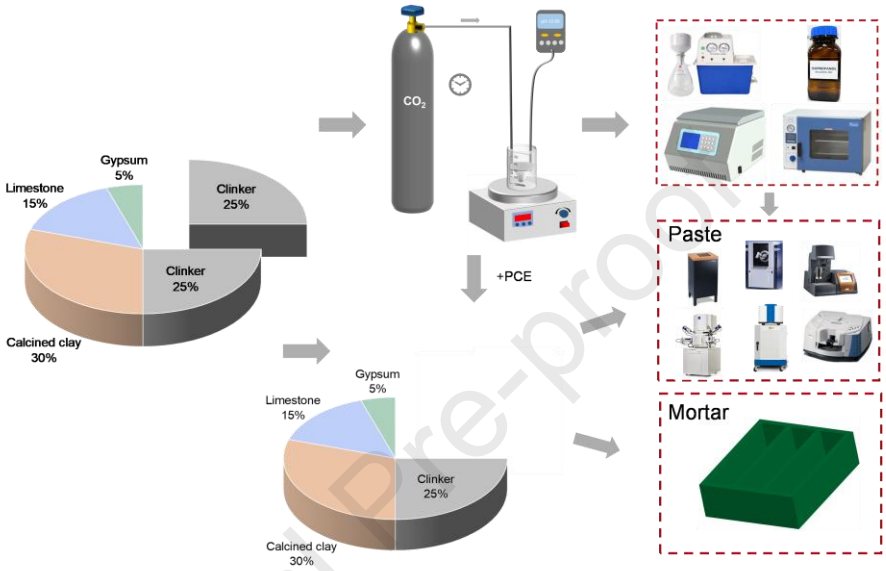

Fig. 2. Schematic view of in-situ carbonation preparation of LC^3.

After carbonation, the suspension was blended with the remaining raw materials to prepare LC^3 mortars and pastes. To investigate the phase assemblage and microstructural changes induced by aqueous carbonation, part of the carbonated cement paste was separated by vacuum filtration, rinsed three times with isopropanol to stop further hydration and carbonation, and then centrifuged at 3000 rpm for 3 min. The recovered solids were subsequently vacuum dried at 40 °C for 72h to ensure complete removal of residual moisture and solvent, according to established procedures [27,32]. The dried samples were then characterised by X-ray diffraction (XRD), thermogravimetric analysis (TGA), N_2 adsorption-desorption (BET), and scanning electron microscopy (SEM).

2.2.2 Preparation of LC^3 mortar and paste

The carbonated cement suspension was blended with a polycarboxylate ether (PCE) superplasticiser and subsequently mixed with the remaining cementitious materials to ensure uniformity and consistency. Standard sand was added at a sand-to-binder mass ratio of 3:1, and the mixture was stirred for 5 min in a rotating mixer to produce mortar specimens. The fresh mortar was cast into 40 × 40 × 160 mm^3 prism moulds in accordance with EN 196-1, compacted by vibration, and covered with plastic film to minimise moisture loss. Curing was first carried out at 95% relative humidity and 20 ± 2 °C for 24h, after which the specimens were demolded and further cured under the same conditions until testing. The paste and mortar specimens were designated LC^3-0, LC^3-10, LC^3-20, LC^3-30, and LC^3-40, corresponding to carbonation durations of 0, 10, 20, 30, and 40 min, respectively, as summarised in Table 1.

Table 2. Mix proportions of LC^3 with and without carbonated cement paste

Sample ID	A (%)	B (%)	CO_2 Duration (min)	Calcined Clay (%)	Limestone (%)	Gypsum (%)	w/b	PCE (%)
LC^3-0	25	25	0	30	15	5	0.5	0.32
LC^3-10	25	25	10	30	15	5	0.5	0.51
LC^3-20	25	25	20	30	15	5	0.5	0.94
LC^3-30	25	25	30	30	15	5	0.5	1.44
LC^3-40	25	25	40	30	15	5	0.5	1.86

*A represents the proportion of cement used for in-situ aqueous carbonation
B represents the remaining proportion of cement in LC^3

2.3 Experimental methods

2.3.1 Paste fluidity and setting time

After mixing the carbonated cement paste with the remaining constituents of the mixture for 3 min, the flowability of the LC^3 paste was tested using a flow table according to GB/T 2419-2005 [33]. A truncated cone mould (36 mm × 60 mm × 60 mm) was filled with the paste and lifted vertically, and the table was operated to complete 25 drops within 25 ± 1 s. The spread diameter was measured in two perpendicular directions, and their average was taken as the flow value. Each mixture was tested in triplicate, and the mean result was reported and quoted in the analyses.

The setting time of the LC^3 paste was measured using a Vicat apparatus in accordance with GB/T 1346-2011 [34]. Fresh paste was placed into the Vicat mould and levelled, and the specimen was kept in a controlled environment at 20 ± 1°C and relative humidity above 90%. The penetration of the Vicat needle was recorded every 5 minutes. Each mixture was tested in triplicate, and the mean value was reported and quoted in the analyses.

2.3.2 Isothermal calorimetry

The LC^3 paste incorporating carbonated cement paste was homogenised via machine-assisted external mixing for 3 min. Subsequently, a sample of approximately 5.39 g was weighed out. The fresh paste was then immediately transferred into a sealed glass ampoule and placed in a TAM Air (8-channel, Thermometric, USA) isothermal calorimeter. Hydration heat flow and cumulative heat release were continuously recorded for 72h at 25 ± 0.1°C to assess the early-age hydration kinetics influenced by the in-situ carbonated products. Two independent replicates were conducted to ensure reproducibility.

2.3.3 Quantitative X-ray Diffraction (QXRD)

Mineralogical identification and quantitative phase analysis of carbonated cement paste and hardened LC^3 paste were performed using a Bruker D8 Advance diffractometer (Cu-Kα radiation, λ=1.54184 Å, 40 kV, 40mA). For quantification, 0.8 g of ground paste (passing a 75 μm sieve) was homogenised with 0.2 g of α-Al_2O_3 as an internal standard (4:1 weight ratio) using ethanol as a dispersant. XRD patterns were recorded over a 2θ range of 5°-70° with a scanning speed of 2°/min and a step size of 0.02°. Phase quantification was performed via Rietveld refinement in TOPAS software. The refinement quality was confirmed by R*p* and R*wp* values below 15%, ensuring the reliability of the resulting phase contents.

The corresponding PDF code numbers used for phase identification are provided below: Alite (PDF# 00-042-0551), Belite (PDF# 00-029-0369), Ettringite (PDF# 00-041-

1451), Gypsum (PDF# 00-021-0816), Portlandite (PDF# 00-004-0733), Calcite (PDF# 00-005-0586), Corundum (PDF# 00-010-0173), Hemi carboaluminate (PDF# 00-041-0221), mono carboaluminate (PDF# 00-041-0219).

2.3.4 Scanning electron microscopy (SEM)

The morphology of cement particles subjected to different carbonation durations was analysed using a ZEISS Gemini SEM 560 (Zeiss, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS). Before imaging, the samples were rinsed with isopropanol to stop hydration, vacuum-dried at 40 °C for 72h, mounted on aluminium stubs, and sputter-coated with a thin gold layer to improve conductivity.

