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Synergistic effects of triethanolamine and nano-SiO_2 on the hydration and hardening properties of Limestone calcined clay cement

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ABSTRACT

This study investigates the synergistic effects of triethanolamine (TEA) and nano-SiO_2 (NS) on the hydration, mechanical properties and microstructure of Limestone Calcined Clay Cement (LC^3). Isothermal calorimetry results reveal that NS primarily enhances the hydration degree of the silicate phase, whereas TEA preferentially accelerates aluminate hydration through Al^{3+} complexation and surface adsorption, which modifies ion availability and delays C-S-H nucleation, thereby regulating the timing of the silicate peak. Both NS and TEA can increase the intensity of the aluminate peak, while their combination produces an even stronger synergistic effect. TEA consistently contributes to LC^3 strength development at all ages, while NS mainly improves early-age strength. The synergistic effect of NS and TEA is more pronounced than either additive alone, with the LC^3-3NS-0.2 %TEA (with 3 % NS and 0.2 % TEA) blend exhibiting the best performance across all ages. TEA leads to a greater consumption of CH compared to NS, while NS-TEA blends yield a higher volume of hydrates, including C-(A)-S-H gel, AFm, and AFt phases. Moreover, TEA primarily influences pore size distribution rather than total porosity, shifting larger, more harmful pores into smaller, less detrimental ones. The NS-TEA synergistic blend achieves the most favourable pore structure, characterised by the lowest content of harmful pores (>100 nm) and the highest proportion of fine pores (4.5–50 nm and <4.5 nm).

1. Introduction

Limestone Calcined Clay Cement (LC^3) has emerged as a promising low-carbon and energy-saving alternative to traditional Portland cement [1,2]. It offers comparable late-age strength while significantly reducing CO_2 emissions [1,3]. However, a major drawback of LC^3 is its low early strength, which limits its widespread application in fast-paced construction projects [4]. To address this issue, many researchers have explored the use of nanomaterials or chemical additives to enhance the strength of LC^3 at early ages [5,6]. Zhang [5] et al. reported that the incorporation of C-S-H seeds significantly enhanced the early-age strength of LC^3 but reduced its late-age strength. This effect occurs because the presence of C-S-H seeds accelerates the reactions of alite and C_3A on the first day but subsequently suppresses their reaction later, resulting in a higher amount of unreacted alite and C_3A. Similarly, the addition of sodium silicate at a silicate modulus of 0.4 and 1 % Na_2O has been shown to increase the early-age strength of LC^3, reaching 22.1 MPa at 1 day (i.e. a 120 % increase over the reference LC^3), owing to the accelerated clinker hydration and the synergistic reactions among portlandite, calcined clay and limestone [6].

In previous studies [7,8], NS has been proven to accelerate the hydration process and improve the early-age strength of LC^3 by promoting the reaction of the silicate phase from the clinker proportion. However, its presence tends to suppress the hydration of the aluminate phase, which plays a crucial role in the early-stage strength development of cementitious systems [8]. Triethanolamine (TEA) is a commonly used chemical admixture in cementitious materials, serving as a component in cement grinding aids, setting regulators, and early strength enhancers for cement and concrete [9,10]. It indicates that TEA promotes the acceleration of aluminate phase reactions, not only in C_3A but more

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Table 1
Chemical compositions of PC, calcined clay, limestone, and gypsum (*wt.*%).

	PC	Calcined clay	Limestone	Gyp
CaO	59.17	0.91	54.78	32.48
SiO_2	18.51	55.95	0.18-	–
Al_2O_3	3.99	34.62	–	–
Fe_2O_3	3.40	1.79	0.02	–
SO_3	3.41	0.14	0.12	46.37
MgO	3.79	1.75	–	0.02
K_2O	1.18	3.86	0.13	0.01
Na_2O	0.23	0.49	–	0.01
TiO_2	0.24	0.28	–	–
LOI	3.48	1.21	43.14	20.93

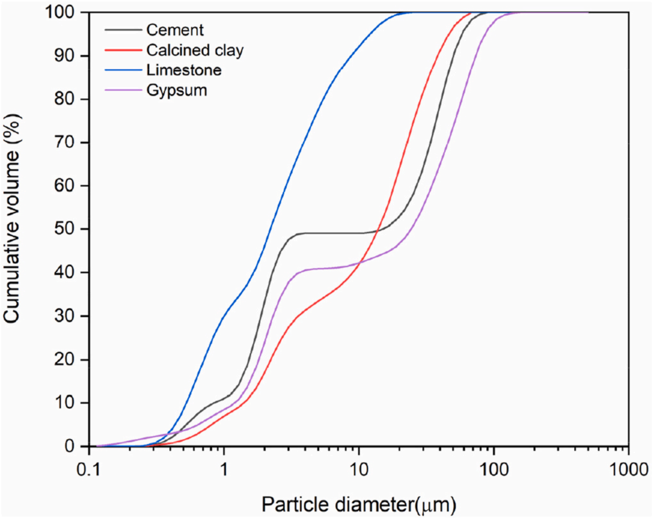


Fig. 1. Particle size distribution of the raw materials.

significantly in C_4AF, primarily through ion complexation and surface adsorption mechanisms. TEA readily complexes with Al^{3+} ions released from C_3A and C_4AF dissolution, which reduces the activity of free Al^{3+} in the pore solution. This promotes further dissolution of aluminate phases according to Le Chatelier's principle, thereby accelerating their hydration. In addition, TEA adsorbs onto the surface of aluminate clinker particles, weakening Al–O bonds and facilitating the breakdown of the crystal structure. These interactions enhance the dissolution rate of C_3A and C_4AF, leading to earlier and more intense aluminate hydration peaks, a mechanism that plays a critical role in governing the overall cement hydration process. [11]. Given their complementary functions, combining NS and TEA could create a synergistic effect, where NS enhances silicate phase hydration while TEA compensates for the suppressed aluminate phase reaction.

Therefore, this research aims to explore the synergistic effects of TEA and NS on LC^3 hydration, evaluating their interaction in terms of hydration kinetics, phase development and mechanical performance to optimise LC^3's properties for sustainable cementitious applications.

2. Materials and methods

2.1. Materials

The raw materials used for this study are reference cement P·I 42.5 (PC), P.W-1 42.5 white cement (WPC), calcined clay (Cc), limestone (LS), gypsum (Gyp), triethanolamine (TEA) and nanosilica (NS) particles. Table 1 presents the chemical composition of these raw materials analysed by XRF. Commercially available PC (i.e. P·I 42.5), complying with the Chinese national standard GB8076-2008, was used as the base material for all mixtures. WPC was purchased from Aalborg Portland Co. Ltd., which was used for the Low-Field Nuclear Magnetic Resonance (LF-NMR) test in this study. It is noted that the concentration of Fe_2O_3 in WPC was rather low to facilitate the accuracy of the LF-NMR test. Commercially available calcined clay, acquired from Nanjing, China, exhibited a strength activity index of 84.2 % in accordance with ASTM C311. Gypsum (AR, 99 %) and limestone (AR, 99 %) sourced from Macklin were also used for the formulations. The NS sourced from Aladdin had a diameter of 7–40 nm, and a specific surface area of 380 m^2/g. PCA®-I high-performance PCE from Jiangsu Sobute New Materials Co., Ltd., China, was used as a superplasticiser to moderate the workability of the mixtures. Analytical reagent triethanolamine (TEA), acquired from Sinopharm Chemical Reagent Co., Ltd., served as an additive of the mixtures. Chinese standard sand was used for preparing mortars for this study. The particle size distribution of the PC, calcined clay, limestone and gypsum was analysed by laser diffraction using the LS Particle Size Analyser, with the results shown in Fig. 1.

Table 2
Compositions of mixes investigated (*wt.*%).

Samples	PC	Cc	LS	Gyp	NS	TEA	PCE
LC^3	55	30	15	2	0	0	0.28
LC^3-0.05TEA					0	0.05	0.25
LC^3-0.2TEA					0	0.2	0.2
LC^3-0.5TEA					0	0.5	0.12
LC^3-3NS					3	0	1.5
LC^3-3NS-0.05TEA					3	0.05	1.12
LC^3-3NS-0.2TEA					3	0.2	0.97
LC^3-3NS-0.5TEA					3	0.5	0.96

2.2. Mixtures and sample preparation

In this study, 8 different mixtures were prepared, with their formulations shown in Table 2. The amount of cement, Cc, LS and Gyp were kept constant by weight. In the first four groups, TEA, as an additive, was dispersed in tap water, with a dosage of 0, 0.05, 0.2 or 0.5 % by mass of the combination of PC, Cc, and LS, to study the effect of TEA alone. In the last four groups, 3 % NS and varied dosages of TEA were added to the mixtures to investigate the synergistic effect of NS and TEA on the hydration of LC^3. NS particles were dispersed in tap water by the ultrasonic method at a frequency of 40 kHz and a power of 200 W for 20 min at room temperature. For all blended pastes and mortars, samples were prepared using a water-to-binder ratio of 0.5. The pastes were prepared in a cement paste mixer according to the following protocol: slow mixing for 120 s, resting for 15 s, followed by fast mixing for 120 s. After specified days of standard curing (relative humidity (RH) > 95 %, 20 °C), hydration of the pastes was stopped. To do so, all samples were immersed in pure isopropanol for 3 h, then moved to new pure isopropanol for another 24 h of curing, followed by being dried in a vacuum oven at 40 °C for 3 days. The dried, hardened pastes were then stored in a vacuum chamber, ready for the thermogravimetric analysis (TGA) and X-ray diffraction (XRD) analysis. Mortars were made with a binder-to-sand weight ratio of 1:3. A polycarboxylate-based superplasticiser (PCE) was used to maintain comparable fluidity across all mortars, which was evaluated using the flow table test in accordance with BS EN 12390-16: 2019.

