Limestone calcined clay cement: mechanical properties, crystallography and microstructure development

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Abstract

Limestone calcined clay cement (LC³) holds promise as a new type of sustainable cement-based material, but the mechanisms underpinning its engineering performance are still poorly understood. Here, a metal intrusion-enhanced imaging approach was employed to quantitatively analyze and link the pore structure development of LC³ to its hydration process, i.e. solid-phase development, and mechanical performance. We found that the early age microstructural development in LC³ is inhomogeneous, with the perimeter of limestone particles displaying higher porosity relative to that surrounding calcined clay and clinker. At later ages, the formation of carboaluminates and calcium-aluminate-silicate-hydrates homogenized the overall microstructure of LC³, thereby delivering improved mechanical performance. Overall, our analysis suggested a more efficient particle packing in LC³ mixes, which decreases the volume/connectivity of micro-pores and can account for LC³’s notable flexural strength. These findings can assist the development of improved LC³ binder formulations alongside other ternary binders with possibly higher limestone additions.
Keywords

Limestone calcined clay cement (LC³); Microstructure development; Metal intrusion; Quantitative SEM analysis; Pore structure; Flexural strength.

1. Introduction

Replacing the clinker in Portland cement with supplementary cementitious material (SCM) in concrete mixtures is a feasible solution to mitigate the carbon footprint of the cement industry [1-4]. However, given that the demands for coal and steel are increasing less rapidly than that for cement [5, 6], the availability of traditional SCMs such as fly ash and slag are expected to decrease. In recent years, a new type of low-carbon cement has been introduced: limestone calcined clay cement (LC³), which consists of cements with up to 60% less clinker via the combined use of calcined clay and limestone as SCM [7-9]. As limestone and clay are widely available worldwide, LC³ features low cost and low embodied CO₂ (30% less than Portland cement) [10, 11]. Furthermore, this new type of cement has demonstrated excellent mechanical properties, with strength comparable to or higher than that of ordinary Portland cement materials from 3 days of hydration, in addition to improved durability [8, 12, 13].

Most of the improved properties of LC³ have been associated with its refined microstructure compared with Portland cement materials [14]. As a ternary binder system, different factors are known for modifying the microstructural development and pore structure of LC³, including physical and chemical effects [15]. Possible physical effects include the filler effect of limestone and calcined clay particles, dilution, and shearing action [15]. Regarding the chemical effects, the SCMs in LC³ can provide additional nucleation sites for the formation
of hydration products and accelerate the Portland cement reaction. Moreover, the pozzolanic reaction of calcined clay, in addition to the synergetic effects between the calcined clay and limestone particles, participate in the hydration process, impacting the cement phase assemblage [14]. A reduction in porosity connectivity may also contribute to the enhanced properties [16]. However, despite playing key role for the superior macro-level performance of LC$^3$-based materials, the LC$^3$’s pore structure characteristics and development from early to late ages are not fully understood.

Scanning electron microscopy (SEM) allows the study of large cross-sectional areas of a sample at a high nanometer-scale resolution [17], and can provide valuable information of cement microstructure such as the identification of pores and hydration products [18, 19], especially non-crystal phases that cannot be recognized via diffraction methods [20], including their morphological features [21]. Previous SEM characterization demonstrated that the pore structure of LC$^3$ is significantly refined, in addition to identifying the phase assemblage [22] and providing the morphology information of the hydration products of LC$^3$ [23]. Furthermore, SEM has also been applied to analyze the morphological changes in LC$^3$ at different temperatures [24]. However, the employed SEM methods were limited by the low contrast between pore and solid phases and, as a consequence, only qualitative information the overall porosity of the samples were obtained.

Intruding the pores of cementitious materials with a low-melting point metal has been proved as an excellent method to overcome the phase-contrast limitation and enable the quantitative study of its pore structure [19, 25, 26]. Possessing an atomic number significantly higher than cement phases, the intruded metal can significantly increase the contrast between pore and solid phases. The slightly contrast reduction between different solid phases is mainly due to the low
voltage of 5 keV used in metal intrusion enhanced BSE imaging compared to a higher voltage applied in other microstructure imaging techniques in BSE imaging, such as at least 15 keV in epoxy impregnation. The theoretical diameters of epoxy impregnation imaging by different emitters (Thermionic emitters (W), Thermionic (LaB₆), Schottky Field Emitter and Cold field emitter) at 15keV are 88.65 nm, 25.46 nm, 3.39 nm, and 0.89 nm, respectively, compared to 5.88 nm on 5keV Schottky Field Emitter applied to metal intrusion-based imaging [27]. As a result, the technique not only provides a higher precision measurement of the overall porosity but also can enable the quantification of the connectivity, aspect ratio, and local pore structure of the samples with enhanced imaging contrast and reduction of imaging noise. For example, Chen et al. and Wang et al. used the metal intrusion enhanced SEM imaging to quantitatively characterize the overall porosity, pore size distribution [28], and particle size distribution of the solid phases of Portland cement [29]. In addition, it has been employed metal intrusion enhanced SEM to investigate the transformation of the pore structure of clay-based materials, including solidity, area-perimeter relationship and pore shape in the nano/micro-scale [30]. Therefore, metal intrusion enhanced SEM can potentially provide a route to understand the pore structure/property relationships and facilitate the construction of robust microstructural models of LC³.