2.3.5 Particle size distribution and specific surface area

The particle size distribution of raw materials and carbonated cement particles was measured using a Malvern Mastersizer 2000 (Malvern Instruments, UK). Specific surface area was determined by the BET method, while pore volume and size distribution were calculated using the BJH model from nitrogen adsorption-desorption isotherms (Kubo X1000). Differential pore volume curves from the adsorption branch were used to characterise pore structure.

2.3.6 Thermogravimetric analysis (TGA)

The hydration of the paste samples was terminated using isopropanol, followed by drying in a vacuum oven at 40 °C for 3 days before TGA. The dried samples were subsequently ground to pass through a 75 μm sieve to ensure homogeneity. Thermogravimetric measurements were performed using a TGA 55 instrument. For each measurement, approximately 7 mg of the prepared powder was heated from 40 °C to 800 °C at a constant heating rate of 10 °C/min. To maintain an inert environment and prevent carbonation, a nitrogen flow of 50 mL/min was continuously applied throughout the heating process.

2.3.7 Compressive strength of LC^3 mortar

The compressive strength of LC^3 mortar was measured from 40 mm-side length cubic specimens broken from 40 × 40 × 160 mm^3 prismatic samples by flexural bending after curing for 1, 3, 7 and 28 days under a loading rate of 2400 ± 200 N/s, and the average strength obtained from six cubic specimens from the same LC^3 formulation was recorded as the corresponding representative strength of the LC^3 at each curing age.

2.3.8 Low field nuclear magnetic resonance (LF-NMR)

Low field nuclear magnetic resonance (LF-NMR) was employed to analyse the pore structure of LC^3 paste at 3d, 7d and 28d. For this purpose, a MicroMR20-025V NMR analyser (Niumag, China) operating at 20 MHz was employed to obtain the transverse relaxation time (T_2) distributions. Cylindrical specimens (Φ20mm × 20 mm) were fully saturated for 24h before testing to ensure complete pore filling. All measurements were conducted at 25 ± 1°C, and the average value of three specimens of the same LC^3 formulation was taken as the corresponding representative value of the mixture for analysis.

3 Results and discussion

3.1 Characterisation of carbonated cement paste

3.1.1 Particle size distribution and specific surface area

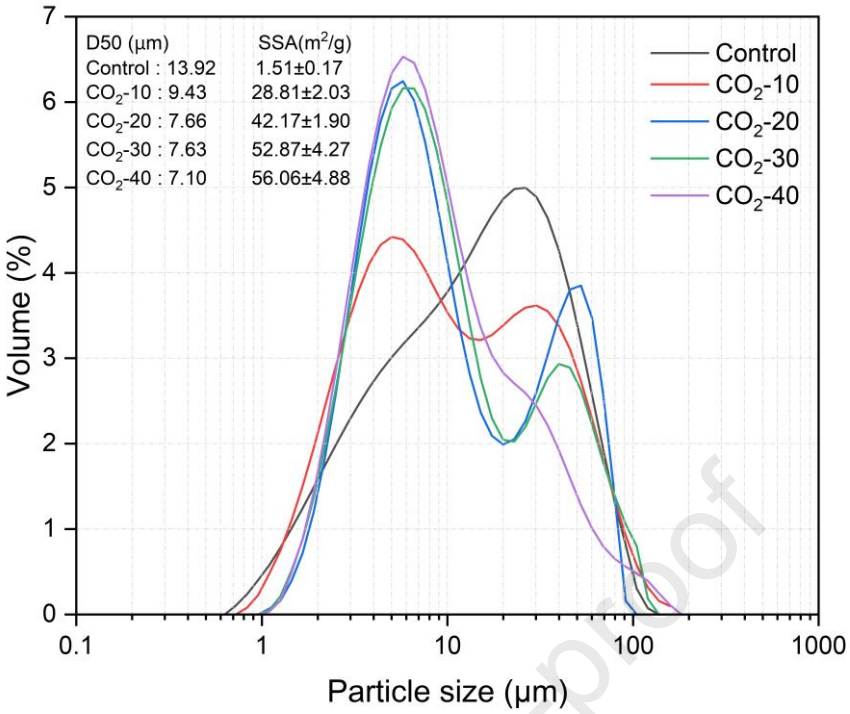

Fig. 3. Particle size distribution of carbonated cement particles.

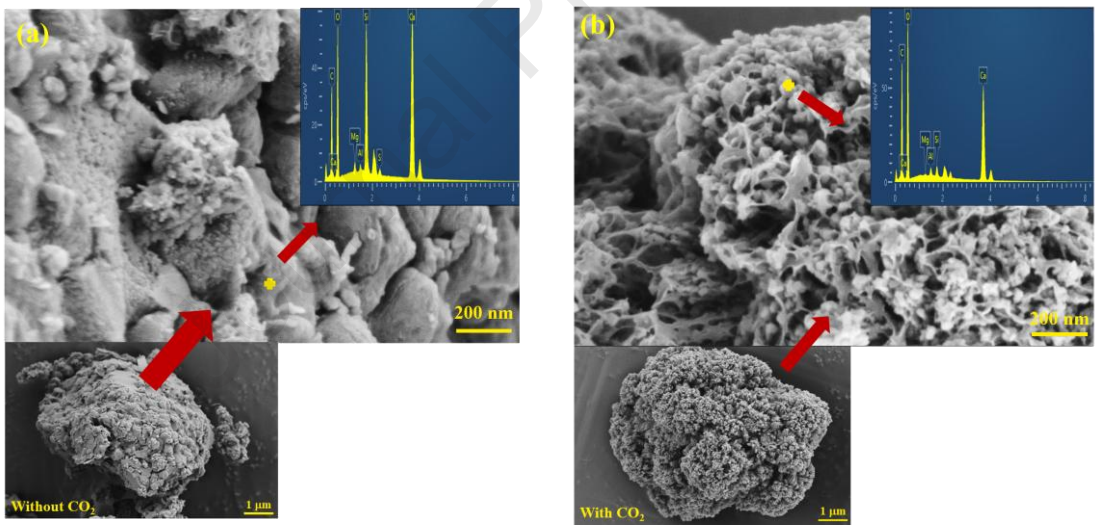

Fig. 4. Cement particles (a) without CO_2 and (b) with CO_2, 30 min.

234 During aqueous carbonation, CO_2 dissolves into the solution to form carbonic acid,
235 which subsequently dissociates into bicarbonate and carbonate ions under the high-
236 alkaline environments. Meanwhile, the progressive dissolution of clinker phases,
237 particularly C_3S, C_2S, and portlandite, reduces the particle size of cement grains and
238 substantially increases their specific surface area (SSA) (Fig. 3), thereby enhancing ion
239 exchange and reactivity. The released Ca^{2+} interacts with carbonate species to

240 precipitate $CaCO_3$, primarily as amorphous or nano-sized crystallites nucleating on
241 cement particle surfaces. As the carbonation duration increases from 0 to 40 min, the
242 particle size distribution of the carbonated cement powders progressively develops a
243 bimodal pattern, indicating the coexistence of very fine particles and larger
244 agglomerates, which suggests partial flocculation and heterogeneous carbonation of the
245 cement grains. This coupled dissolution-precipitation process also refines the particle
246 morphology (Fig. 4(b)) and increases the density of nucleation sites. SEM-EDS
247 analysis confirms the formation of nanoscale $CaCO_3$, and it can be observed that
248 nanoscale $CaCO_3$ and gel phases are interspersed on the surface of carbonated cement
249 particles.