2.3. Methods

2.3.1. Hydration heat

The heat release during hydration of the mixtures was measured in an isothermal calorimeter (TAM Air) for 72 h 10 g of the sample was mixed, and 5.39g of the sample was poured into a glass ampoule, which was then sealed and placed in the calorimeter.

2.3.2. Compressive strength

In accordance with BS EN 12390–16:2019, prismatic mortar samples

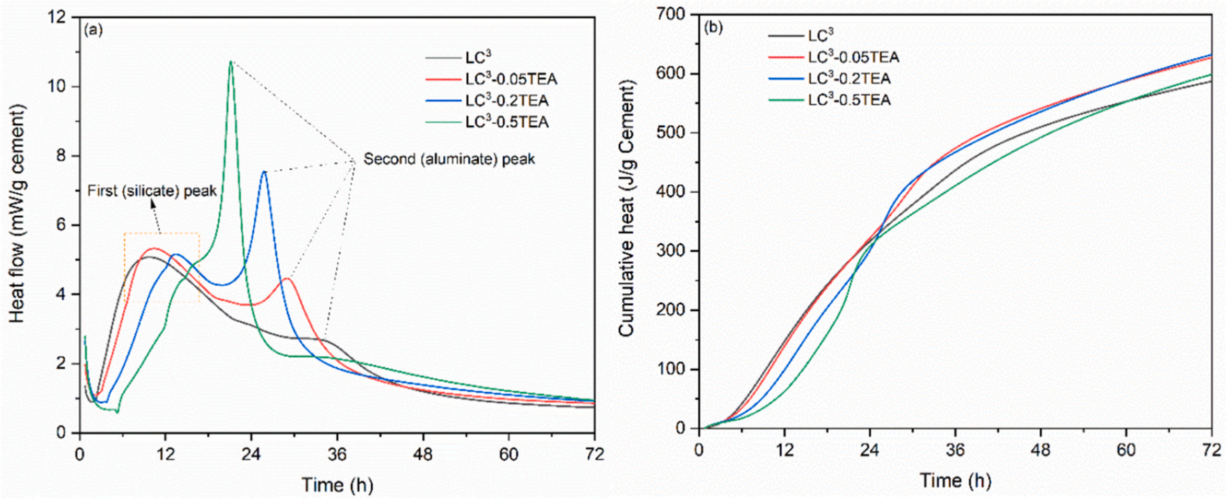


Fig. 2. Heat flow (a) and cumulative heat (b) of LC^3 with different ratios of TEA.

with the sizes of 4 × 4 × 16 cm^3 were prepared, and their compressive strength was measured at 3, 7, 28, and 90 days.

2.3.3. *XRD*

XRD tests (D8-Advance, Bruker International Corporation, Germany) with Cu-Kα radiation (λ = 1.54184 Å, 40 kV, 40 mA) were carried out on freshly cut slices of hardened paste to assess the phase assemblage of the relevant samples. To do so, the samples were crushed to a fine powder and pressed into a sample holder. The scanning program consisted of rotating between 5° and 70° 2θ with a 10°/min scanning speed.

2.3.4. *TGA*

TGA of the pastes was performed using a simultaneous TGA55 instrument (TA Corporation, USA). The heating rate was set at 10 °C/min under a nitrogen atmosphere, and the temperature range was between 30 and 800 °C.

2.3.5. *LF-NMR*

The porosity of hardened LC^3 pastes at 3 and 28 days was measured by Low-Field Nuclear Magnetic Resonance (MicroMR20-025V, Niumag, China). The samples were cast into cylinders of size Φ20 mm × 20 mm. These cylindrical specimens were then saturated with water for 24 h through high-pressure intrusion at 20 MPa before the test.

3. Results and discussions

3.1. *Kinetics of hydration*

The effect of TEA alone on LC^3 hydration is illustrated in Fig. 2. Compared with the control group (LC^3) without TEA, the addition of TEA prolonged the induction period and delayed the occurrence of the silicate peak (first peak). Consequently, the cumulative heat release of LC^3 containing TEA is lower than that of the control sample within the first 24 h, although the peak intensities remain at a comparable level to that of the control group. The delayed occurrence of the silicate peak after TEA addition can be attributed to its chelation with Al^{3+} and Ca^{2+} ions, which delays C-S-H nucleation and consequently postpones the silicate hydration peak [12].

In contrast, the aluminate peaks are shifted to earlier ages and exhibit significantly higher intensities. This behaviour is likely due to the acceleration of aluminate phase dissolution (C_3A and C_4AF) through TEA's ion complexation and surface adsorption mechanisms, which enhances the availability of Al^{3+} and Ca^{2+} ions in the pore solution. The increased ion concentration promotes the rapid precipitation of ettringite (AFt), generating a greater number of nucleation sites. These additional nucleation sites further accelerate aluminate hydration and amplify the heat evolution associated with these reactions, resulting in earlier and more intense aluminate peaks compared to the system

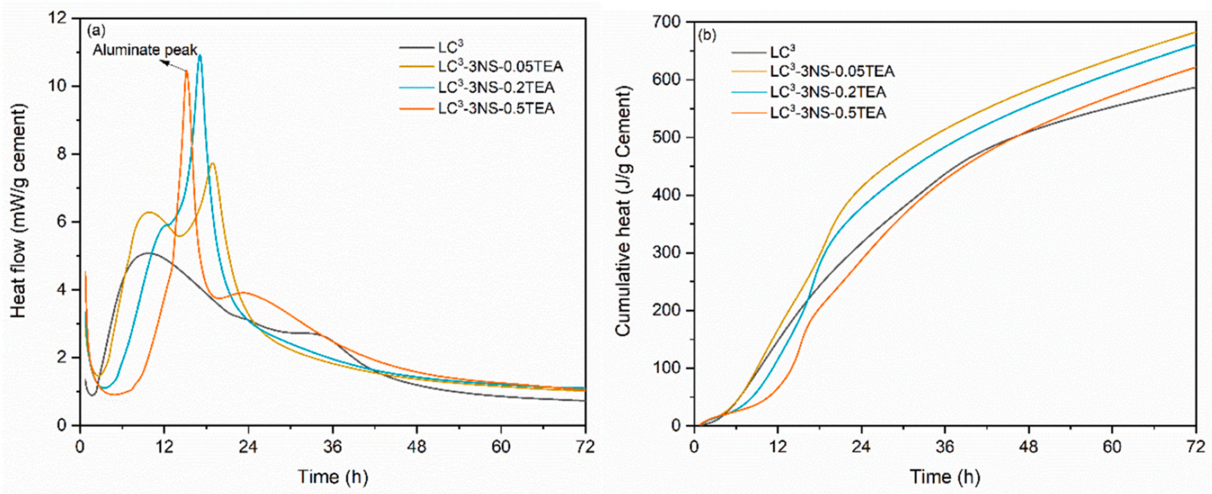


Fig. 3. Heat flow (a) and cumulative heat (b) of LC^3 with the addition of 3 % NS and varying dosage of TEA.

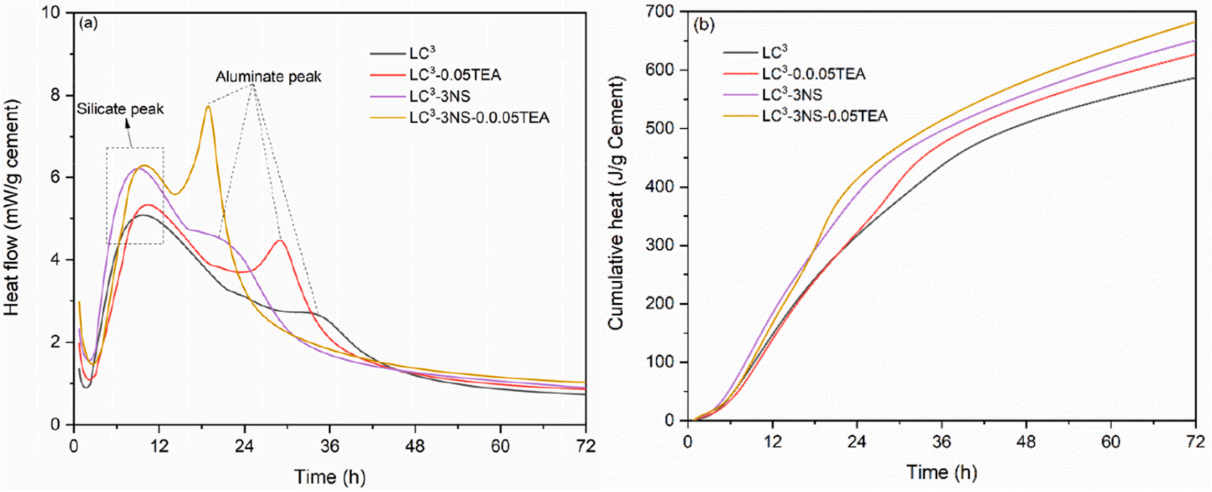


Fig. 4. Heat flow (a) and cumulative heat (b) of LC^3 with NS and/or TEA.