Here, we analyzed the microstructural development and pore structure of LC³ via the SEM-imaging analysis using low-melting point metal intrusion. The intruded metal increased the contrast between solid and pore phases and enabled extracting quantitative information of LC³’s microstructure at the curing of 7, 28, and 180 days. Our analyses demonstrated that the pore refinement in LC³ is associated with the decrease in the connectivity of micro and nanopores. Furthermore, we found that microstructural development in LC³ is inhomogeneous at early ages, with the local structure at the perimeter of limestone particles
being more porous than the local structure surrounding calcined clay and clinker. At later ages, on the other hand, the formation of carboaluminates appears to densify the perimetral structure of limestone, which thus homogenize the overall microstructure of LC$^3$. The pore shape analyses suggested that pores $>10 \ \mu\text{m}$ in LC$^3$ display a lower aspect ratio, further substantiating the lower connectivity between the pores. These findings can assist the development of LC$^3$ systems with optimized microstructure and, thereby, mechanical and durability properties.
2. Materials and Test Methods

2.1 Raw materials

The calcined clay used in this study was obtained from kaolin tailings with 50.7% kaolinite content from Maoming, Guangdong Province, China. The chemical composition of the kaolin tailing is presented in Table 1. The kaolin tailings were calcined using an industrial rotary kiln at temperatures of 800–850 °C.

Industrial limestone with a purity of 91% and pure gypsum were used in this study. Cement clinker was supplied by China Shanshui Cement Group. The chemical composition of the cement is listed in Table S1. Cement, calcined clay and limestone were ground separately in a lab mill, with the physical characterizations demonstrated in Table 2. Natural sand, in accordance with ISO 679 standard, was used for the preparation of mortars.

The Field’s metal and epoxy used to prepare samples for microscopy analysis were obtained from Rotometals, Inc. and Agar Scientific, Inc., respectively. The composition by weight, melting point and contact angle of the Field’s metal are 32.5% Bi, 51% In, 16.5% Sn [31], 62 °C [31], and 130° [32], respectively. The surface tension of the Bi-In-Sn alloy is 9.77 N/m at 80°C (temperature employed in the intrusion process) [33].

2.2 Preparation of cement paste samples

OPC and LC3 paste samples were prepared to examine the crystal phases and microstructure of the cementitious materials. The mixes had the same proportions shown in Table 3 but without the sand portion. After moisture-curing for 24 hours at 20 °C, the samples were demolded and immersed in saturated Ca(OH)2 solution until reaching the specified age. Then,
the hardened samples at certain ages were cut into small pieces and immersed in isopropanol to arrest the hydration.

2.3 Preparation of cement mortar samples

Portland cement (OPC) and LC$^3$ mortar samples were prepared to examine the strength of the cementitious materials. The calcined clay to limestone weight ratio in the LC$^3$ specimens was fixed at 2:1 while maintaining the clinker to cement ratio of 50% in LC$^3$. The cement for comparison (CC30) was prepared using 30% of calcined clay as the replacement for clinker. The mixture design of the samples is presented in Table 3. 5% of gypsum was added to all mixtures to avoid the under sulfation conditions, according to the standard EN 197-1 [31].

Mortar samples were molded into prisms with the dimensions of 40 mm × 40 mm × 160 mm, as defined in EN-197-1 [34]. After moisture-curing for 24 hours at 20 °C, the samples were demolded and immersed in saturated lime solution until reaching the specified age. 0.1% polycarboxylic based superplasticizer was applied for LC$^3$ mortars to maintain a flow rate comparable to the OPC mortar. The average slump values of OPC and LC$^3$ were 219 mm and 170 mm, respectively, as measured according to the standard EN 196-1 [35].

To examine the reactivity of calcined clay according to the strength activity index (SAI) test described in the EN 196-1 standard [35], mortar samples with 30% of calcined clay as the replacement for clinker were also prepared (CC30 in Table 3). The calcined clay’s SAI was calculated according to Equation (1):

$$\text{SAI} = \frac{R_{\text{CC30}}}{R_{\text{OPC}}} \times 100\% \quad (1)$$
where $R_{OPC}$ represents the 28-day compressive strength of the OPC samples, while $R_{CC30}$ represents that of the CC30 samples.

### 2.4 Mechanical testing

Compressive strength and flexural strength tests and data processing were conducted following the EN-196-1 standard [35]. In total, twenty-four mortar specimens of LC$^3$ and OPC were prepared and examined for compressive strength and flexural strength tests (six specimens for each of four curing ages: 3-day, 7-day, 28-day and 180-day). Six specimens of CC30 were also tested for compressive strength at the age of 28-day to calculate the SAI. Following the EN-196-1 standard, the SAI test is one of the widely used and recognized methods for testing the reactivity of the SCMs [36], and it is a reliable method to evaluate the pozzolanic activity of SCMs in cementitious materials [37].

### 2.5 Microstructure characterization

XRD analysis was implemented on a D8 Advance (NH) using Cu Kα radiation at 20 kV and 20 mA at room temperature. The XRD scanned from 5 to 70° with the step size of 0.0167113 degrees 2θ. After the hydration stoppage, the cement paste samples were ground into a fine powder and put in a sample holder for XRD testing.