250 3.1.2 Mineralogical phase

251 As shown in Fig. 5, the XRD patterns reveal that calcite peaks became more distinct
252 with prolonged carbonation and the pH monitoring indicated that all carbonated
253 specimens maintained a high alkalinity, with values remaining above 11.20 throughout
254 the testing period. This high alkalinity, combined with the formation of calcite, indicates
255 the ongoing hydration and carbonation of the calcium silicates (C_3S and C_2S).
256 Meanwhile, the progressive reduction and disappearance of the gypsum peak at 11.62°
257 were observed, suggesting their decomposition and transformation during carbonation.

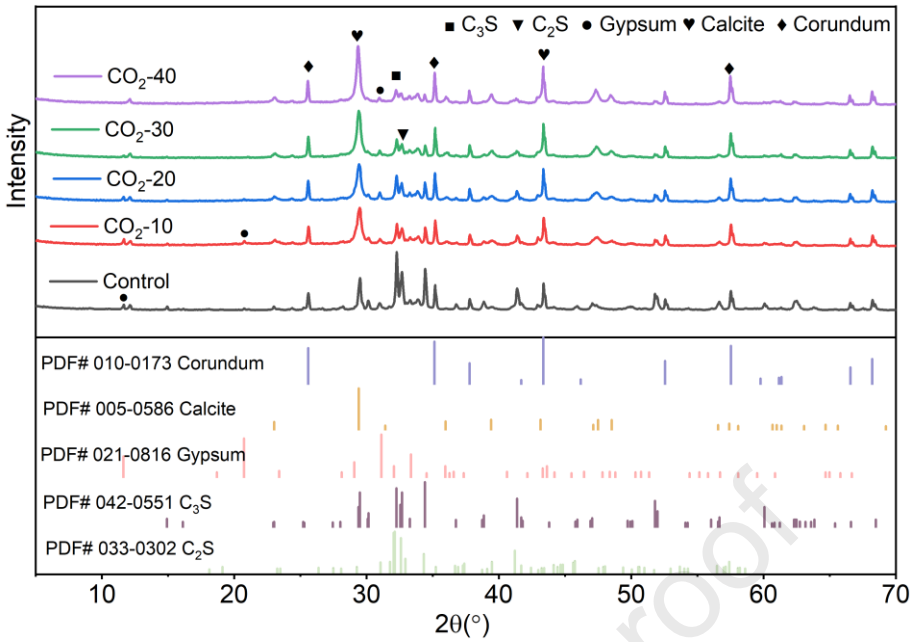

Fig. 5. XRD patterns of carbonated cement particles at different carbonation durations.

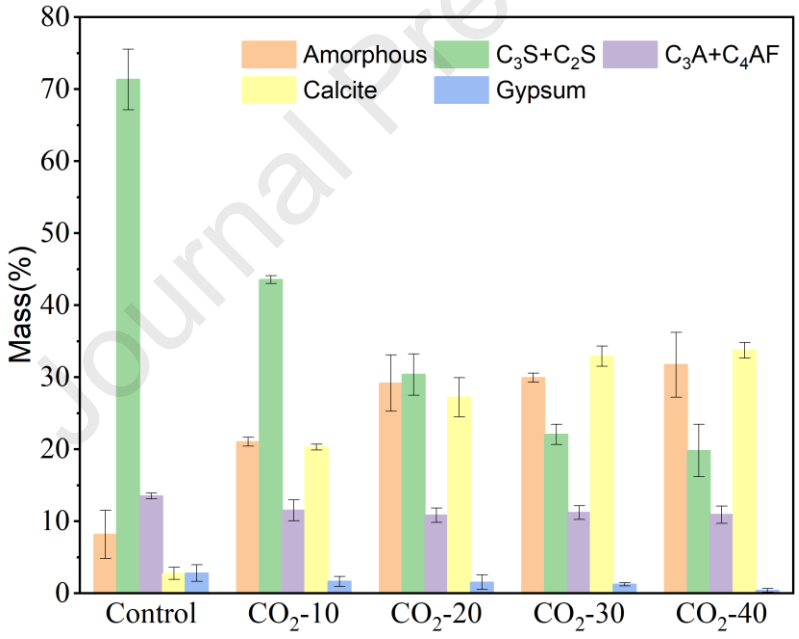

Fig. 6. Mineralogical evolution via QXRD.

The quantitative changes in major phases were analysed by Rietveld refinement. As shown in Fig. 6, the contents of the amorphous phase and calcite varied markedly with carbonation duration, while the $CaCO_3$ content remained nearly constant after 30 and 40 min of carbonation. The crystallite size was evaluated by Rietveld refinement based on the Fundamental Parameter Approach via TOPAS [35], ranging from 36 to 75 nm. This nanoscale morphology is consistent with the SEM-EDS observations shown in Fig.

4, which reveal the formation of nanoscale $CaCO_3$ particles. The formation of these nanoscale $CaCO_3$ is associated with an increase in specific surface area, thereby providing nucleation sites for continued hydration, as reported by Monkman et al. [20,36].

The formation and content variation of $CaCO_3$ were further supported by the subsequent DTG analysis, which quantified the CO_2 uptake and phase evolution during the aqueous carbonation. As shown in Fig. 7(b), the broad peak in the 40-80 °C range and the sharp peak at approximately 105 °C are attributed to the dehydration of minor amounts of gel phases (including C-(A)-S-H and silica gel) and gypsum, respectively. With the progression of carbonation, C-(A)-S-H was readily decalcified to form $CaCO_3$ and silica gel, resulting in an increased intensity of the broad peak at 40-80°C, while the gypsum peak diminished. Concurrently, the broad peak between 400 and 580 °C, associated with amorphous $CaCO_3$ [37], was observed. Furthermore, the sharp peak in the range of 580-700 °C, corresponding to the decomposition of calcite [38], exhibited a significant increase in intensity. The progressive increase in peak intensity with extended carbonation duration reflects the accumulation of stable carbonate phases within the cement matrix. Fig. 8 compares the CO_2 uptake obtained by the QXRD and DTG analyses, calculated based on Equations (1) and (2), respectively, in which m_{co_2} denotes the molar mass of CO_2, while M_n denotes the mass percentage of the sample at n°C.

$$\text{QXRD:}\quad CO_2\ \text{uptake (wt.\%)} = M_{CaCO_3} \times \frac{m_{CO_2}}{m_{CaCO_3}} \tag{1}$$

$$\text{DTG:}\quad CO_2\ \text{uptake (wt.\%)} = \frac{M_{400} - M_{700}}{M_{105}} \times 100 \tag{2}$$

The results show that the CO_2 uptake determined by DTG is slightly higher due to the presence of amorphous $CaCO_3$. Nevertheless, both methods indicate that the CO_2 uptake was in the range of 15-16% after 30 min of carbonation.