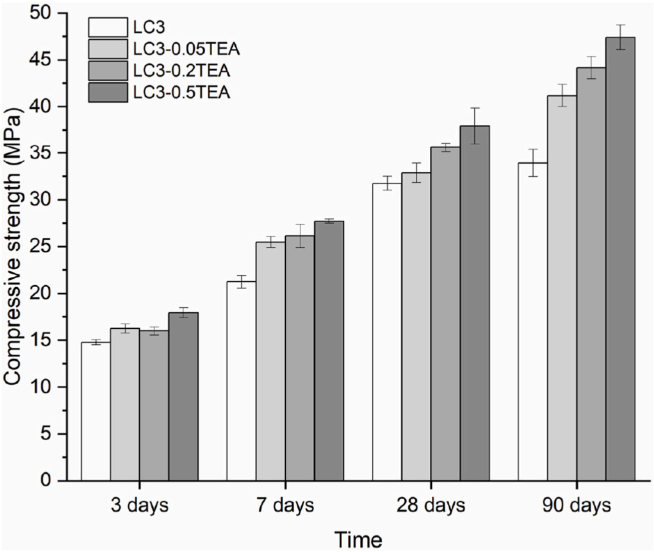


Fig. 5. Influence of TEA dosage (0 %, 0.05 %, 0.2 % and 0.55 %) on the compressive strength evolution of LC^3.

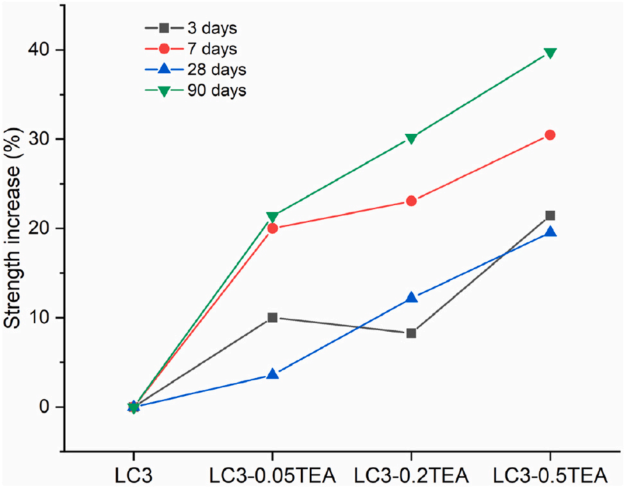


Fig. 6. Influence of TEA dosage (0 %, 0.05 %, 0.2 % and 0.55 %) on the compressive strength increase of LC^3.

without TEA [13,14]. At a dosage of 0.5 % TEA, the aluminate peak is markedly advanced and overlaps with the silicate peak. This behaviour can be explained by the accelerated aluminate hydration, which consumes sulfate rapidly, leading to early sulfate depletion [15].

The synergistic effect of NS and TEA on the hydration heat of LC^3 is illustrated in Fig. 3. Compared with the control group LC^3 without NS and TEA, the addition of NS and TEA extends the induction period. The aluminate peak appears earlier and is significantly enhanced. With 0.05 % and 0.2 % TEA, the silicate peak becomes more intense and is slightly delayed. It indicates that the addition of TEA still retards the reaction of the silicate phase, even though in the presence of NS. Especially for the mix containing NS and 0.2 % TEA, the significant increase in the aluminate peak in the heat flow curve can be attributed to the combined effects of TEA and NS. TEA accelerates the dissolution of aluminate phases (C^3A and C_4AF) through ion complexation and surface adsorption, increasing the availability of Al^{3+} ions in the pore solution. Meanwhile, NS provides additional nucleation sites for AFt formation. The combination of accelerated aluminate dissolution and enhanced nucleation results in a more rapid and intensified aluminate reaction, reflected in the higher heat flow peak observed. With a further increase in TEA dosage to 0.5 %, the silicate peak is completely overlapped by the aluminate peak. The broad peak observed at 24 h is associated with overlapping silicate hydration and ongoing aluminate-ferrite reactions. Compared with the control group, the initiation of the aluminate phase reaction remains similar, while the silicate phase reaction is retarded.

Fig. 4 depicts the synergistic effect of NS and TEA, as well as their individual effects, on the hydration heat of LC^3. Compared with the control group LC^3 without NS and TEA, the addition of NS alone does not affect the duration of the induction period, whereas TEA alone and the combination of NS and TEA both prolong it. NS alone significantly increased the intensity of the silicate peak but did not alter the timing of its occurrence. In contrast, TEA alone slightly increased but delayed the silicate peak, while the combined addition of NS and TEA markedly increased its intensity and caused a slight delay. These results suggest that NS primarily influences the hydration degree of the silicate phase, whereas TEA predominantly governs the timing of the silicate peak. For the aluminate peak, both NS and TEA advanced its occurrence, with NS showing a stronger effect. Either additive enhanced the intensity of the aluminate peak, while their combination produced a synergistic effect, advancing and intensifying the peak to a greater extent.

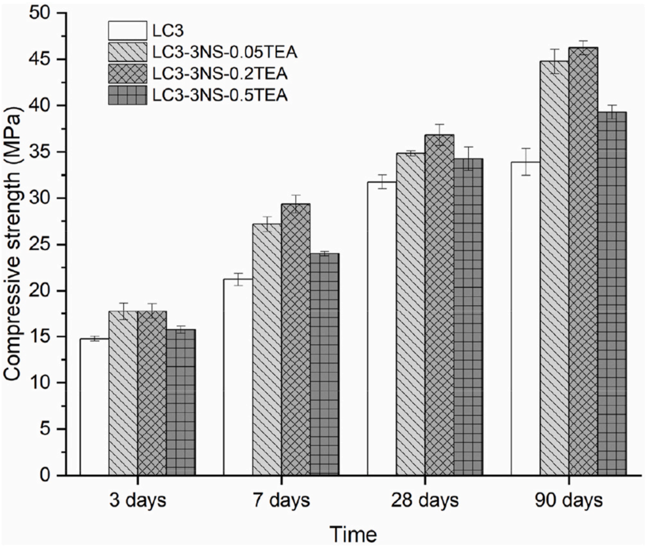


Fig. 7. Influence of NS with varied TEA dosages on the compressive strength evolution of LC^3.

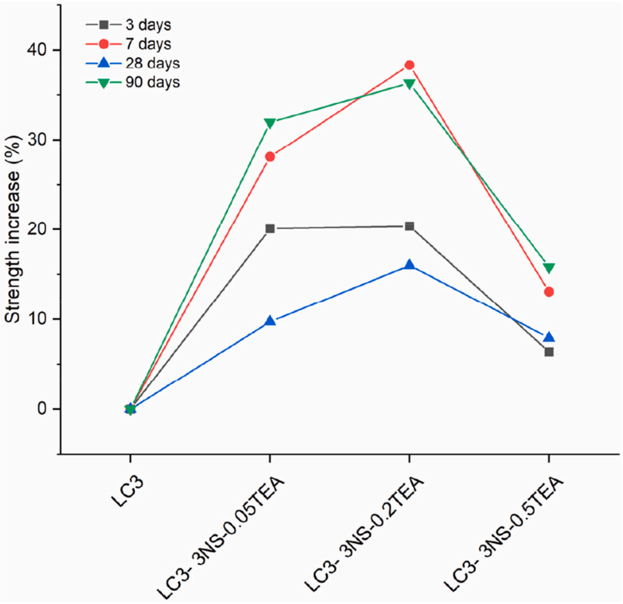


Fig. 8. Influence of NS with varied TEA dosages on the compressive strength increase of LC^3.

3.2. Compressive strength

The compressive strength of LC^3 mortar with different dosages of TEA at four ages is presented in Fig. 5. Furthermore, Fig. 6 quantifies the enhanced compressive strength observed from LC^3 blends with various dosages of TEA compared to that of the control group. Basically, the compressive strength at all four ages exhibits a positive correlation with the dosage of TEA. Moreover, strength enhancement became more pronounced with increasing curing age. Notably, the incorporation of 0.5 % by mass TEA yielded the most substantial increase in compressive strength across all ages, with a rise of 21.4 % at 3 days and 39.8 % at 7 days, respectively. Although the mixes with 0.05 % and 0.2 % TEA show higher cumulative heat after 72 h, as shown in Fig. 2, this heat is mainly associated with intensified aluminate reactions, which contribute less to early strength development. In contrast, 0.5 % TEA more effectively promotes silicate hydration and C-(A)-S-H formation at later ages, resulting in higher 3-day compressive strength despite the lower total heat release.

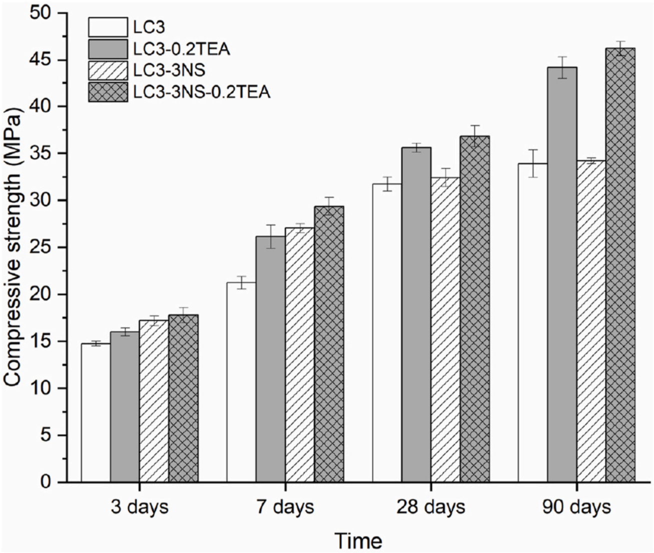


Fig. 9. Influence of NS and TEA, individually and in combination, on the compressive strength evolution of LC^3.