The steps below were followed to 1) characterize the pore structure of the cementitious materials via SEM-imaging analysis using a low-melting point metal intrusion method and 2) calculate their pore volume, pore size distribution, local porosity and pore average aspect...
Field’s metal intrusion: Low-melting point Field’s metal was melted at a temperature of 80 ± 2°C and intruded into hardened paste samples using a steel die. A Shimadzu AG-X testing machine was used to apply pressure gradually up to 400 MPa (12.5 MPa min-1), the pressure required to intrude pore of the size of ~3.6 nm [38]. Based on the Monte-Carlo simulations of the backscattered electron image across pore-solid boundaries on Schottky Field Emitter at 5 keV, the theoretical minimum imaging resolution was 5.88 nm in this study [27]. The surface temperature of the steel die was controlled at 80 ± 2 °C during the process to ensure the sample temperature was above 70 °C. The peak pressure was maintained for over 30 minutes before the samples were cooled to room temperature.

Polishing: Then, the samples were mounted in epoxy (with epoxy/hardener ratio fixed at 25:3), followed by a 2-stage polishing process. In the first stage, the sandpaper of four grades (125 μm, 58.5 μm, 25.8μm, and 15.3 μm) were used. In the second stage, fine polishing was proceeded by using polishing cloths with four grades of ethanol/diamond grit polishing suspensions (6 μm, 1 μm 0.25 μm, and 0.1 μm). After each grit size, the samples were rinsed with ethanol and sonicated in an ethanol bath to remove any polishing debris. It has been confirmed that by adopting epoxy impregnation, the surface of the cement sample will be flat with no dropping of soft cement paste matrix [32].

SEM-BSE imaging: A FEI Nova NANOSEM 450 FEG-SEM instrument was used to image the microstructure of the cement pastes. The polished cross-section of all specimens was coated with a 10 nm thin carbon layer. The samples were imaged using the backscattered electrons (BSE/SEM). Unless otherwise stated, a voltage of 5 kV, the magnification of
1000x, and an electron beam dwell time of 10 µs were used. More than five images were taken at random non-overlapping positions near the center of each sample, with more than 50,000 pore profiles being captured in each image. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed at the operating voltage of 7 kV. It has been reported for cementitious materials, as isotropic materials, 3D microstructural information can be obtained from high-resolution 2D SEM cross-section images [39-41]. As the 2D fractal dimension of cements has a linear correlation with the 2D porosity of the images, the pore size distribution, the pore shape distribution and the two-point correlation function of the 2D cross-section of the reconstructed microstructure were comparable with the original binarized SEM images [40, 42]. These results demonstrate that SEM 2D analysis utilized here can provide accurate information on the pore structure of cementitious materials.

**Data analysis:** The BSE images were first analyzed with the image processing software ImageJ. The images were converted into an 8-bit grayscale, and the greyness threshold level was determined by an iterative selection method, which isolated the pore and solid phases based on the grey level histogram of the image [43]. This method can automatically determine an optimum threshold at which to segment a picture by successive Gaussian distribution that provides increasingly cleaner extractions of the object region. Due to its independent and identically distributed normal distribution, the Gaussian distribution has less human intervention during the image analysis process compared to other methods, such as the overflow criterion [44]. The detailed process of Gaussian distribution fitting is demonstrated in the previous study [30]. The BSE images were then binarized according to the acquired greyness threshold. The white pixels in the binary picture obtained were considered to be pores. Details of setting the grayscale threshold to distinguish solids and pores have been reported elsewhere [28]. After the grayscale threshold was set for each group of images,
Gaussian distributions were used to fit the different phases. To ensure the fitting accuracy, iteration was performed until the standard and mean deviations corresponded to an \( R^2 > 0.99 \). On the basis of the corresponding Gaussian distribution, the pore volume was quantified by integrating the area of the pores. The average volume fraction of pores was calculated from all the corresponding images. The comparison between the original BSE image and the binary image after segmentation has been illustrated in Fig. S1 in Supplementary Information. An adequate sampling size is required for image analysis to ensure high representativeness of the microstructure. According to previous studies on the 2D image microstructure analysis, the minimum sampling size recommended for cementitious composites is at least 40 million pixels with a size of 67.6 nm [40, 42, 45]. Thus, ten BSE images with the pixel size of 67.6 nm (BSE imaging with a resolution of 6144 pixel \( \times \) 4096 pixel), with a total scanning area of \( 1.143 \times 10^6 \text{μm}^2 \), were included for each sample in this study, ensuring the sampling size is sufficient enough for cement microstructure analysis [46]. To maintain the consistency of the image analysis, the local porosity was also calculated from the binary images. The unhydrated particle surrounded by hydration products were treated as one particle. Thus, the highest porosity was observed from the surface the solid particles. The particles were extracted for local porosity analysis via a flood-fill algorithm from the binary images and analyzed through the binary dilation method [47, 48]. The algorithms were computed using MATLAB software. The aspect ratio of pores, which fits the pore shape in an ellipse before dividing the length of the major axis by that of the minor axis, can describe overall pore slenderness [30]. Furthermore, the aspect ratio has less correlation with curing time and w/c [28] and can be used to reconstruct the 3D pore structure of cementitious materials [49].
3. Results and Discussion