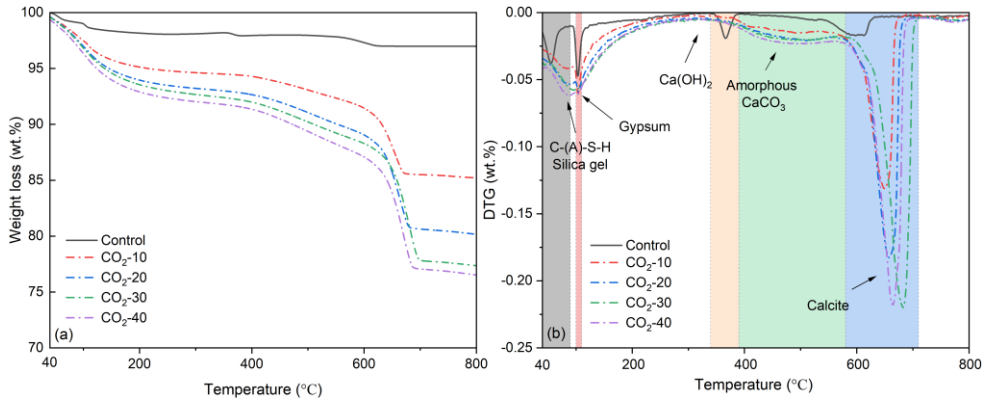

Fig. 7. (a) TG and (b) DTG results of carbonated cement particle.

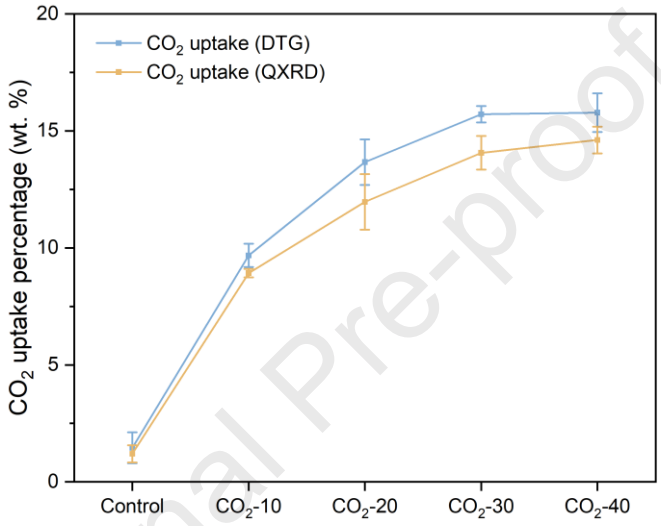

Fig. 8. Comparison of CO_2 uptake calculated by QXRD and DTG

289 3.2 Integration of in-situ carbonation with LC^3

290 3.2.1 Fluidity and setting time of LC^3 paste

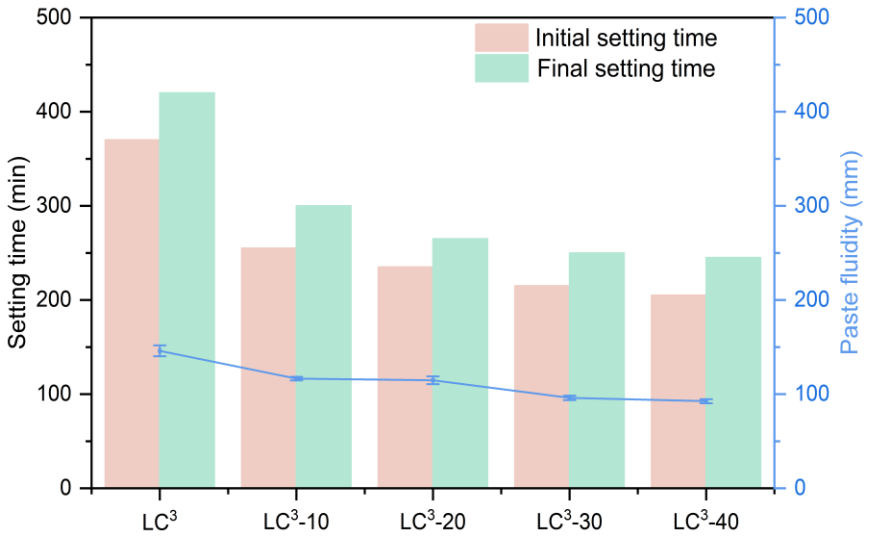

Fig. 9. Setting time and fluidity of LC^3 paste with carbonated cement paste

As shown in Fig. 9, the calcium carbonate generated during pre-carbonation markedly reduced both the fluidity and setting time of LC^3. Specifically, the initial and final setting times of LC^3-40 decreased by 44.60% and 41.67%, respectively, while the fluidity of LC^3-30 and LC^3-40 decreased by 34.25% and 36.64%. These changes can be primarily attributed to the participation of free water in hydration and carbonation reactions during pre-carbonation, which promotes the in-situ formation of nano-$CaCO_3$ and silica gel. The presence of these in-situ nucleated nano-$CaCO_3$ significantly accelerates subsequent cement hydration by providing abundant nucleation sites, thereby shortening the setting time and reducing workability [39]. Moreover, although carbonation decreases the amount of reactive clinker, the metakaolin fraction remains unchanged and retains its high specific surface area. Consequently, its strong water demand and pronounced thickening effect become more dominant, further contributing to the reduction in fluidity and the acceleration of setting [40].

3.2.2 Compressive strength

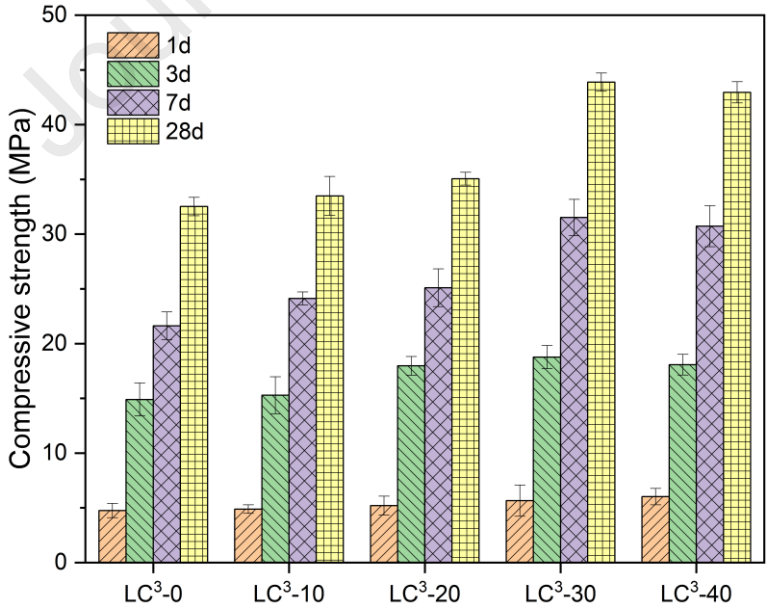

Fig. 10. Compressive strength of LC^3 subject to different carbonation durations.