The enhancement of compressive strength in LC^3 with TEA addition is primarily attributed to its accelerating effect on aluminate hydration, which promotes the formation of ettringite and C-(A)-S-H gel [16]. In addition, the relative strength increase is more significant at late ages because the early acceleration primarily enhances initial ettringite and C-(A)-S-H formation, whereas at later stages TEA promotes the continued reaction of calcined clay alumina with calcium carbonate to form stable carboaluminate phases such as Hc and Mc. These secondary hydrates progressively densify the microstructure and refine pore connectivity, leading to a greater cumulative gain in compressive strength at later ages compared to the early period [17]. In addition, the hydration of the silicate phase is initially decelerated, as evidenced by the heat evolution results in Section 3.1, but it becomes reactivated and more pronounced at later stages.

The compressive strength of LC^3 mortars containing 3 % NS and different dosages of TEA at four curing ages is shown in Fig. 7, while Fig. 8 quantifies the strength enhancement rate observed from LC^3 blends with 3 % NS combined with various dosages of TEA compared to the control group. All TEA-modified mixes exhibited markedly higher strength at 3 days compared to the control group with no TEA, with the 0.2 % TEA dosage delivering the most pronounced improvement. This initial acceleration is attributed to TEA's role in chelating metal ions, which promotes the dissolution and hydration of cementitious phases, primarily the alite and aluminate phases from cement and calcined clay [18]. Crucially, the 0.2 % TEA mix maintains this superiority, achieving the highest compressive strength at all subsequent testing ages (7, 28, and 90 days), establishing it as the optimum dosage for the LC^3-3NS system.

Conversely, the highest dosage tested (0.5 % TEA) demonstrated clear limitations. Although it accelerated early strength gain, its relative performance declined at later ages, with 28- and 90-day strengths only marginally exceeding that of the control group. This behaviour suggests that while low-to-medium TEA dosages primarily enhance hydration kinetics, excessive dosage introduces adverse secondary effects. The most plausible mechanism is excessive air entrainment, where surplus TEA promotes void formation, increases porosity, and reduces the overall density of the hardened matrix, thereby constraining ultimate strength development.

These observations are corroborated by the relative strength increase trends presented in Fig. 8, which show substantial improvements across

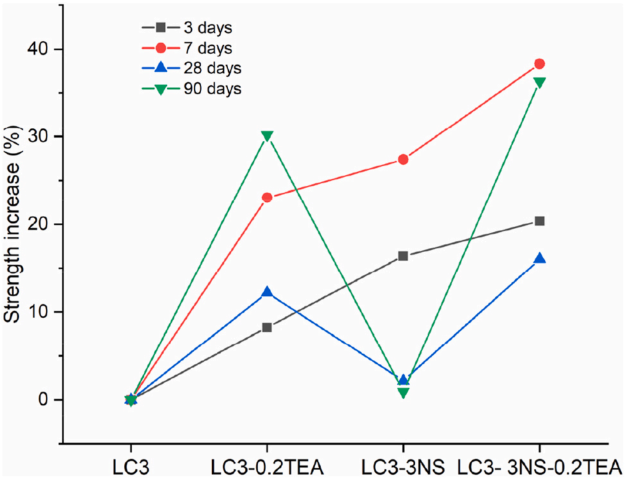


Fig. 10. Influence of NS and TEA, individually and in combination, on the compressive strength increase rate of LC^3.

all TEA dosages, with the greatest benefits achieved in the low-to-medium range (0.05–0.2 %). The 0.5 % TEA mix, although still beneficial, produced the smallest relative gain, reinforcing the existence of a dosage ceiling beyond which further addition yields diminishing or even negative returns.

In summary, the incorporation of TEA into LC^3-NS mortars is highly effective in mitigating the typically slower early strength development of LC^3 systems. However, the results underscore the critical importance of dosage optimisation. For the system studied here, 0.2 % TEA is identified as the optimum dosage, providing superior strength enhancement across all ages. These findings highlight the necessity of a balanced approach when using chemical admixtures in multi-component LC^3 systems.

Figs. 9 and 10 illustrate the effects of NS and TEA, both individually and in combination, on the compressive strength development of LC^3 at various curing ages. The results reveal a clear synergistic effect between the two additives, with their combined application yielding significantly higher performance than either component applied alone. When evaluated individually, each additive exhibits distinct mechanisms and degrees of effectiveness. The sample containing 0.2 % TEA (LC^3-0.2TEA) shows a pronounced acceleration of early-age strength, with significantly higher strength gains at 3 and 7 days compared to the LC^3 reference.

In contrast, the sample with 3 % NS demonstrates a different enhancement pattern. While early-age strength (at 3 and 7 days) shows moderate improvement, the strength development at later ages (28 and 90 days) is diminished. NS primarily contributes to early strength development in LC^3 by accelerating the hydration of clinker phases.

Importantly, the combined use of NS and TEA results in a pronounced synergistic effect. As indicated in Fig. 9, this group achieves the highest compressive strength of all ages. Furthermore, Fig. 10 demonstrates that the strength development of LC^3 incorporating both TEA and NS surpasses the individual contributions of both additives, confirming a truly synergistic rather than merely one additive effect. This mechanism can be explained as follows: NS accelerates the early hydration of cement, particularly C_3S, while TEA not only promotes early hydration but also facilitates the continued reaction between calcined clay and calcium carbonate, leading to the formation of stable carboaluminate phases such as Hc and Mc [8,19].

3.3. Evolution of phase assemblage of hardened LC^3 pastes

XRD patterns at 3 and 28 days of hydrated LC^3 blends with NS and various dosages of TEA are shown in Fig. 11. At 3 days, the intensity of portlandite (CH) was decreased with the increase of TEA. The consumption of CH in the presence of TEA could be attributed to its ability to chelate calcium ions, thereby enhancing the dissolution of calcium hydroxide. This process may lead to the consumption of CH through the chemical interaction between TEA and calcium ions, which could promote further hydration or result in the formation of soluble complexes [11]. The incorporation of NS also contributes to the consumption of CH, albeit to a much less extent than TEA. Notably, at 3 days, the compressive strength of LC^3 with 3 % NS surpasses that of LC^3 with 0.2 % TEA. The most pronounced CH reduction in all samples happened in the one with NS combined with TEA, particularly LC^3-3NS-0.5TEA, where CH is nearly consumed. However, an excessively high TEA content (LC^3-3NS-0.5) hinders the hydration of C_3S and C_2S.

At 28 days, ongoing hydration led to the formation of Mc, which contributes to the strength of the cement paste. Numerous studies have