3.1 Mechanical properties

The compressive strength results of the OPC and LC\textsuperscript{3} mortars at different ages are presented in Fig. 1 (a). Compared with OPC, it is seen that the LC\textsuperscript{3} mortar exhibits a slower strength development but presents comparable and even higher strength values at late ages. At the 3-day curing age, the compressive strength of the LC\textsuperscript{3} is approximately 75% of that of the OPC. The lower strength is possibly due to the lack of clinker resulting in insufficient early reaction at the low rate of pozzolanic reactions\cite{50}. The SAI test compares the 28-day compressive strength with 30% replacement of Portland cement with SCM (CC30) relative to a reference mortar with only OPC (as detailed in Table 3) to analyze the reactivity. An activity index higher than 70% represents a high reactivity due to a 30% clinker replacement ratio. We found that the average SAI of CC30 mortar was 93.2%, indicating the high reactivity of the calcined clay in the cementitious environment. Notably, the compressive strength of LC\textsuperscript{3} is about 97% of that of OPC from 28 days. This finding demonstrates the positive synergy between the calcined clay and limestone employed in this study, which contributes to the high strength of the LC\textsuperscript{3}. At 180 days, the compressive strength of the LC\textsuperscript{3} continued to increase, slightly exceeding that of the OPC. These results were consistent with the argument that the compressive strength of LC\textsuperscript{3} is initially lower than that of OPC but increases more rapidly and becomes comparable from 7 days \cite{51}.

Regarding the flexural strength, we found that LC\textsuperscript{3} displayed excellent performance. As shown in Fig. 1(b), the flexural strength of LC\textsuperscript{3} is comparable to that of OPC (about 89%) as early as 3-day of curing and becomes greater than that of OPC from 7-day curing. At 180-day curing, the flexural strength of LC\textsuperscript{3} exceeds that of OPC by more than 20%. The improved
performance could be attributed to the products formed due to the synergy between calcined clay and limestone. For example, systems with calcined clay and limestone display an increased formation of ettringite (AFT), carboaluminates and other crystalline hydrates [50]. A similar effect has also been found for the addition of limestone in the cement binder, which improved the flexural strength from 7 days [52].

To further demonstrate the improved performance of LC3 under flexural loads, a power correlation between flexural strength and compressive strength of LC3 and OPC was established. As shown in Fig. 1(c), the results obtained in our study were compared with four classical flexural-compressive strength empirical equations.

This work: \( f_{f,OPC} = 0.9 \times f_c^{0.527} \) (2) with the determination coefficient \((r^2)\) of 0.975
\[ f_{f,LC3} = 0.34 \times f_c^{0.83} \] (3) with the determination coefficient of 0.983

Ahmad and Shah: \( f_f = 0.44 \times f_c^{0.67} \) [53]

ACI 1992: \( f_f = 0.94 \times f_c^{0.5} \) [54]

ACI 1995: \( f_f = 0.62 \times f_c^{0.5} \) [55]

and TS 500: \( f_f = 0.62 \times f_c^{0.5} \) [56]

It is seen that the apparent flexural-compressive strength equation derived for OPC coincided with that proposed in ACI 1992 [54]. On the other hand, the flexural-compressive strength equation derived for LC3 presents a higher slope than OPC, with higher flexural-compressive strength ratios for samples with higher compressive strength (i.e., for samples with more days of curing). These results contrast previous studies, in which the flexural-compressive strength ratio of LC3 remains similar to that of OPC at the late ages [57]. They also demonstrate that LC3 materials can possess significantly improved tensile strength, generally low in OPC.
3.2 Analysis of the hydration products

In order to understand the crystalline phases affecting the LC\(^3\) microstructure and, thereby, its mechanical properties, hardened paste samples of LC\(^3\) and OPC were analyzed using XRD. The XRD patterns of LC\(^3\) and OPC paste at the curing age of 7, 28, and 180 days are shown in Fig. 2. From the XRD results, it is seen that LC\(^3\) displays more crystalline phases compared with OPC in all the analyzed curing ages. The LC\(^3\)'s main phases include AFt, portlandite, Hc, Mc, in addition to unhydrated/unreacted minerals.

According to the patterns, the strong peaks of clinker minerals C\(_2\)S and C\(_3\)S (32-33°) remain at least until 28 days in Portland. The C\(_2\)S and C\(_3\)S peaks are weaker compared to OPC, which indicates the dilution of the system. Similar to OPC, the peaks also become less intense after 28 days. In the LC\(^3\) system, no obvious kaolinite diffraction peak from calcined clay could be identified due to its non-crystalline nature. Muscovite, another mineral from calcined clay, appear to react as hydration proceeds increasingly. On the other hand, a small and unchanged reflection representing quartz from calcined clay is found at 26.5°. The main peak (29.4°) and subordinate peak (23°) of calcite characterize the unreacted limestone in LC\(^3\), indicating that limestone particles are only minimally dissolved in the LC\(^3\) system.