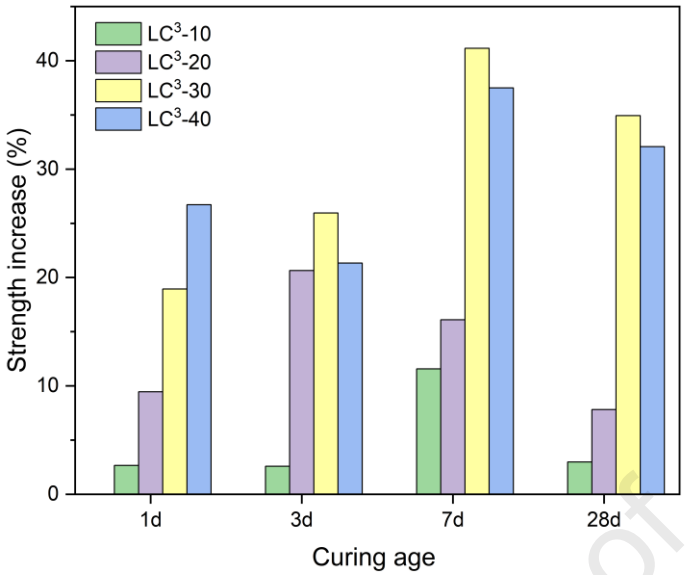

Fig. 11. Compressive strength increasing rates compared to LC^3-0 at various ages.

The compressive strength results demonstrate that the in-situ formation of $CaCO_3$ significantly enhanced the compressive strength of LC^3 mortar over the curing period. For LC^3-10, short-duration carbonation had a negligible influence, showing values only comparable to the control group (Fig. 10). With longer carbonation duration, LC^3-20, LC^3-30, and LC^3-40 exhibited significantly higher strength. At 28d, the compressive strength of LC^3-10, LC^3-20, LC^3-30, and LC^3-40 increased by 2.98%, 7.81%, 34.93%, and 32.07%, respectively, compared to that of the control group, as shown in Fig. 11. Despite the relatively low reactivity of the calcined clay used in this study (Reactivity index of only 84.23%), LC^3-30 and LC^3-40 achieved compressive strengths of 43.88 and 42.95 MPa, respectively, at 28d, comparable to the EN 197-1 strength class CEM I 42.5 (28d standard mortar strength ≥ 42.5 MPa).

Although part of the clinker was consumed during aqueous carbonation to form $CaCO_3$ and amorphous phases, the carbonated LC^3 mortar still exhibited higher compressive strength than the control group, underscoring the positive role of carbonate products in hydration. However, further prolongation of the carbonation duration did not lead to continuous strength development. The slightly lower early-age strength observed in LC^3-40 relative to LC^3-30 may be attributed to excessive carbonation, which consumed reactive clinker phases and produced a dense carbonate layer, thereby hindering subsequent hydration[41]. In contrast, significant strength gains were observed at later

ages. This pronounced late-age strength gain is ascribed to the filler and nucleation effect of $CaCO_3$. Furthermore, the pozzolanic reactivity of silica-rich gel may have also contributed to this enhancement, as reported by Zajac et al. [42]. These points highlight the positive contribution of aqueous carbonation to the strength development of LC^3.

3.2.2 Isothermal calorimetry

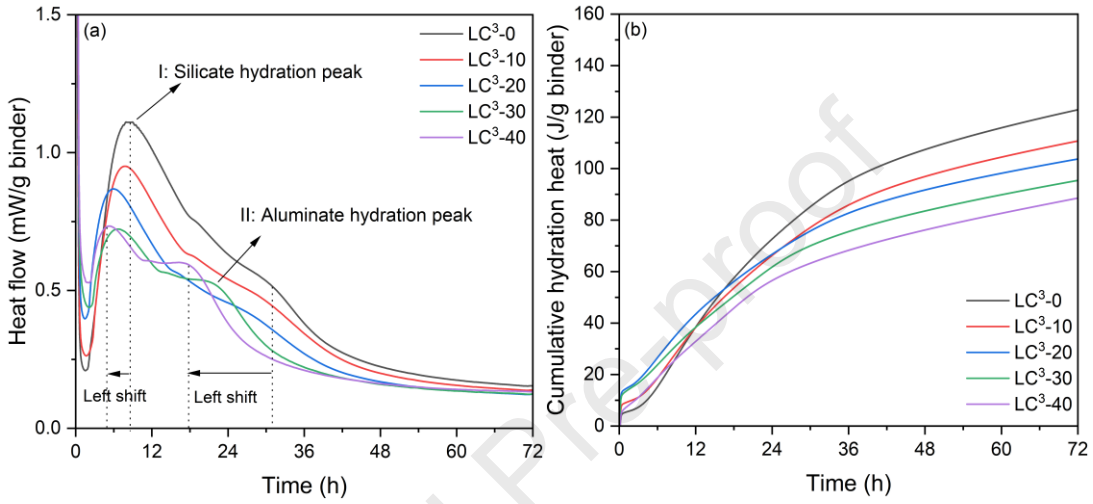

Fig. 12. (a) Hydration heat flow per unit binder mass. (b) Cumulative heat release per unit binder mass

Fig. 12 illustrates the heat flow and cumulative hydration heat curves of LC^3 pastes with and without carbonated cement paste over 72 hours. As shown in Fig. 12(a), the silicate hydration peak (Peak I) for LC^3-40 appeared approximately 3.5 h earlier than that of LC^3-0, signifying accelerated hydration kinetics. Regarding aluminate hydration (Peak II), the impact of carbonation was even more pronounced. The onset of LC^3-40 advanced to 17.6 h, which is nearly 13 hours earlier than that of LC^3-0, where the reaction only initiated after 24 h. Similarly, LC^3-30 also exhibited an onset before 24 h. These results confirm that $CaCO_3$ effectively promotes and accelerates the aluminate hydration process [7].

3.2.3 QXRD analysis of LC^3 paste

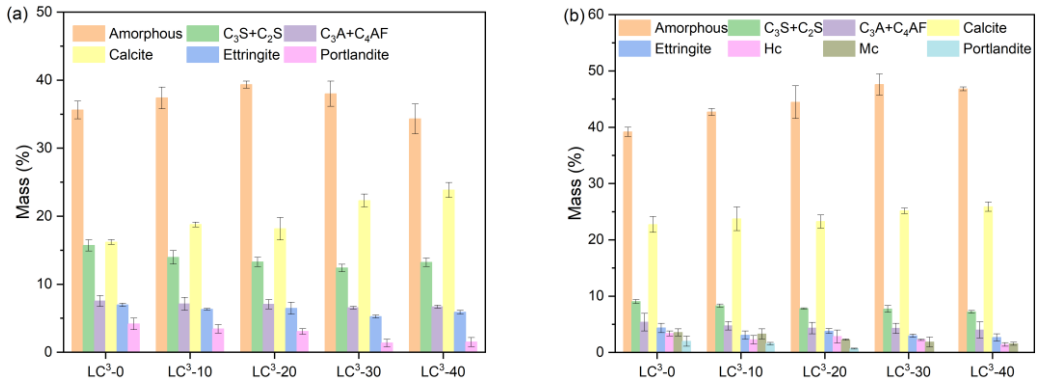

Fig.13. QXRD results of LC^3 paste at (a) 1d and (b) 28d.