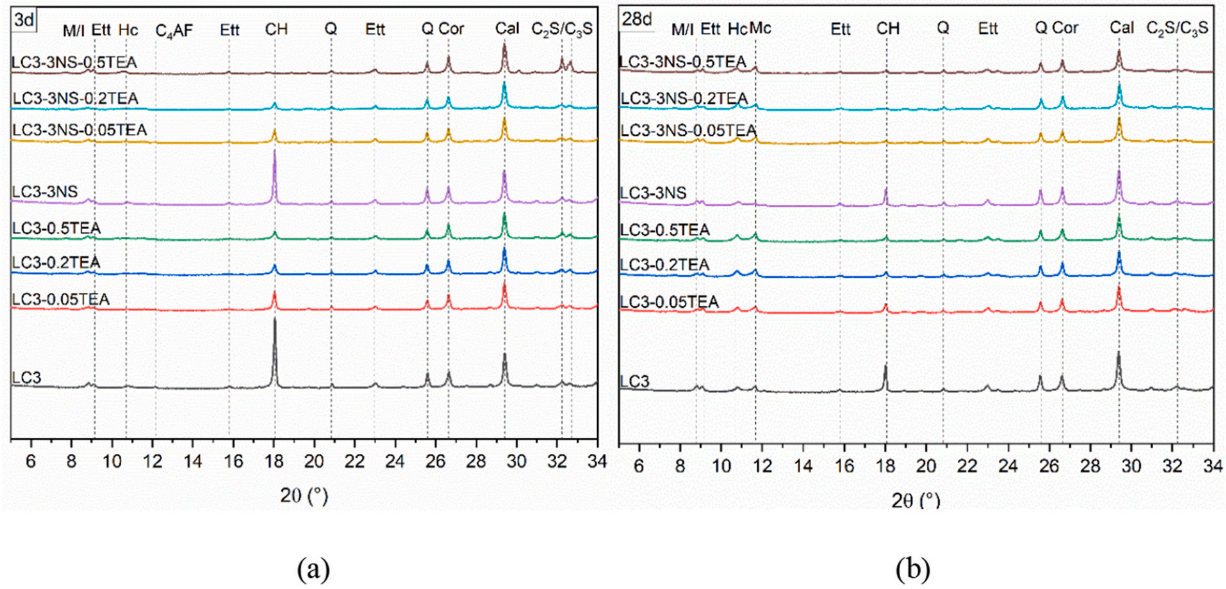
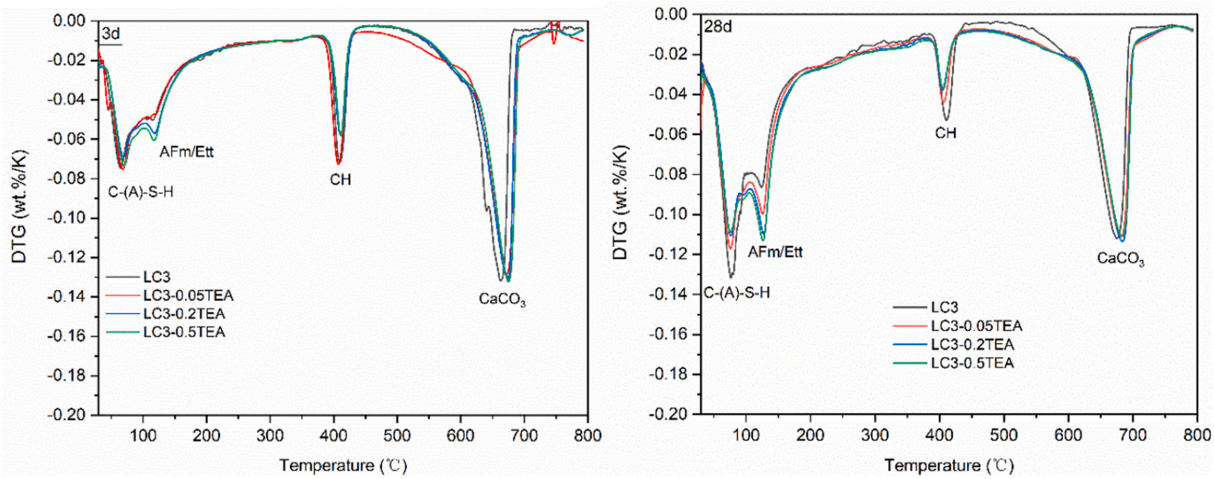
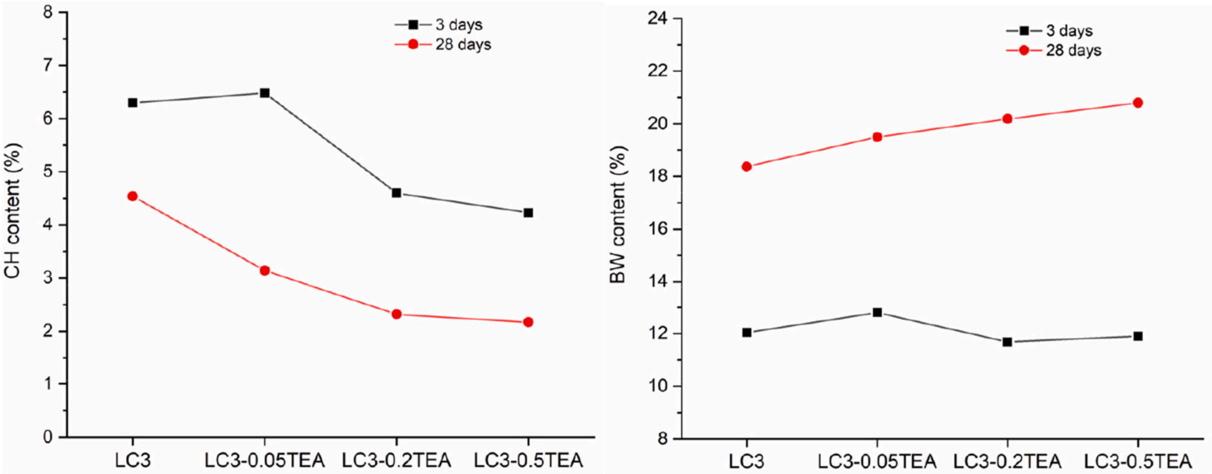


Fig. 11. XRD patterns of LC^3 pastes at 3 days (a) and 28 days (b) (M/I: Mullite/Illite, Ett: ettringite, Hc: hemicarboaluminate, Mc: monocarboaluminate, CH: portlandite, Q: quartz, Cal: Calcite, Cor: Corundum).



(a) (b)

Fig. 12. Thermogravimetric analysis of LC^3 pastes with TEA at 3 days (a) and 28 days (b).



(a) (b)

Fig. 13. CH (a) and BW (b) content of LC^3 pastes with TEA.

demonstrated that carboaluminate hydrates enhance strength by filling pore spaces [20,21]. In addition, portlandite was nearly depleted as hydration progressed. The amounts of hydration products, such as ettringite, Hc, and Mc, were generally comparable across all LC^3 pastes. However, pastes containing TEA exhibited lower $CaCO_3$ contents, suggesting that at later hydration stages, TEA promotes greater participation of $CaCO_3$ in the reactions. This further confirms that calcined clay consumes CH to generate additional amorphous C-A-S-H gel.

3.4. Thermogravimetric analysis

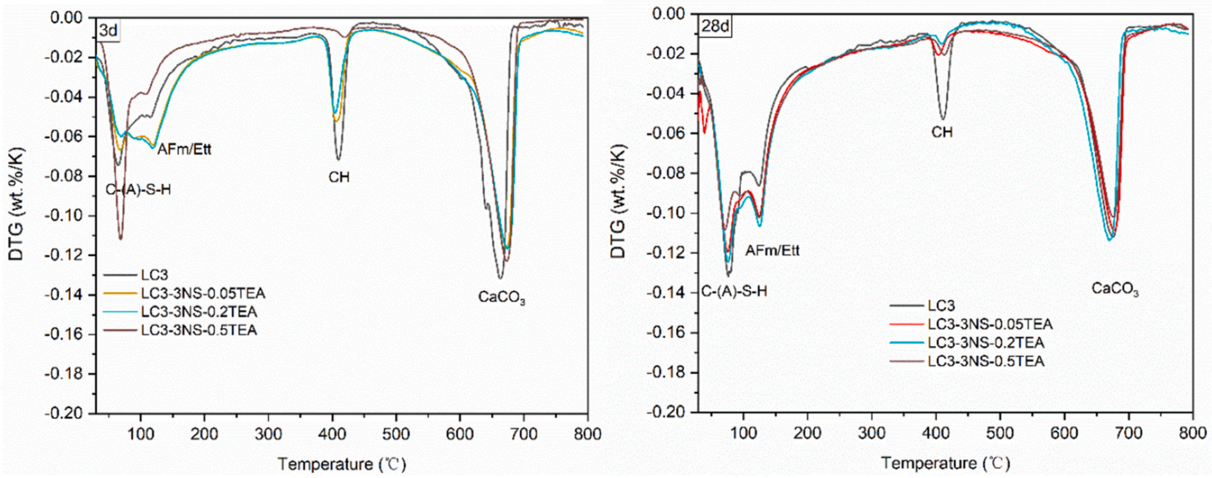
3.4.1. Thermogravimetric analysis of LC^3 with TEA only

Fig. 12 presents the DTA curves of LC^3 mixes with TEA only at 3 and 28 days. The C-(A)-S-H content shows no significant difference between the control and TEA-modified samples. In contrast, the AFt and AFm phases increase with TEA addition. This increase is mainly attributed to the acceleration of aluminate phase hydration. TEA enhances the reactivity of C_3A and alumina dissolved from calcined clay, thereby promoting greater formation of AFt at early ages and subsequently AFm as sulfate becomes depleted.

Fig. 13 depicts the evolution of CH and BW contents in LC^3, calculated from the DTA curves using the tangent method. At 3 days, the CH content decreases in the TEA-containing samples, particularly at 0.2 % and 0.5 % dosages. By 28 days, CH content decreases significantly with ongoing hydration. Comparing the weight loss attributed to BW at 3 and 28 days, an increase is observed with the progression of hydration. At 3 days, there is little difference in BW content among the samples with different TEA dosages. However, by 28 days, BW content increases with higher TEA addition, indicating the formation of more hydration products.

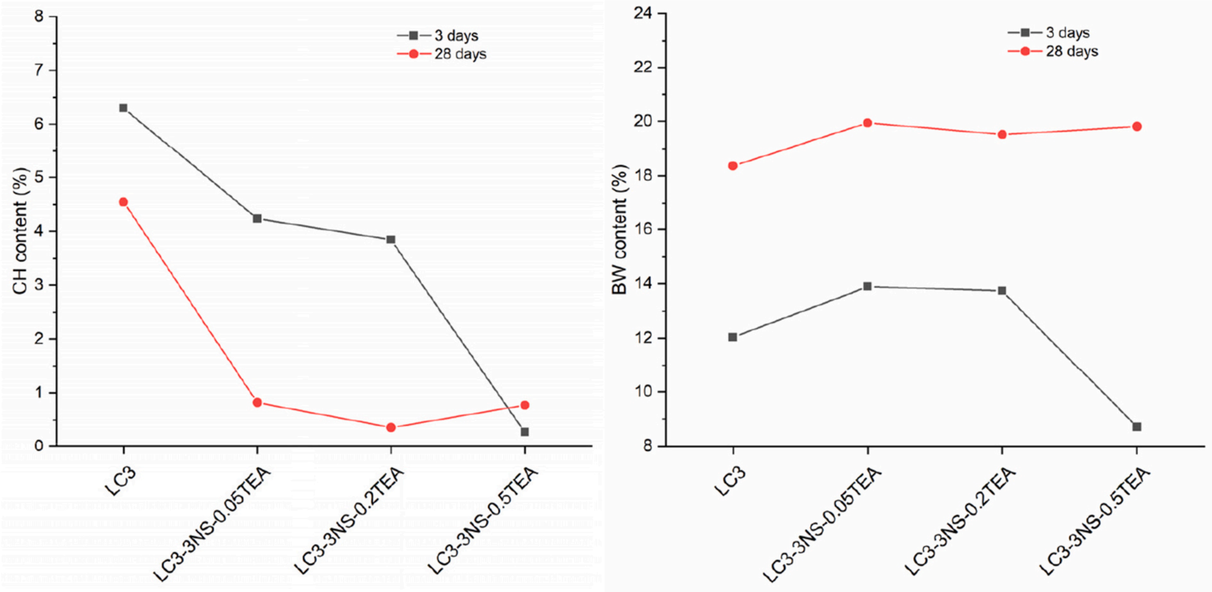
3.4.2. Thermogravimetric analysis of LC^3 incorporating NS and TEA

Figs. 14 and 15 present the DTA curves and the quantitative analysis of CH and BW for LC^3 with 3 % NS and varying TEA contents at 3 and 28 days. At both ages, mixes containing NS and, particularly, the LC^3-3NS-0.2TEA mix, exhibit markedly lower CH content and higher BW content compared to the plain LC^3 reference. This concurrent decrease in CH and increase in BW indicates that TEA accelerates early hydration of the aluminate phase, consuming Portlandite more rapidly, while NS efficiently consumes this CH through pozzolanic reactions to generate



(a) (b)

Fig. 14. Thermogravimetric analysis of LC^3 with NS and different dosages of TEA at 3 days (a) and 28 days (b).