Despite its low dissolution, the inter-mixed limestone in LC\(^3\) not only demonstrated a physical filler effect but also induced a reaction between aluminate ions and calcium carbonate to form carboaluminates such as Hc and Mc, in agreement with previous studies [58-60]. The favored formation of Hc and Mc crystalline phases in LC\(^3\) can be attributed to
the portion of the calcium carbonate from limestone that took part in the reaction with the dissolved aluminate ions from the calcined clay when subjected to a highly alkaline pore solution. The peak intensity of Mc was found to be higher than that of Hc in our study, which indicates that relatively lower percentage of kaolinite in the calcined clay [14]. Interestingly, the intensity of the carboaluminates and AFt crystals markedly increases after the curing age of 7-day. This finding suggests that the increased mechanical properties of LC3 after 7 days, particularly the flexural strength, are possibly associated with the increased formation of these crystals. Due to their elongated shape [61], they may possibly present a bridging effect within the cement matrix.

AFm was not detected at all the tested ages of LC3. That is due to the presence of dissolved carbonates in the LC3 solution, which stops the conversion of the AFt to Ms and favors the formation of Hc and Mc [62]. In contrast, Hc and Mc were not observed in the XRD pattern of OPC samples, but both AFt and AFm co-existed at the 7-day, 28-day and 180-day curing ages. The ratio between Ms and AFm constantly increases as hydration proceeds, indicating that the phase transformation of AFt into AFm also occurs at late ages.

The amount of portlandite was much lower in the LC3 paste than in the OPC at all ages. At early ages, the decreased amount of portlandite is possibly attributed to the dilution effect due to the reduction of clinker in the mix [63]. At later ages, the XRD peak for portlandite further decreases mostly due to the pozzolanic reaction with the silicate and aluminate ions from the calcined clay in LC3, which leads to the formation of C-A-S-H gel [23].

3.3 Microstructure characterization
To understand the underlying mechanism of the hydration process, microstructure development and improved mechanical performance, the microstructure development and pore structure of LC\textsuperscript{3} was thoroughly investigated and compared with that of OPC via SEM-BSE imaging analysis.

### 3.3.1 SEM-BSE imaging and morphology data analysis

Fig. 3 (a) shows the SEM-BSE image under 7000× magnification of the microstructure of LC\textsuperscript{3} intruded with Field’s metal. In Fig. 3 (b)-(d), we identified the three main binder components in LC\textsuperscript{3}, namely the clinker, limestone and calcined clay, respectively. It is seen that the clinker phase in Fig. 3 (b) has a thin outer hydrated ring (dark grey/black) surrounding the unhydrated phase (light grey) (Fig. 3 (e)). Compared with clinker, limestone phases shown in Fig. 3(f) have the typical rod-like shape with limited morphological changes around the boundary. The color contrast throughout the limestone phase is small. That agrees with our previous XRD observations, which noted that only a small portion of the crystalline limestone is dissolved. The typical layered structure is observed in Fig. 3 (g) regarding the calcined kaolinite phases. It can be seen that its surface acted as nucleation sites for the growth of C-S-H with a fibrous texture, consistent with previous literature [64]. Furthermore, it has been reported that the images with more isolated pores from epoxy impregnation method may not provide quantitative analyses due to the limited resolutions and blurred pore boundaries that would cause more errors than metal intrusion enhanced BSE imaging [30].

Due to the significant difference in atomic numbers between the Field’s metal alloy and cement, high contrast can be observed between the pore structure and the solid phases. Therefore, the Field’s metal intrusion method enabled extracting quantitative pore characteristics and structure of LC\textsuperscript{3} compared with OPC, including the pore volume and size
3.3.2 Overall pore structure characteristics

Based on the high contrast between solid and pore phases, a color map with the equivalent pore diameters in the LC$^3$ and OPC samples was generated. The comparison between the original BSE image and the binary image after segmentation has been illustrated in Fig. S1 in Supplementary Information. As shown in Fig. 4, the color map was converted from the typical BSE images of Field’s metal intrusion. Due to the irregular pore shapes within the cement microstructure, $d_p$ indicated the equivalent pore diameter in Fig. 4. It was defined by a descriptor of the pore size and computed by the diameter of a circle with an equivalent area of each specific pore, as described in Eq. 8. The pore sizes from small to large are characterized by different colors, as demonstrated in the color bar, in which darker parts are related to hydrates and unhydrated cement. Thus, information about the global pore structure can be directly visualized, providing important insight into the microstructure of the cementitious materials.

\[
d_p = 2 \times \sqrt{\frac{\text{area}}{\pi}} \quad (8)
\]

Clearly, both OPC and LC$^3$ pastes demonstrated a densification process as the hydration proceeded. Furthermore, it can be observed that the LC$^3$ pastes presented a more refined pore structure compared with OPC, with reduced pore size at corresponding curing ages. For example, the equivalent pore diameter of LC$^3$ from 7 days illustrates marked refinement compared with that of OPC. More specifically, the largest pore diameter of OPC is
approximately 50 μm, whereas the largest pore diameter of LC³ is about 30 μm. Similar findings can be drawn from both the 28-day and 180-day equivalent pore diameter-based color maps. For instance, the equivalent pore diameter map of LC³ at 180 days shows its significantly compact microstructure. The largest pore diameter is about 15 μm, whereas the majority of pore diameters are less than 5 μm. On the other hand, the largest pore diameter of OPC at 180 days corresponds to approximately 30 μm. In addition, many pores larger than 10 μm were detected, thus confirming the refined pore structure of the LC³ samples, particularly at late ages.