Fig. 13 quantifies the hydration product contents of the samples at 1d and 28d following duplicate sampling and Rietveld refinement. It reveals distinct differences in $CaCO_3$ and amorphous phase contents among the samples at 1d (Fig. 13(a)) and further indicates that extended carbonation results in a marked rise in calcite content with a concomitant reduction in clinker phase content. Notably, the amorphous phase in LC^3-40 did not show a significant increase compared to that of LC^3-0. It appeared slightly lower than that of LC^3-20. However, the compressive strength results indicate that appropriate carbonation promotes early strength gain, suggesting that the early-age strength enhancement is not driven by the formation of additional C-S-H gel (amorphous phase) but primarily by the filler effect of the in-situ formed nanoscale $CaCO_3$, which densifies the microstructure.

Fig. 13(b) illustrates the quantitative phase assemblage of hydration products at 28d. In contrast to the results at 1d, the amorphous phase content increased significantly in all samples, becoming the dominant phase. Specifically, the amorphous content in carbonated samples (LC^3-10 to LC^3-40) ranged from 42% to 48%, surpassing that of the LC^3-0, which is around 39%. This substantial growth corresponds to the extensive formation of C-S-H gel and silica-rich gel derived from the pozzolanic reaction [37]. The 28d QXRD results reveal a marked reduction in Hc and Mc in LC^3-30 and LC^3-40, attributed to portlandite depletion, which constrains carboaluminate crystallisation [43]. Nevertheless, the long-term strength development was sustained by the high content of amorphous gel and residual calcite. The in-situ $CaCO_3$ served as effective nucleation

sites, accelerating the precipitation of hydration products (C-(A)-S-H) and creating a dense matrix despite the limited presence of carboaluminate.

3.2.4 DTG analysis

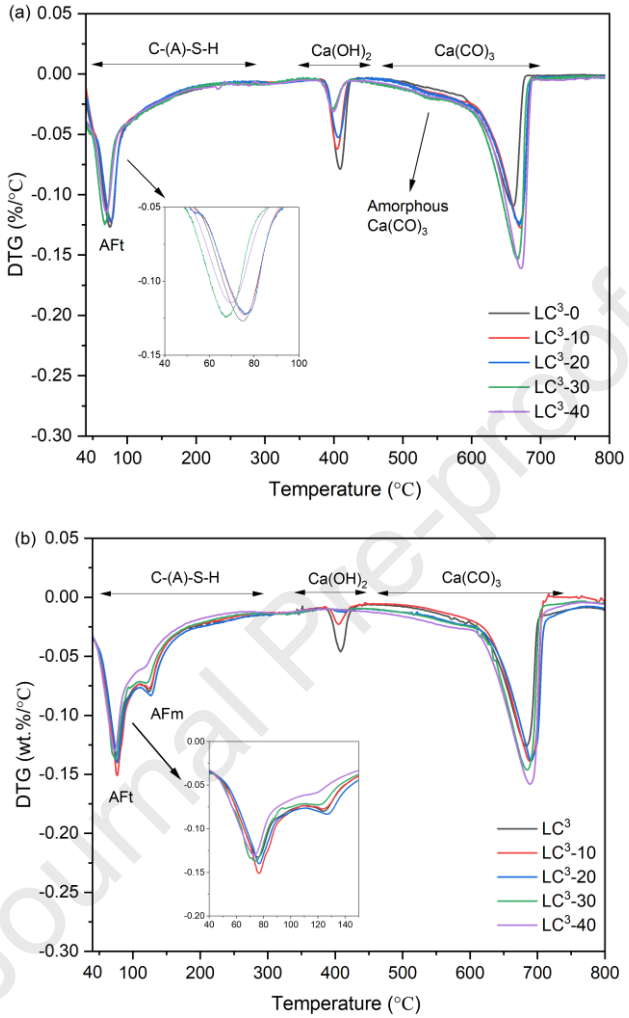

Fig. 14. DTG curve of LC^3 paste at (a)1 d and (b) 28 d.

Fig. 14 presents the DTG curves of samples at 1d and 28d, where four distinct peaks can be identified. The weight loss between 40 °C and 300 °C corresponds to the dehydration of C-(A)-S-H. The sharp peaks at around 80°C and 120 °C correspond to the dehydration of AFt phase (ettringite) and AFm phases (Hc and Mc), respectively. The peak between 360 °C and 430 °C is associated with the dehydroxylation of calcium hydroxide, while the weight loss from 430 °C to 600 °C corresponds to the decomposition of amorphous calcium carbonate (ACC), which is less thermally stable than crystalline calcite. A strong peak at 600 °C - 700 °C is attributed to decarbonation of calcite.

Thermogravimetric analysis reveals a progressive increase in $CaCO_3$ content with longer carbonation durations, accompanied by enhanced compressive strength of early age, suggesting a positive correlation between carbonation products and mechanical performance. At 28d, a pronounced reduction in portlandite content was observed in all samples by DTG and QXRD. This reduction arises from early carbonation of clinker phases, the pozzolanic reaction of metakaolin, and the formation of Hc and Mc. These results further demonstrate that early-age pre-carbonation depletes part of the reactive C_3S and C_2S, which consequently reduces the portlandite produced at later ages. In LC^3-30 and LC^3-40, excessive carbonation caused a pronounced deficiency of portlandite, thereby constraining AFm formation, whereas in the other groups, the peak intensity of AFm phases and C-(A)-S-H exhibited significant variation. As shown in Fig. 15, LC^3 with carbonated cement paste contained more $CaCO_3$ but less bound water (40 - 300 °C) compared to the control group. This suggests that the in-situ carbonation promotes a more uniform distribution of hydration products, which contributes positively to strength development.

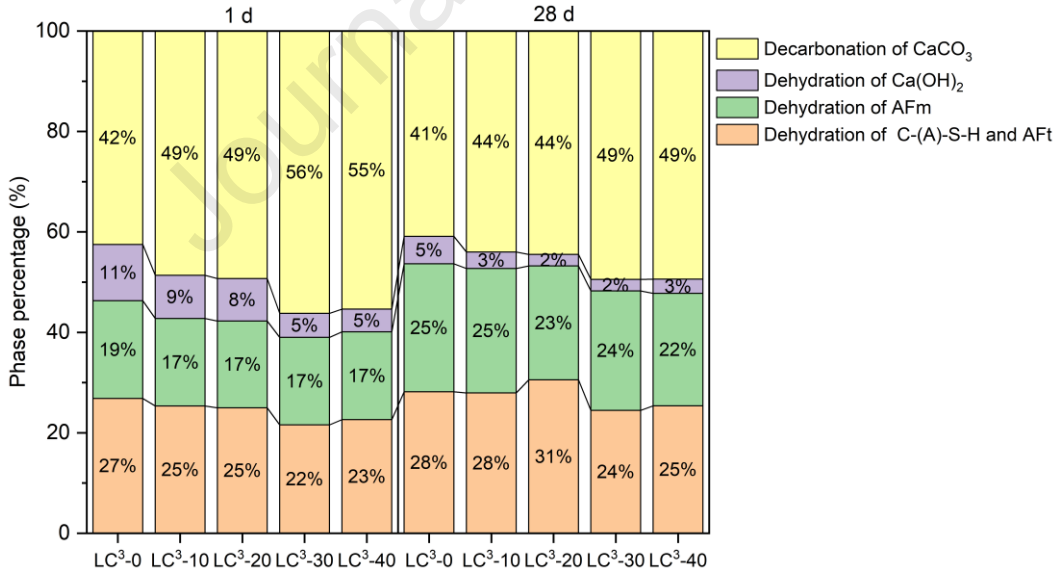

Fig. 15. Mass loss percentage of different hydration products in the samples.