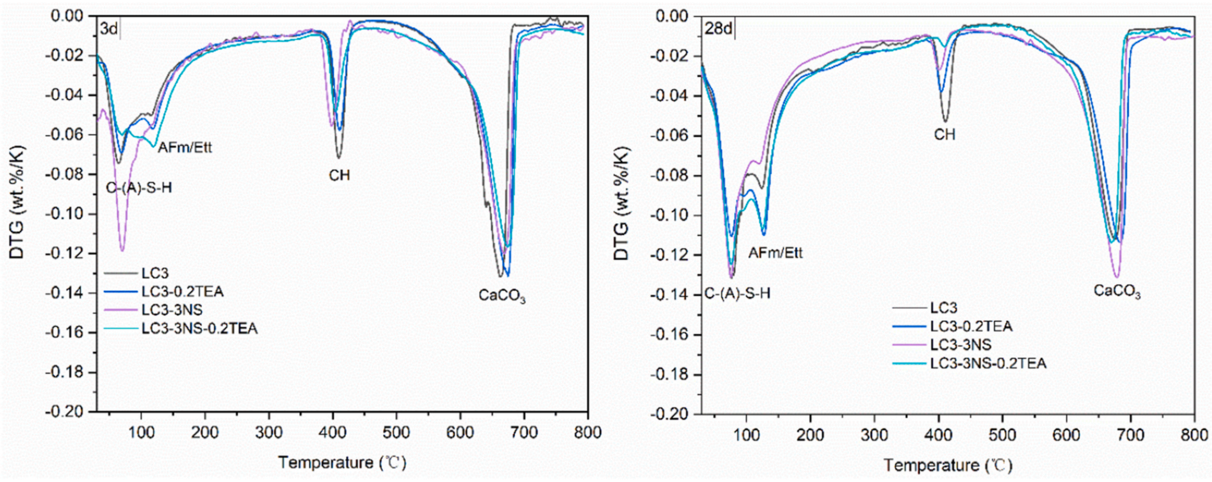
(a) (b)

Fig. 15. CH (a) and BW (b) content of LC^3 with NS and different dosages of TEA.

additional C-S-H and other hydrates. The optimal synergy achieved with 0.2 % TEA yields the lowest residual CH and highest BW, reflecting maximum reaction efficiency and hydrate formation, which translate directly into enhanced microstructural density and mechanical strength. By contrast, the higher dosage (i.e. LC^3-3NS-0.5TEA) exhibits somewhat higher CH and reduced BW relative to the 0.2 % TEA mix, confirming that excessive TEA introduces physical defects like air voids, which hinder complete hydration and compromise microstructural development despite continued chemical activity. Overall, these findings highlight that the interaction between NS and TEA is primarily controlled by reaction kinetics and microstructural evolution, with an optimal TEA dosage being critical to maximise performance.

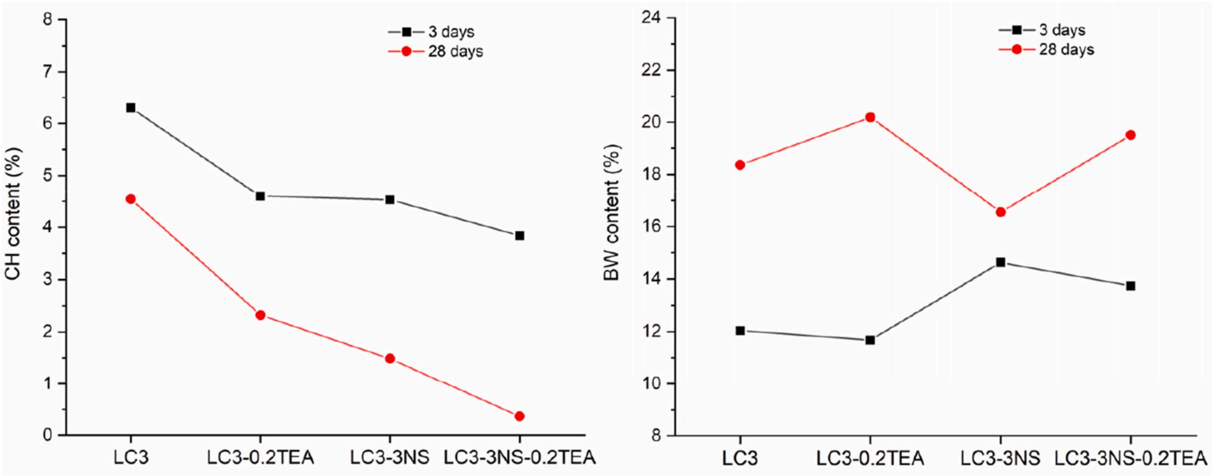
3.4.3. Thermogravimetric analysis of LC^3 with NS and TEA: individual and synergistic effects

Figs. 16 and 17 illustrate the DTA curves and the corresponding quantitative analysis of CH and BW for LC^3 incorporating NS and TEA, examined individually and in combination, at 3 and 28 days. At 3 days, the CH decomposition peak is most pronounced in plain LC^3, reduced with TEA alone due to accelerated clinker hydration, and further diminished with NS alone owing to its pozzolanic activity. The combination LC^3-3NS-0.2TEA exhibits the smallest CH peak, demonstrating early synergy where TEA enhances CH generation and NS consumes it efficiently. This trend intensifies at 28 days, with LC^3-3NS-0.2TEA showing near-complete CH consumption, suggesting that their cooperation drives sustained pozzolanic reaction. Concurrently, the enhanced low-temperature mass loss (50–200 °C) in NS-TEA blends indicates a greater volume of hydrates (C-S-H, AFm, ettringite). These results quantitatively validate that the NS-TEA synergy optimises reaction kinetics and microstructural density, with the 0.2 % TEA dosage maximising hydration completeness and solid phase formation, directly correlating with the observed mechanical performance.



(a) (b)

Fig. 16. Thermogravimetric analysis of LC^3 with NS and TEA: Individual and synergistic effects at 3 days (a) and 28 days (b).



(a) (b)

Fig. 17. CH (a) and BW (b) content of LC^3 pastes with NS and TEA, individually and in combination.

3.5. *Porosity*

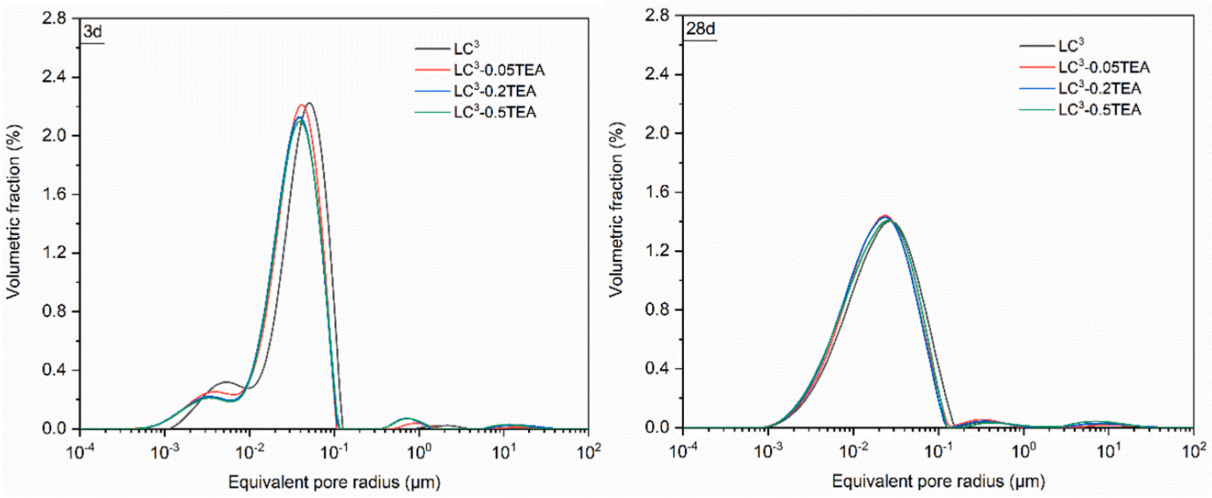
3.5.1. *Porosity of LC^3 with TEA*

As shown in Figs. 18 and 19, the pore size distribution and volume fractions of LC^3 with varying TEA contents (0.05 %, 0.2 %, and 0.5 %) were evaluated at 3 and 28 days. In the LC^3 system, the addition of TEA slightly reduced the critical pore entry radius (Fig. 18). Following the method proposed by Mehta et al. [22], the pore size classification was divided into four pore groups, as illustrated in Fig. 19. Pores with a radius below 50 nm contribute positively to strength development, whereas those exceeding 50 nm have a detrimental effect. Although the total porosity remains relatively consistent across all mixes at both ages (ranging from 42.8 % to 44.9 %), indicating that TEA does not drastically alter the overall pore volume, significant changes occur in the pore size distribution, which have profound implications for performance.