Based on the corresponding Gaussian distribution results via SEM/BSE imaging analysis, the total pore volume at different hydration ages was derived. Fig. 5 indicates the pore volume obtained from the SEM/BSE images. It is seen that the average porosity of LC³ is approximately 8% higher than that of OPC at the 7-day curing age. However, the average porosity of LC³ decreases rapidly and becomes slightly lower than that of OPC at 28 days, illustrating the intensified formation of hydration products and the densification of the LC³ microstructure between 7 and 28 days. As hydration proceeds, the porosity of LC³ is further densified, becoming approximately 14% lower than that of OPC at 180 days. These results agree with the mechanical properties measurements, which indicated a lower strength of LC³ at early ages but a larger strength increase rate with the continued hydration. Therefore, the microstructure development of LC³ is slower than OPC before 7 days, but the continued pozzolanic reaction and associated synergetic effects of metakaolin in the calcined clay combined with limestone promote significant changes in the LC³ pore structure after 7 days, as evidenced by the increase in carboaluminates and the decrease in portlandite in the XRD analysis.
The refinement of the pore structure of LC\(^3\) was seen not only in the reduction of the total porosity as mentioned but also imparted modifications in the distribution of pore sizes. Fig. 6 demonstrates the pore size distribution of LC\(^3\) and OPC as obtained via SEM/BSE imaging analysis. The curves were acquired from the derivative of the cumulative pore size distribution (R-square set higher than 0.999) through a moving mean to smooth and reduce the noise.

At the 28-day and 180-day curing ages, the fraction of finer pores is much greater in LC\(^3\) than in OPC, although both increases in the fraction of finer pores compared with the 7-day age. It is also notable that the fraction of larger pores of LC\(^3\) reduces significantly from the 28-day curing to the 180-day curing. Combined with the findings for porosity and hydration, it could be anticipated that the LC\(^3\) paste has a refined microstructure than the OPC, which justify the superior strength and, as evidenced in previous studies, improved durability properties [8, 65]. Given the complexity of the cement pore structure and limitations of different characterization methods, including the 2D analysis, MIP and micro-CT were conducted to compare the porosity and pore size distribution trend of 28 days LC\(^3\) and OPC and further corroborate the data from the 2D cross-section image analysis, as illustrated in Fig. S2 and Fig. S3 in Supplementary Information.

In addition to providing the overall pore characteristics of the samples, the high contrast between pore and solid also enabled obtaining insights on why the pore structure of LC\(^3\) is significantly refined. Fig. 7 shows in higher magnification SEM/BSE images of LC\(^3\) and OPC pastes at the age of 28 days. It can be observed that both samples exhibit pores with similar shapes. However, the pores in the OPC paste have visibly more points of connection with neighboring pores, which account for the higher number of larger pores observed in Fig.
4 and Fig. 7. On the other hand, the pores in LC\textsuperscript{3} are surrounded by a solid phase, suggesting that more hydration products are formed in regions farther from the cement grains in the LC\textsuperscript{3} system. In addition, pores are also blocked by calcined clay particles, indicating the filler effect of the SCM. Although the reduced pore connectivity of LC\textsuperscript{3} had been inferred from MIP in previous literature, these findings provide direct visualization and further insights on this important phenomenon.

### 3.3.3 Local pore structure

The image-based SEM-BSE data analysis made it possible to quantitatively characterize local microstructure features of LC\textsuperscript{3}. Given that clinker, calcined clay, and limestone possess different reactivity rates, they would be expected to have different contributions to the microstructure development of the paste. To investigate this aspect, we analyzed the pore structure of LC\textsuperscript{3} at the perimetric region around the different solid phases.

The clinker, calcined clay, and limestone particles were identified using SEM-EDX elemental mapping. Corresponding to the SEM-BSE image shown in Fig. 8 (a), elemental maps of calcium (Ca), silicon (Si), carbon (C) and aluminum (Al) derived by the SEM-EDX are shown in Fig. 8 (b). Although the coated thin carbon layer may slightly influence the accuracy of SEM-EDX carbon mapping results, limestone can still be correctly identified when combined with the calcium mapping results, as illustrated in Fig. 8 (b). Similarly, the unreacted calcined clay has been identified via a combination of Al and Si mappings, in addition to recognizing their layered morphology. Clinker particles were identified based on silicon and calcium mappings, in addition to recognizing their morphology consisting of a hydrated shell with an unhydrated core. The main phases in LC\textsuperscript{3} were indicated in Fig. 8 (a),
for which five random particles for each solid phase were selected and characterized. A distance within two micrometers around the solid particles in LC\(^3\) was maintained, on the one hand, to avoid the influence of other solid particles in cement and, on the other hand, to calculate the corresponding local porosity of LC\(^3\) and OPC.

The local porosity results of LC\(^3\) and OPC are shown in Fig. 9. For both OPC and LC\(^3\) samples, it was observed that the highest porosity occurred on the perimetric region of the solid-phase particles, and the porosity tended to decrease with increasing distance until around 0.8 \(\mu\)m. The perimetric porosity of LC\(^3\) then became approximately constant at thicknesses between 1 and 2 \(\mu\)m, particularly for the 28-day and 180-day ages. This trend is similar to that observed in radial distribution functions and indicates that the cement particles, due to their roughly spherical shape, cannot effectively pack close to each other [66].