3.2.5 Porosity analysis

To clarify the role of in-situ $CaCO_3$ in LC^3 hydration, pore structure analysis was performed using LF-NMR. Fig. 16 presents the total porosity of all samples at 3d and

28d as a function of carbonation duration. Short carbonation times, as in LC^3-10 and LC^3-20, resulted in higher porosity than the control group, whereas LC^3-30 displayed a porosity evolution comparable to the control group, suggesting that carbonation for 30 min exerts little influence on pore development. This behaviour can be explained by the evolution of PSD and SSA during carbonation: initially smooth cement grains progressively transformed into porous structures (Fig. 4). After 30 min, both D50 and SSA stabilised, confirming that carbonation duration governs the subsequent hydration and pore refinement of LC^3 paste. For LC^3-40, the porosity exhibits an initial increase followed by a subsequent decrease with hydration time, indicating that a carbonation duration of 40 min is already approaching an over-carbonation stage. From the SSA and fluidity results, it can be observed that after 30 minutes of carbonation, the SSA and fluidity of the cement particles gradually stabilise. At this stage, the silicate phases within the clinker undergo more pronounced dissolution and decalcification, together with significant alterations in their microstructural integrity, thereby reducing the amount of clinker that remains hydraulically active [44]. The progressively reduced compressive strength of LC^3-40 further supports these findings.

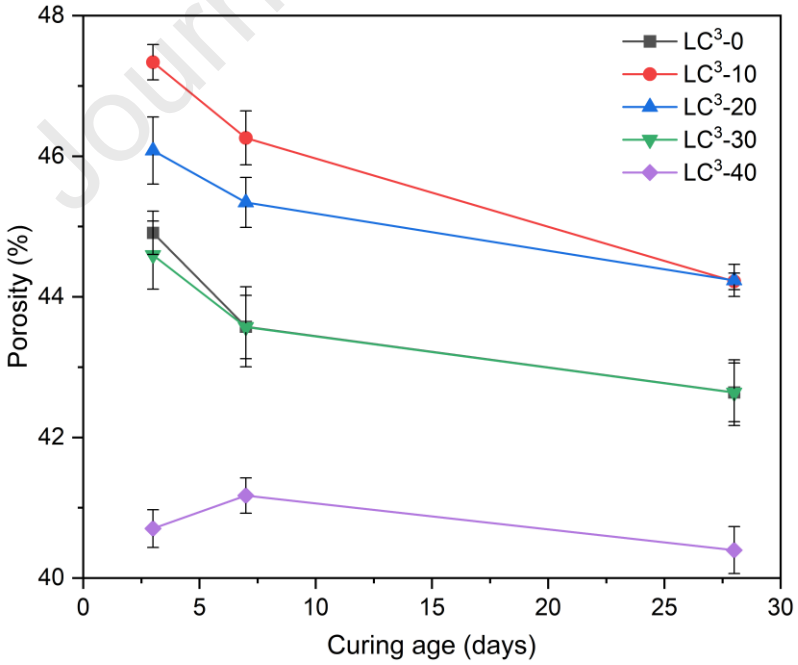

Fig.16. Porosity evolution of LC^3 paste at different ages.

The LF-NMR results further reveal the pore size distribution of samples at 3d and 28d.

Pore sizes were classified into four ranges: d < 10 nm (gel pores), 10-50 nm (fine capillary pores), 50 -100 nm (medium capillary pores), and d > 100 nm (coarse capillary pores) [45,46]. Macro-pores (50 nm-1 μm) are widely recognised as the dominant factors governing the strength and permeability of cementitious materials [47,48]. In this study, the pore volume distribution of all samples was mainly concentrated between 10 and 100 nm, indicating a predominantly mesoporous structure with limited macro-pore development, as shown in Fig. 17.

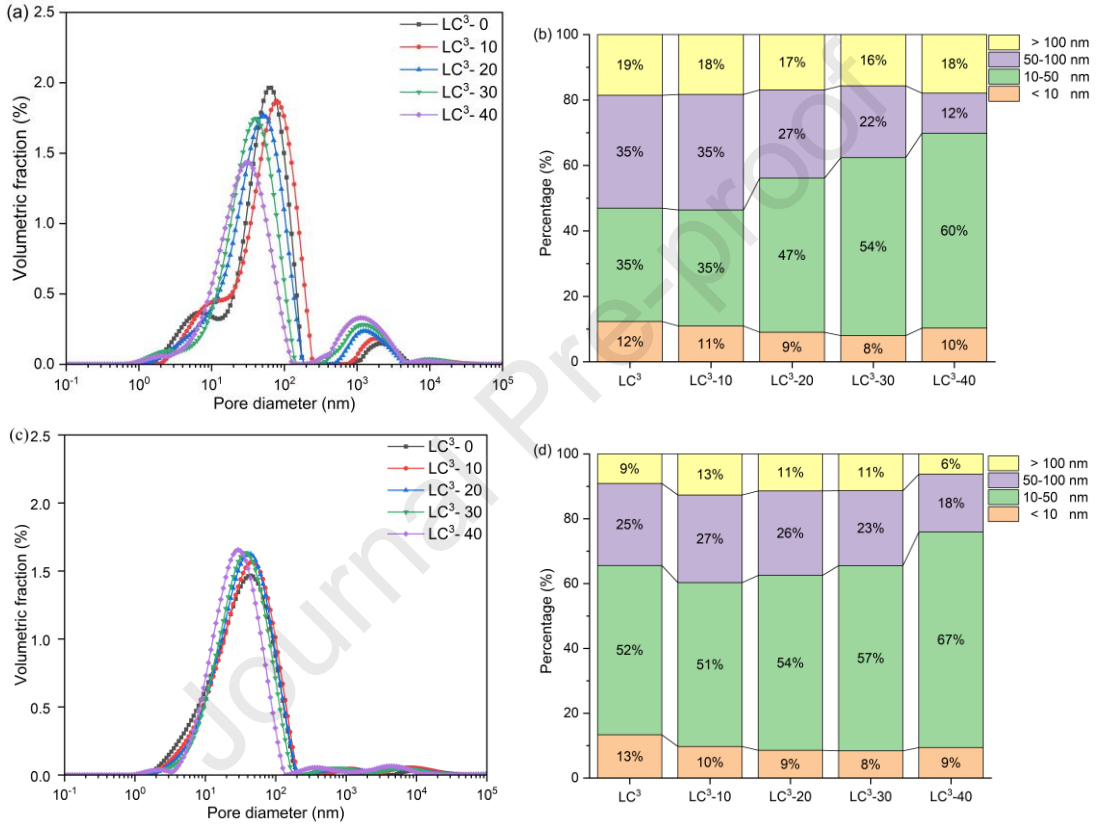

Fig. 17. Pore size distribution of samples at (a) (b) 3d and (c) (d) 28d.