At 3 days, the total porosity is highest in the LC^3-0.05TEA mix (44.93 %) and lowest in LC^3-0.5TEA (44.22 %), but these differences are marginal. The most notable trend is the shift in pore size distribution: as the TEA dosage increases, the volume of larger capillary pores (>100 nm) decreases, while the volume of finer pores (4.5–50 nm) increases. This suggests that TEA accelerates hydration, leading to a more refined microstructure at an early age. The reduction in large pores is beneficial for strength increase, as verified in section 3.2.

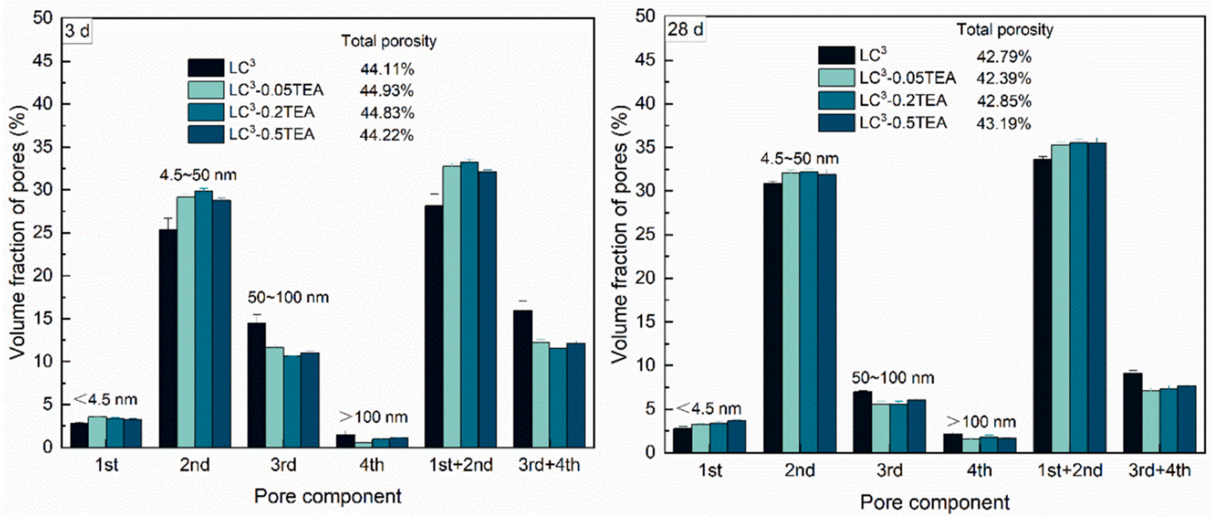
By 28 days, the total porosity decreases across all mixes due to ongoing hydration, but the differences between them remain small. However, the pore refinement trend becomes even more pronounced. The volume of harmful large pores (>100 nm) continues to decrease with higher TEA dosages, particularly in the LC^3-0.2TEA and LC^3-0.5TEA mixes, while the volume of finer pores (4.5–50 nm) increases. This indicates that TEA not only accelerates early hydration but also contributes to continued microstructural densification over time. The increase in finer pores is associated with enhanced gel porosity within the C-S-H matrix, which is advantageous for strength development. Interestingly, the LC^3-0.5TEA mix shows a slight increase in total porosity at 28 days (43.19 %) compared to other mixes, which may be attributed to the air-entraining effect of high TEA dosage, introducing additional voids that offset some of the refinement benefits. Despite this, the pore size distribution has improved, with fewer large pores.

In summary, TEA dosage primarily influences the pore size distribution rather than the total porosity, promoting a shift from larger, more



(a) (b)

Fig. 18. The pore size distribution from NMR for LC^3 pastes with TEA at 3 days (a) and 28 days (b).



(a) (b)

Fig. 19. Volume fractions of four types of pores for LC^3 pastes with TEA at 3 days (a) and 28 days (b).

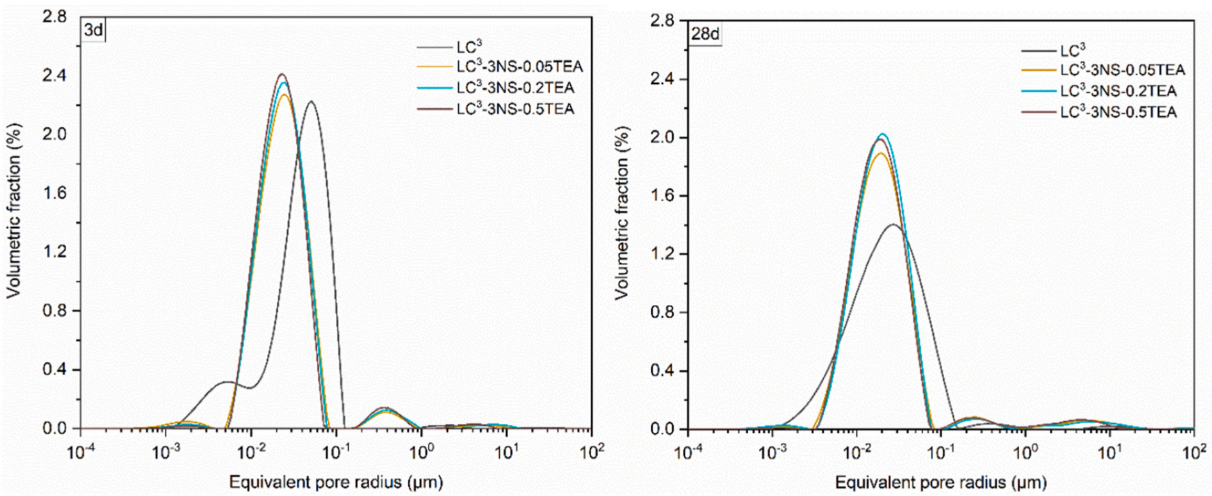
harmful pores to smaller, less detrimental ones. This refinement is most effective at moderate TEA dosages (i.e. 0.2 % TEA), where the acceleration of hydration optimally enhances microstructure without significant adverse effects.

3.5.2. *Porosity of LC^3 with NS and TEA*

Figs. 20 and 21 present the pore size distribution and volume fractions of LC^3 with 3 % NS and with varying TEA contents (0.05 %, 0.2 %, and 0.5 %) on 3 and 28 days. In the LC^3 system, the addition of NS and TEA reduced the critical pore entry radius (Fig. 20). At 3 days, the total porosity increases in all NS-TEA blends (46.02–46.6 %) compared to the plain LC^3 reference (44.11 %). This rise is attributed to the dual effects of TEA-induced air entrainment and the initial spacing effect of NS nanoparticles. Despite the higher total porosity, the pore size distribution shifts favourably: the volume of large capillary pores (>100 nm) decreases markedly, while the volume of finer pores (4.5–50 nm) increases. This refinement indicates that TEA accelerates early hydration, leading to faster precipitation of hydration products that fill larger voids, while NS contributes to pore narrowing through its filler and pozzolanic effects. The LC^3-3NS-0.2TEA mix shows the most pronounced reduction in large pores and the highest volume of finer pores, suggesting optimal synergy at this dosage.

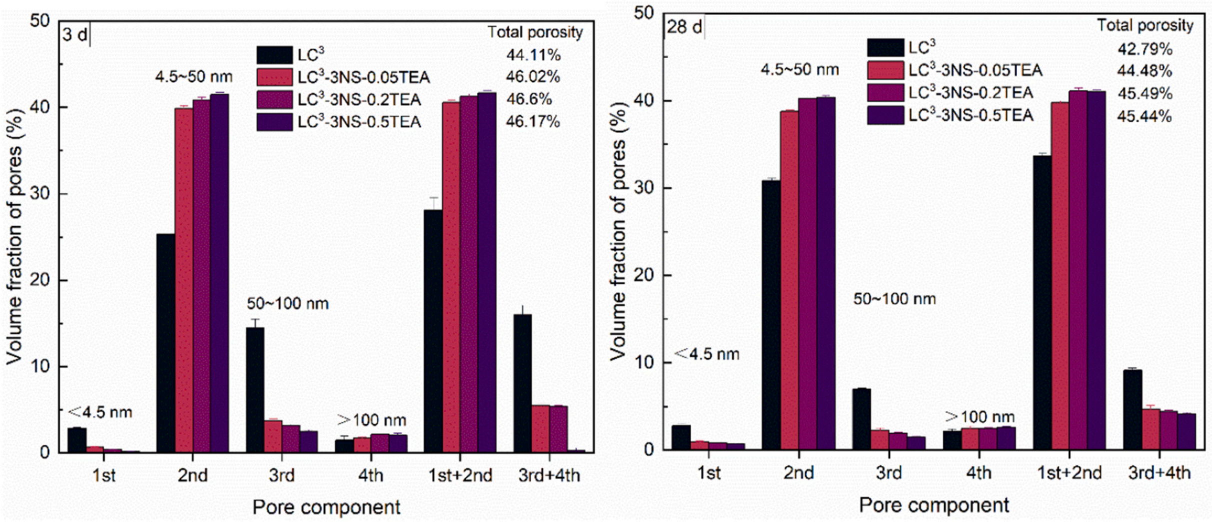
At 28 days, the total porosity decreases across all mixes due to continued hydration, but the NS-TEA blends still exhibit higher porosity (44.48–45.49 %) than plain LC^3 (42.79 %). The persistence of elevated porosity is likely due to the stable air voids entrained by TEA, which are not easily filled by hydration products. However, the pore refinement trend intensifies: the volume of large pores (>100 nm) further declines, while the fraction of finer pores (4.5–50 nm) continues to increase. The LC^3-3NS-0.2TEA mix again demonstrates the most refined microstructure, with the lowest proportion of large pores and the highest volume of gel pores. This aligns with its superior mechanical performance, as finer pores contribute more to strength and durability than total porosity alone.

The increase in total porosity with NS-TEA addition is primarily physical (air entrainment), while the refinement in pore size distribution



(a) (b)

Fig. 20. The pore size distribution from NMR for LC^3 pastes with NS & TEA at 3 days (a) and 28 days (b).



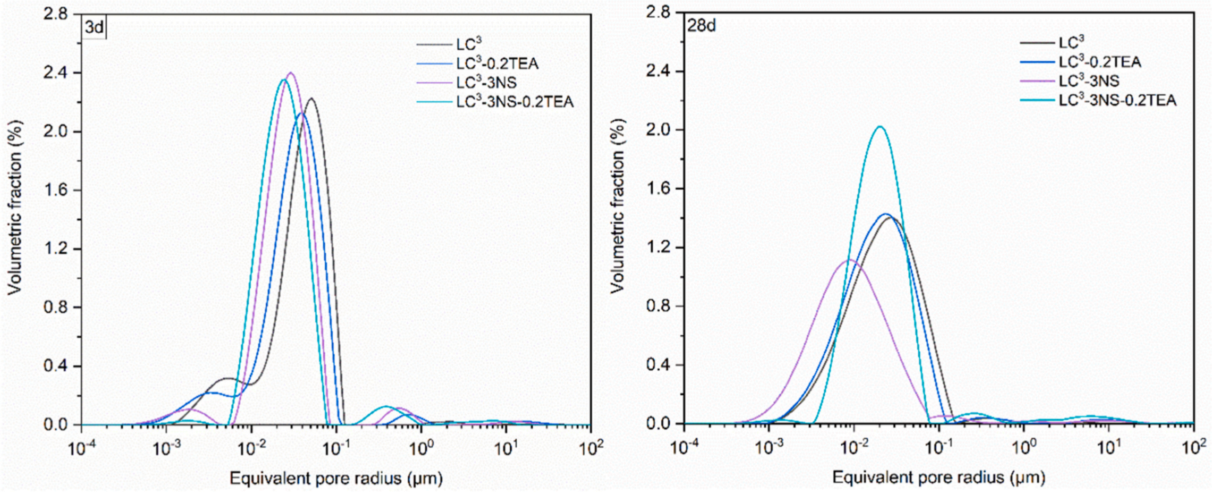
(a) (b)

Fig. 21. Volume fractions of four types of pores for LC^3 pastes with NS & TEA at 3 days (a) and 28 days (b).

is chemical (enhanced hydration and pozzolanic reaction). The synergy between NS and TEA is evident: TEA accelerates clinker hydration, generating more CH and promoting early pore refinement, while NS consumes CH to produce additional C-S-H, further filling and subdividing pores. The optimal dosage of 0.2 % TEA balances these effects, minimising large pores without excessive air entrainment. Higher TEA dosages (0.5 %) exacerbate porosity due to increased air void content, offsetting some of the refinement benefits.

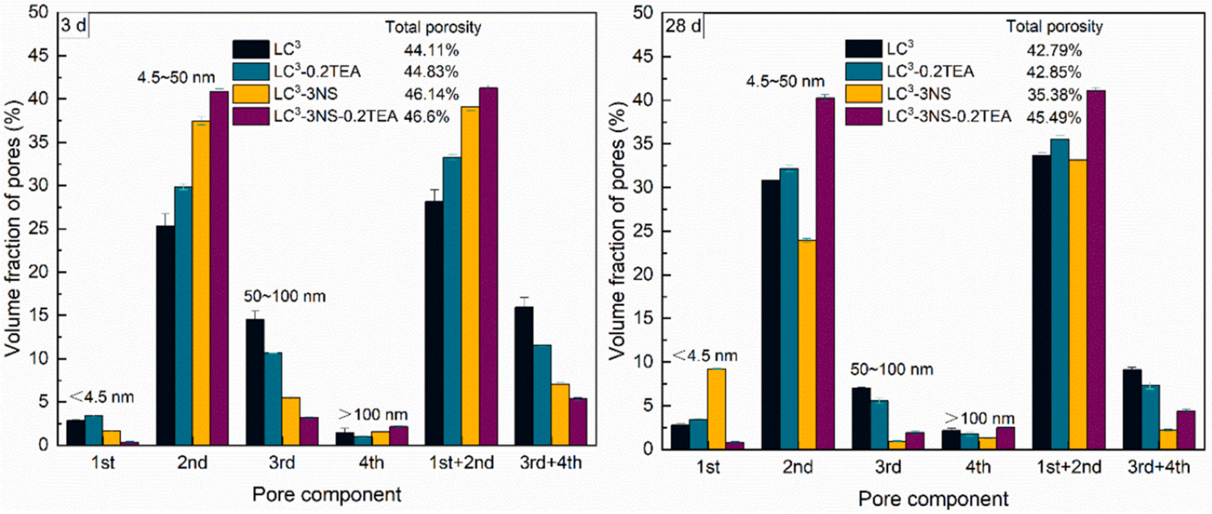
3.5.3. Porosity of LC^3 with NS and TEA: individual and synergistic effects

Figs. 22 and 23 illustrate the individual and synergistic effects of NS and TEA on the pore size distribution and volume fractions of LC^3 at 3 and 28 days. At 3 days, the addition of TEA alone slightly increases total porosity (44.83 %) compared to plain LC^3 (44.11 %), likely due to mild air entrainment, yet it reduces the volume of large capillary pores (>100 nm) by accelerating early hydration and promoting finer pore formation. In contrast, NS alone significantly refines the microstructure, drastically reducing total porosity to 35.38 % by 28 days and shifting the pore size distribution toward finer categories (4.5–50 nm and <4.5 nm), owing to its dual filler effect and pozzolanic consumption of CH to form additional C-S-H. However, the combination of NS and TEA (LC^3-3NS-0.2TEA) results in higher total porosity at both ages (46.6 % at 3 days and 45.49 % at 28 days) than plain LC^3, primarily due to TEA-induced air entrainment introducing macro voids. Despite this, the synergistic blend achieves the most favourable pore size distribution: it exhibits the lowest volume of large harmful pores (>100 nm) and the highest volume of fine pores (4.5–50 nm and <4.5 nm), as TEA accelerates hydration to rapidly generate CH, while NS consumes it to produce dense C-S-H, refining the pore network. This indicates that pore quality (size distribution) outweighs total porosity in determining performance, as the NS-TEA synergy optimally densifies the matrix at the nanoscale, explaining its superior mechanical and durability properties despite elevated overall porosity. The data underscores the importance of balancing chemical enhancement (hydration and pozzolanic reactions) with physical effects (air entrainment) in admixture design.



(a) (b)

Fig. 22. The pore size distribution from NMR for LC^3 pastes with NS and TEA: Individual and synergistic effects at 3 days (a) and 28 days (b).



(a) (b)

Fig. 23. Volume fractions of four types of pores for LC^3 pastes with NS and TEA: Individual and synergistic effects at 3 days (a) and 28 days (b).

4. Conclusions

This paper presents the individual and synergistic effects of NS and TEA on the hydration and hardened properties of the LC^3 system, focusing on hydration heat, compressive strength, phase assemblage and pore size distribution. Based on the analysis and discussions, the following conclusions can be drawn:

(1) Isothermal calorimetry results reveal that NS primarily influences the hydration degree of the silicate phase, whereas TEA governs the timing of the silicate peak. For the aluminate peak, both NS and TEA advanced its occurrence, with NS showing a stronger effect. Either NS or TEA enhanced the intensity of the aluminate peak, while their combination produced an even stronger synergistic effect, both advancing and intensifying the peak to a greater extent.

(2) Compressive strength: TEA alone contributes to the strength development of LC^3 at all ages, while NS only contributes to the early strength of LC^3. In addition, the synergistic effect of NS and TEA is more pronounced than TEA or NS alone, especially LC^3-3NS-0.2 %TEA, which shows the highest performance at all ages.

(3) Hydration products: TEA contributes more significantly to the consumption of CH compared to NS. NS-TEA blends indicate a greater volume of hydrates of C-(A)-S-H gel, AFm and AFt phase, leading to a denser structure and enhanced strength.

(4) Porosity: TEA primarily influences the pore size distribution rather than the total porosity, promoting a shift from larger, more harmful pores to smaller, less detrimental ones. Synergistic blend with NS and TEA achieves the most favourable pore size distribution: it exhibits the lowest volume of large harmful pores (>100 nm) and the highest volume of fine pores (4.5–50 nm and <4.5 nm).

CRediT authorship contribution statement

Mingqing Liu: Writing – original draft, Software, Formal analysis, Data curation, Conceptualization. **Zhonghao Niu:** Writing – review & editing, Software, Data curation. **Xiangming Zhou:** Writing – review & editing, Conceptualization. **Pengkun Hou:** Writing – review & editing, Conceptualization. **Ran Hai:** Writing – review & editing. **Shuang Liang:** Writing – review & editing. **Yuzhou Sun:** Writing – review & editing.

Declaration of competing interest

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.

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Data availability

Data will be made available on request.

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