As shown in Fig. 9 (a), local pore structure analysis of the LC\(^3\) pastes reveal important features of the LC\(^3\) microstructure. At the early age of 7 days, we found that the localized porosity near limestone particles was much higher than other solid particles. On the other hand, the localized porosity near calcined clay is slightly lower than that of clinker, likely due to its amorphous nature, which induces the nucleation and growth of C-A-S-H on its surface. These results demonstrate that the reactivity of the SCM plays a key role in the early structural features of LC\(^3\). In particular, the limited reaction of limestone particles and thereby the porous perimetric structure surrounding them is possibly responsible for higher pore volume (Fig. 5) and lower mechanical properties (Fig. 1(a) and (b)) of LC\(^3\) at 7 days compared with OPC.

At 28 days, the perimetric pore structure around the clinker decreased significantly and was
the lowest, while that of both limestone and calcined clay was also reduced. Notably, the local pore structure around limestone is still significantly higher than that around clinker and calcined clay particles. At 180-day curing, no significant further changes can be observed for clinker, which implies that the hydration of clinker was almost complete after 28 days. However, it has also been found that the localized porosity of both calcined clay and limestone decreased considerably, and the perimetric pore structure around limestone is now comparable to the other phases. This result indicates that the late formation of the carboaluminates leads to a denser and more uniform microstructure and, thereby, the higher mechanical properties of LC³.

These findings indicate that the pore structure of LC³ is not homogenous across the paste, which confirmed that the LC³ system containing particles with different chemical compositions and reaction rates indeed lead to microstructure heterogeneity, as assumed in previous SEM and MIP studies. In fact, the pore structure appears to be highly heterogeneous at the early ages due to the different reactivity rates of the binder phases. This information is important as the mechanical and durability properties of cementitious materials are influenced by localized porous regions. For example, it is well known that the porous interfacial transition zone between cement paste and aggregates govern many of the concrete properties [67, 68]. In this case, the thickness of an analogous interfacial transition zone, named peripheral microstructure, around the different solid phases in LC³ is only approximately two-thirds of that of OPC. Our results thus provide a more precise characterization of the pore structure of LC³, which can facilitate the construction of robust microstructural models of the ternary cementitious material.

For comparison, Fig. 9 (b) shows the local pore structure of OPC at different ages. Firstly, it
is seen that the local porosity around the clinker in OPC is higher at all ages compared with that around the calcined clay in OPC. This further demonstrates the positive synergetic effect of the ternary LC$^3$ system, which can enhance the reaction of the clinker phase (in agreement with previous XRD Rietveld analysis [14]). Moreover, while the thickness of the porous perimetric region is approximately 0.8 μm in LC$^3$, this value is higher in the OPC system (about 1 μm), indicating the less efficient packing (and also the filler effect of the SCMs in the LC$^3$ system).

3.3.4 Aspect ratio of pores

The SEM/BSE imaging using Field’s metal intrusion method also enabled the analysis of the average pore aspect ratio. In Fig. 10, the scatter plots with different colors represent the experimental data acquired from the SEM/BSE images, and the lines represent the average aspect ratios of LC$^3$ and OPC. The aspect ratio limit has been set to 4.0 because more than 95% of the pores lies below this limit. The results indicate that LC$^3$ and OPC exhibit similar aspect ratios at all ages, mostly from 1.8 to 2.0. However, it is seen that the LC$^3$ paste presents a slightly lower aspect ratio for pores with a nominal diameter larger than 10 μm, which indicates the lower pore connectivity of LC$^3$ compared with OPC.

In addition to comparing the pore structure of OPC and LC$^3$ pastes, our results indicate that the pore aspect ratio (which relates to a decrease in pore circularity) in cementitious materials is higher than 1. This evidence points out that pore shape cannot be defined simply as a cylinder (cross-section aspect ratio =1), a universal assumption in studying the pores of cementitious materials with MIP [69]. Based on these results, the actual shape of pores should be taken into consideration to improve the accuracy of pore structure evaluation,
especially when calculating the porosity and pore size distribution of cementitious materials. On the other hand, further research is needed to explore how the shape of the pore and solid phases affect the mechanical properties of cementitious materials.

4. Conclusions

Based on quantitative SEM image-based analysis, the microstructural development and pore structure of LC$^3$ compared with OPC at ages up to 180 days were thoroughly examined and linked to crystallography investigations and mechanical performance. The main conclusions of the study are as follows.

1. Mixtures of LC$^3$ presented more than 30% higher flexural strength than OPC at 7 days to 180 days while exhibiting higher reactivity via strength index test compared to OPC incorporating 30% calcined clay. A statistically derived correlation between the compressive and flexural strengths yielded a distinctive flexural-compressive strength empirical equation for LC$^3$ of: $f_f = 0.34 \times f_c^{0.83}$ with a correlation coefficient of 0.975.

2. The synergetic reaction between calcined clay and limestone in LC$^3$ was evidenced by the formation of a considerable amount of carboaluminate hydrates. Among the different carboaluminates, mono-carboaluminate was found as the dominating phase in the LC$^3$ paste. Unlike OPC, neither formation of Monosulfoaluminate nor transformation of Monosulfoaluminate to Ettringite was identified during LC$^3$ hydration, in agreement with previous studies [9, 23].
3. Lower overall porosity and a reduced number of larger pores characterized the refinement of the pore structure in LC$^3$ from 7 days compared to OPC, resulting eventually in about 17% lower pore volume in LC$^3$ than OPC at 180 days. This observation has been linked to the reduced pore connectivity of LC$^3$ relative to OPC.

4. The metal intrusion enhanced SEM imaging technique provided direct visualization and important insights into the LC$^3$ microstructure development. At early ages, the local structure surrounding limestone particles is more porous than that surrounding calcined clay and clinker, indicating a heterogeneous to homogeneous microstructural development in LC$^3$. At later ages, the formation of carboaluminates and C-A-S-H was found to densify the structure surrounding limestone particles and homogenize the overall microstructure of LC$^3$. The decreased pore connectivity in LC$^3$ was also directly visualized via the SEM/BSE images.

5. A consistent peripheral microstructure of ~0.8 μm was found around selected solid particles in LC$^3$ pastes at all curing ages from 7 days to 180 days. This transition zone was only two-thirds of that of OPC, which discloses improved particle packing in LC$^3$. Overall, the thinner peripheral microstructure contributes to a denser microstructure in LC$^3$ which contributes to its improved mechanical performance.

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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.

**CRediT author statement**

**Hao Sui**: Conceptualization, Methodology, Software, Visualization, Investigation, Writing-Original draft; **Pengkun Hou**: Resources, Verification, Data curation; **Yanming Liu**: Methodology, Software, Writing- Reviewing and Editing; **Kwesi Sagoe-Crentsil**: Writing- Reviewing and Editing; **Felipe Basquiroto de Souza**: Writing- Reviewing and Editing; **Wenhui Duan**: Supervision, Funding acquisition, Writing- Reviewing and Editing.

**Data Availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Tables

Table 1. Chemical composition of the kaolin tailing from X-ray fluorescence (weight %).

<table>
<thead>
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<th>Compounds</th>
<th>Percentage</th>
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<tr>
<td>SiO$_2$</td>
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<tr>
<td>Al$_2$O$_3$</td>
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<tr>
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Table 2. Physical characterization of cement, calcined clay, and limestone.

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<th>Materials</th>
<th>Grinding time [min]</th>
<th>Specific surface area [m$^2$/kg]</th>
<th>D$_{50}$ [µm]</th>
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<td>Cement</td>
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<td>341.5</td>
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<tr>
<td>Calcined clay</td>
<td>15</td>
<td>620.8</td>
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<tr>
<td>Limestone</td>
<td>30</td>
<td>812.9</td>
<td>5.88</td>
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</table>

Table 3. Mix composition of OPC, CC30, and LC$^3$ binders

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clinker</th>
<th>Calcined clay</th>
<th>Limestone</th>
<th>Gypsum</th>
<th>Binder/sand ratio</th>
<th>w/b</th>
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<tbody>
<tr>
<td>OPC</td>
<td>95%</td>
<td>0</td>
<td>0</td>
<td>5%</td>
<td>1:3</td>
<td>0.5</td>
</tr>
<tr>
<td>LC$^3$</td>
<td>50%</td>
<td>30%</td>
<td>15%</td>
<td>5%</td>
<td>1:3</td>
<td>0.5</td>
</tr>
<tr>
<td>CC30</td>
<td>65%</td>
<td>30%</td>
<td>0</td>
<td>5%</td>
<td>1:3</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figures

Fig. 1. (a) Compressive strength of LC$^3$ and OPC mortar, (b) Flexural strength of LC$^3$ and OPC mortar, and (c) Flexural-compressive strength correlation of OPC and LC$^3$. 
Fig. 2. XRD patterns of hardened LC$^3$ and OPC pastes at the age of 7, 28, and 180 days.
Fig. 3. Typical SEM-BSE images of hardened pastes (polished) after Field’s metal intrusion (a) LC$^3$ at 28 days under 7000× magnification. Selected areas are showing (b) Clinker, (c) Limestone, (d) Metakaolin in LC$^3$. (e) Extracted representative areas from (b); (f) extracted representative areas from (c); and (g) extracted representative areas
from (d). Bright areas represent Field's metal intruded into capillary pores.

Fig. 4. Equivalent pore-diameter-based original and color map of metal-intruded OPC and LC$^3$ based on BSE imaging. OPC: (a) 7 days, (b) 28 days, and (c) 180 days; LC$^3$: (d) 7 days, (e) 28 days, and (f) 180 days.
Fig. 5. The total pore volume of OPC and LC$^3$ pastes from 7 to 180 days as extracted from SEM/BSE images. The line plot was created by averaging the porosity data of OPC (Avg. OPC) and LC$^3$ (A. LC$^3$) pastes, respectively.

Fig. 6. Frequency of the pore size distribution of LC$^3$ and OPC from 7 days to 180 days.
Fig. 7. High-magnification SEM-BSE of (a) LC$^3$ and (b) OPC at 28 days.

Fig. 8. The chemical distribution characterization of LC$^3$ via EDX-SEM technique. (a) An example of SEM-BSE image showing limestone (LS), clinker and calcined clay (CC) in hydrated LC$^3$, and (b) the corresponding elemental maps of Ca, Si, C, and Al.
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Fig. 10. The aspect ratio of pores of LC³ and OPC pastes at 7 days, 28 days and 180 days.
Figure Captions

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