Figure 17(a) shows the presence of distinct pore size peaks (d < 10 nm) in LC^3-0 and LC^3-10 at 3d, while the accompanying data in Fig. 17(b) quantifies the shifts in peak intensity and volume proportion. In contrast, samples subjected to longer carbonation durations displayed no pronounced peaks in this region, possibly due to the formation of nano $CaCO_3$, which promoted the densification of C-(A)-S-H. Compared with the control group, the primary pore volume distribution peaks of all samples, except LC^3-10, shifted toward smaller pore sizes and exhibited lower intensities, indicating refinement of gel pores and a reduction in overall gel pore volume. A small fraction of

coarse capillary pores (> 100 nm) was also detected in the carbonated samples. This may be attributed to the local dissolution of cement particles during aqueous carbonation and subsequent precipitation of nano $CaCO_3$, which can leave larger voids at original sites.

By 28d, the proportion of coarse capillary pores disappeared, as shown in Fig. 17(c). Meanwhile, the peak intensity of all samples incorporating carbonated cement paste was higher than that of the control, and the peak positions exhibited a progressive shift toward smaller pore sizes with increasing carbonation duration. A reduction in the proportion of pores > 100 nm was identified, accompanied by an increase in fine capillary pores (10-50 nm), as shown in Fig. 17(d), the in-situ carbonation promoted the in-situ formation of calcium carbonate particles on the cement surface, which facilitated the further hydration of LC^3 cement clinker, thereby densifying its microstructure and improving its strength. The refinement effect was also particularly evident at 3d, with the fraction of fine capillary pores increased by 2.49%, 36.00%, 57.04%, and 71.95% for carbonation durations of 10, 20, 30, and 40 min, respectively. Although this refined distribution weakened over time, the proportion of fine capillary pores remained higher at 28d than that of the control. Such pore refinement, induced by $CaCO_3$ and amorphous phases, is expected to contribute positively to the strength development of LC^3, as shown in Fig. 18.

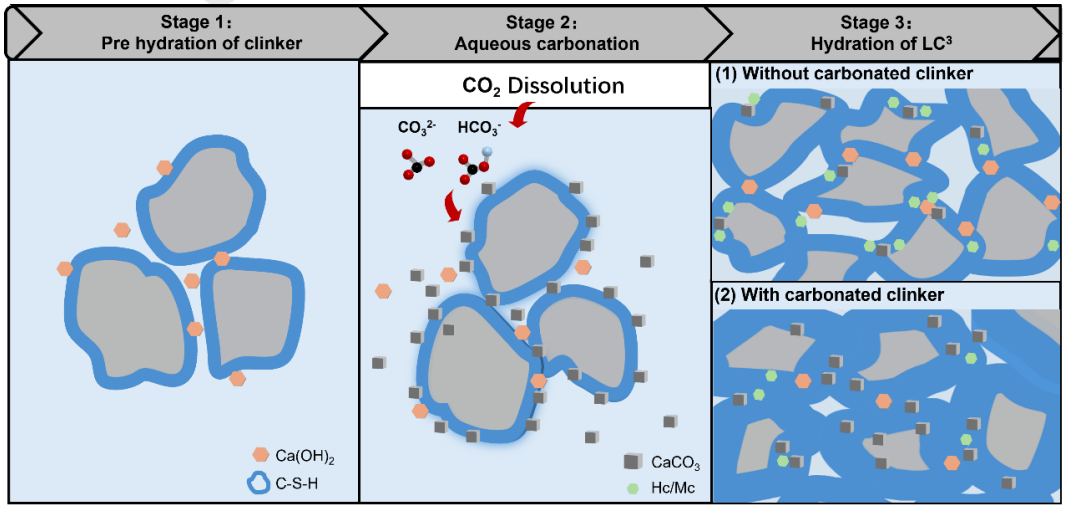

Fig. 18. Schematic diagrams of in-situ $CaCO_3$ formation and its impact on LC^3

Conclusion

This study demonstrates that partial pre-carbonation of the LC^3 cement fraction produces in-situ nano sized $CaCO_3$ that reshapes early hydration, microstructure development, and mechanical performance through nucleation and dilution effects. First, in situ $CaCO_3$ supplies abundant nucleation sites that advance both the silicate (Peak I) and aluminate (Peak II) hydration events, increasing early cumulative heat on a binder basis. Afterwards, this nucleation advantage translates into rapid refinement within the mesopore band (10-50 nm), as evidenced by the leftward shift and intensification of PSD peaks and the elevation of the fine-capillary fraction to 28d. Moreover, the same pre-carbonation converts part of the reactive clinker into carbonate, progressively depleting portlandite and moderating the extent of carboaluminate (i.e. Hc and Mc) formation at later ages. Consequently, nucleation-driven densification surpasses clinker dilution within an optimal dosage, achieving pronounced strength gains. Considering both the process and property, 30 minutes of carbonation (CO_2 uptake ≈ 15%) was believed to be an optimum. LC^3-30 and LC^3-40 mortars exhibit about 30% higher 28d strength than the control group, approaching the EN 197-1 CEM I 42.5 strength class, despite the relatively modest reactivity of the calcined clay used. Nevertheless, at later ages, strength development is controlled by microstructural densification, indicating that the nucleation/filler roles of in situ $CaCO_3$ effectively compensate dilution up to a threshold. Based on the experimental results and analyses, the main conclusions can be drawn:

1) Aqueous carbonation led to the in-situ formation of nanoscale $CaCO_3$, which is interspersed with gel phase and adheres to the surface of cement particles. The increased specific surface area of the cement provided additional nucleation sites, effectively accelerating the hydration kinetics of silicate and aluminate phases in LC^3. However, the progressive consumption of portlandite during pre-carbonation restricted the later formation of hemicarboaluminate and monocarboaluminate, highlighting a trade-off between enhanced early hydration and limited availability of secondary hydration products.
2) In-situ generated nano $CaCO_3$ significantly improved the compressive strength of

LC^3 mortar. At 28d, the strength of LC^3-30 and LC^3-40 increased by 34.93% and 32.7%, respectively, compared with the control, with 30 min identified as the optimum carbonation duration, corresponding to a CO_2 uptake of 15.71%.

3) The presence of in-situ formed nano-$CaCO_3$ refined the pore structure of LC^3, particularly within the 10-50 nm range. The proportion of fine capillary pores increased markedly at early ages and remained higher than the control at 28d, corresponding to long-term strength development.

From a sustainability perspective, the approach established in this study couples clinker reduction intrinsic to LC^3 with measurable CO_2 uptake during aqueous carbonation. The observed maximum uptake and the concurrent strength enhancement indicate a pathway to lower embodied CO_2 per unit performance. Practically, aqueous carbonation offers a controllable route to dispense nanoscale $CaCO_3$ without the dispersion challenge commonly associated with ex-situ nano-additions, mitigating agglomeration and improving spatial uniformity of nucleation sites. However, further investigation of long-term durability is needed, as the reduction in portlandite content resulting from in-situ carbonation limits AFm formation, which may influence durability that depends on $Ca(OH)_2$ and AFm (e.g., sulfate attack and chloride attack).

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: