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Enhancing Early-Age Strength of Low-Clinker Limestone Calcined Clay Cement Using Sodium Carbonate and Chemical Accelerators

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Abstract

While limestone calcined clay cement (LC3) can reduce CO_2 emissions by up to 50%, low early-age strength in low-clinker formulations limits its structural adoption. This study investigates practical strategies to accelerate early strength development in low-clinker LC3 mortars (clinker fraction ~42.5%) using sodium carbonate (1–3%) and a commercial chemical accelerator (1.5–3%), evaluated individually and in combination. Eleven mortar mixes were tested for compressive and flexural strength at 3, 7, and 28 days per BS EN 196-1, alongside ATR-FTIR hydration characterization and dry versus wet mixing comparisons. Results show that 2% sodium carbonate is the optimal single dosage, increasing 7-day compressive strength by ~29% (from 6.8 to 8.8 MPa) and flexural strength by 22% (from 2.46 to 3.00 MPa). Combining 1% sodium carbonate with 1.5% accelerator produced a pronounced synergistic effect, boosting 7-day compressive strength by 38% (9.4 MPa) and flexural strength by 34% (3.30 MPa). FTIR spectra confirmed enhanced silicate polymerization and carboaluminate precipitation. These findings provide construction practitioners with a scalable, low-cost chemical activation method to facilitate early demoulding and formwork stripping in sustainable low-carbon construction.

Keywords: limestone calcined clay cement (LC3); early-age strength; sodium carbonate; chemical accelerator; low-carbon concrete; FTIR spectroscopy

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1. Introduction

Portland cement-based concrete is the most extensively used engineered material worldwide due to its exceptional versatility and durability [1]. Consequently, it is a fundamental material for modern civilization, extensively used in civil engineering and architectural construction. However, like many industrial processes, the production of Portland cement poses significant environmental challenges due to its high-energy demand and substantial carbon dioxide emissions. Calcination during clinker production is the primary source of CO_2 emissions, in addition to those generated from the combustion of fossil fuels required to heat the kiln. Overall, the global cement industry is responsible for approximately 7% of total worldwide CO_2 emissions [2]. The United Nations Intergovernmental Panel on Climate Change (IPCC), during COP27 held in Sharm El-Sheikh [3], emphasized that global CO_2 emissions must be reduced by 45% by 2030 in order to meet the target of limiting the global temperature increase to below 2 °C by 2050 [3]. In practical

construction engineering, achieving these aggressive decarbonization targets requires immediate material-level innovations that can be implemented seamlessly in ready-mixed concrete batching plants, precast element manufacturing, and on-site structural repair operations without disrupting standard construction schedules or productivity.

Consequently, cement manufacturers and structural engineers have been encouraged to intensify research efforts aimed at developing more sustainable and cost-effective cementitious materials. In this context, continued investigation into the application and optimization of limestone calcined clay cement (LC3) is strongly recommended. This ternary cement system can reduce CO_2 emissions by approximately 30–50% [4], as up to half of the clinker content is replaced by a synergistic blend of calcined clay (metakaolin) and limestone powder. Calcined clay is a naturally occurring aluminosilicate clay that is thermally activated at temperatures of around 700–850 °C [5,6]. This temperature is considerably lower than the ~1450 °C required for conventional Portland cement clinker kilns, making the manufacturing process substantially more energy-efficient and environmentally sustainable. In real-world construction practice, LC3 offers tremendous potential to reduce the embodied carbon of building components, bridge decks, and precast infrastructure elements.

The mechanical performance of LC3 has shown competitive or superior ultimate strength compared to OPC and other blended cements at mature ages (28–90 days). Multiple studies have successfully achieved increased compressive strength in standard LC3 formulations while using water-to-binder ratios and mixing proportions similar to those employed for OPC [7,8]. However, a major technical hurdle restricting the widespread commercial and structural adoption of LC3 in real construction is its slower strength development at early ages (1–7 days) compared to OPC, primarily due to the lower initial clinker content, reduced early C-S-H formation, and the inherently slower dissolution and pozzolanic kinetics of calcined clay at early curing times [9,10]. In fast-track construction, precast fabrication, and cold-weather concreting, this delayed early strength gain translates to extended formwork stripping times, slower cycle times, and increased overall project costs.

Several studies have explored methods to overcome the inherent low early-age strength of Limestone Calcined Clay Cement (LC3) and improve its structural performance at early curing times. One effective approach is the incorporation of reactive silica sources such as silica fume (SF) and rice husk ash (RHA), which provide additional nucleation sites for cement hydration products and accelerate the formation of calcium silicate hydrate (C-S-H). For example, adding 5% SF to LC3 was shown to improve compressive strength by more than 30% at 3 days and achieve strength comparable to OPC by 14 days, with enhanced hydration kinetics and microstructural development confirmed by XRD and FTIR analyses [9].

In addition to silica-based additives, research has investigated nanomaterials such as nano-silica, which significantly accelerates early hydration reactions and increases early compressive strength at 1–3 days due to its extremely high pozzolanic activity and ability to refine pore structure. For instance, the addition of 2% nano-silica increased the strength at 1 day by 56% [11]. However, although the addition of nano-silica significantly enhances early strength, its high commercial cost, dispersion difficulties, and potential agglomeration limit its practical applicability on large-scale construction job sites.

Another promising category of early strength enhancers includes inorganic salts (e.g., sodium carbonate, sodium chloride, and sodium sulfate), which promote early hydration reactions and accelerate aluminate and pozzolanic processes in LC3, with sodium carbonate showing particularly strong activation potential [12]. Specifically, sodium carbonate (Na_2CO_3) provides an immediate source of soluble alkali (Na^+) and carbonate (CO_3^{2-}) ions,

elevating the pore solution alkalinity, which accelerates the breakdown of the tetrahedral aluminosilicate framework in calcined clay and promotes the precipitation of calcium carboaluminate phases [12,13]. In parallel, the incorporation of limestone powder ($CaCO_3$) provides supplementary carbonate ions and fine nucleation surfaces that stabilize monocarboaluminate and hemicarboaluminate phases, preventing the conversion of ettringite to monosulfate [13,14]. Furthermore, gypsum ($CaSO_4 \cdot 2H_2O$) supplies essential sulfate ions (SO_4^{2-}) to regulate early tricalcium aluminate (C_3A) hydration and maintain the optimum sulfate-to-aluminate ratio in LC3 systems [13,14]. Recent studies on low-clinker LC3 formulations with clinker contents below 50% have highlighted their tremendous potential to further minimize embodied CO_2, while emphasizing the urgent need for cost-effective chemical activation to overcome early-age hydration deficits [13,14].

In areas with abundant volcanic ash deposits, Portland pozzolanic cements (PPCs) or blended cement have been utilized since the 1950s. These cements are composed of a blend of clinker, naturally occurring pozzolanic materials (volcanic ashes), and gypsum. In recent years, the production of blended Portland cements, slag cements, and pozzolanic cements in Europe and Asia has surpassed that of pure Portland cement. The use of these blended cements has led to reductions of at least 25% in CO_2 emissions, energy consumption, and overall costs [15]. The clinker content in blended cement varies from 80 to 50% depending on cement type and class [14]. Natural pozzolans typically exhibits lower reactivity than calcined clays [16,17], which often results in blended cements exhibiting lower strength than ordinary Portland cement (OPC) during the 1–28 day curing period [18–21]. Nevertheless, natural pozzolans can enhance durability [22–24] and are widely employed in the production of structural concrete [25].

Zunino et al. [14] investigated the hydration kinetics, phase evolution, and strength development of low-clinker limestone calcined clay cements (LC3) with clinker contents of 50%, 35%, and 25%, and compared these to Portland pozzolanic cements (PPC) made with natural pozzolans (NP). The study combined experimental measurements and thermodynamic modeling to analyze how different blends evolve during hydration, focusing on phase assemblage, sulfate requirements, porosity, and mechanical performance. Low-clinker LC3 systems showed faster hydration kinetics, greater carboaluminate precipitation, and improved pore refinement compared with PPC, which the authors attributed to the higher reactivity and alumina content of calcined clays relative to natural pozzolans. As a result, LC3 produced a larger volume of solid hydration products at equivalent reaction degrees, enabling clinker reductions of 40–46% while still meeting standard strength requirements for PPC-type cements. These findings demonstrate that low-clinker LC3 is a viable low-carbon alternative to PPC, offering significant CO_2 reduction potential without compromising mechanical performance in markets where pozzolanic cements are commonly used.

This research was initiated to advance the work of Zunino et al. [14] and Sun et al. [13] on low-clinker LC3 made with limestone powder. Despite the growing body of research on conventional LC3 systems (typically ~50% clinker), limited studies have systematically investigated early-age strength enhancement strategies for low-clinker LC3 formulations with clinker contents below 50%. Existing work has primarily focused on standard LC3 compositions or on single, high-cost activation approaches, such as nano-silica or caustic alkali hydroxides (e.g., NaOH, KOH), which pose workplace safety hazards, severe workability loss, and economic penalties in real-world construction. In contrast, sodium carbonate (Na_2CO_3) represents a safer, non-caustic, readily available activator, while liquid chemical accelerators (such as nitrate/alkanolamine-based commercial accelerators) are already widely accepted in precast and ready-mix concrete operations.

The present study addresses this research gap by experimentally evaluating the effectiveness of sodium carbonate activation and a commercial chemical accelerator, both individually and in combination, on the early-age compressive and flexural performance of low-clinker LC3 mortars (actual clinker content ~42.5% of total binder). Unlike previous studies, this work explicitly examines flexural response alongside compressive strength and links mechanical performance to hydration mechanisms using Fourier Transform Infrared Spectroscopy (FTIR) analysis. Furthermore, the practical influence of mixing protocol (dry blending vs. wet pre-dissolution) on activation efficiency and workability is assessed to provide actionable insights for field implementation. However, the scope and limitations of the present study should be noted: the experimental programme is conducted at the mortar scale under controlled ambient laboratory curing (20 ± 2 °C), evaluating mechanical performance up to 28 days and FTIR phase assemblage at 28 days; full-scale concrete structural testing, rheological characterization, long-term durability (e.g., carbonation, chloride penetration), and elevated/cold-temperature curing are beyond the immediate scope and are recommended for future investigation. The outcomes of this research provide practical and mechanistic insights into achieving early-strength-competitive, low-carbon LC3 systems suitable for structural, precast, and repair applications.

2. Experimental Program

The experimental program involved preparing and testing eleven mortar mixes with variations in clinker content, sodium carbonate dosage, accelerator dosage, and mixing method. Two control mixes were also included: one consisting of ordinary cement mortar and the other of LC3 mortar without any additives, aside from admixtures used to maintain workability.

2.1. Test Matrix

Eleven mortar mixes were prepared and tested to investigate the effects of cement/clinker content, sodium carbonate dosage, accelerator dosage, and mixing procedure on mortar performance. The mix designations and binder compositions are presented in Table 1. The first term in each designation indicates the cement content as a percentage of the total binder (where cement refers to CEM II/A-L 32.5R containing ~85% clinker and ~15% limestone; hence 50% cement corresponds to ~42.5% clinker, 70% cement to ~59.5% clinker, and 100% cement to ~85.0% clinker by mass of binder). The letter S denotes the incorporation of sodium carbonate, with the accompanying number indicating its dosage by mass of binder (1%, 1.5%, 2%, 3%), while the letter A represents the use of the commercial chemical accelerator (SikaRapid®-1) which was supplied by Sika Limited, UK, with the adjacent number referring to its dosage (1.5%, 3%). The letters D and W identify the mixing procedure, corresponding to dry and wet mixing, respectively. In the dry mixing procedure (D), all solid constituents (cement, calcined clay, limestone powder, gypsum, and sodium carbonate powder) were thoroughly dry-blended prior to water and liquid admixture addition. In contrast, for wet mixing (W), sodium carbonate was first dissolved in the mixing water prior to introduction to the dry materials. For example, the mix C50-S1-A1.5-D represents a mortar containing 50% cement (~42.5% clinker), 1% sodium carbonate, and 1.5% accelerator, prepared using the dry mixing method. Control mixes were prepared without sodium carbonate or accelerator to provide baseline references, designated as CEM II-Control (100% cement, ~85% clinker) and LC3-Control (50% cement, ~42.5% clinker).

Table 1. Test matrix.

Mix	Mixing Method	Cement (%)	Clinker Content (%)	Sodium Carbonate (%)	Accelerator (%)
CEM II-Control	Dry	100	~85.0	0	0
LC3-Control		50	~42.5	0	0
C50-S1-D		50	~42.5	1.0	0
C50-S1-A3-D		50	~42.5	1.0	3.0
C50-S1.5-D		50	~42.5	1.5	0
C50-S1-A1.5-D		50	~42.5	1.0	1.5
C50-S1-W	Wet	50	~42.5	1.0	0
C50-A1.5-D	Dry	50	~42.5	0	1.5
C50-S2-D		50	~42.5	2.0	0
C50-S3-D		50	~42.5	3.0	0
C70-D		70	~59.5	0	0

2.2. Materials

2.2.1. Cement

Portland-limestone cement CEM II/A-L 32.5R, conforming to BS EN 197-1 [26], was used as the reference cement. According to manufacturer specifications and EN 197-1 criteria, this cement contains approximately 15% limestone and 85% clinker (within the standard 6–21% limestone range), with a small gypsum fraction for setting regulation. It exhibits a standard 28-day compressive strength of 32.5 MPa and rapid early strength development (R-class). In this study, the clinker content of each binder mix is calculated directly from this base cement fraction: a 100% cement mix (CEM II-Control) contains ~85.0% clinker; a 70% cement mix (C70-D) contains ~59.5% clinker; and 50% cement mixes (LC3-Control and C50 series) contain ~42.5% clinker by total binder mass. Consistent distinction between total cement content and actual clinker content is maintained throughout this manuscript.

2.2.2. Calcined Clay

Calcined clay was used in the preparation of the LC3 mixes, with the following properties in Tables 2 and 3 provided by the manufacturer.

Table 2. Chemical properties of calcined clay.

Compound	%
Aluminium Oxide Al_2O_3	38–44
Silicon Dioxide (SiO_2)	48–54
Ferric oxide Fe_2O_3	0.6 max
Titanium dioxide TiO_2	1.5 max
Magnesium Oxide (MgO)	0.3 max
Calcium Oxide CaO	0.5 max
Kaolinite Content	98%

Table 3. Physical properties of calcined clay.

Property	%
Moisture	2.5% Max
Loss in ignition	1–2%
PH	5–6.5
Retention on 325 Mesh	3.0%
Lime Reactivity ($Ca(OH)_2$)	Min 850 mg/gm
Color	Off white

2.2.3. Fine Aggregate

Thames River fine aggregate with a maximum size of 5 mm and specific gravity of 2.6 conforming to BS EN 12620 [27] was used.

2.2.4. Water

Potable water was used in the mixing and curing of specimens free from any contamination and conforming to BS EN 1008 [28].

2.2.5. Sodium Carbonate

Anhydrous sodium carbonate (Na_2CO_3) powder (analytical grade, 99.5% purity, molecular weight 105.99 g/mol, Supplied from Fisher Scientific at the UK) was used as the chemical activator. Sodium carbonate was selected because it is non-hazardous, safe for handling on construction sites compared to caustic alkalis (e.g., NaOH, KOH), and rapidly supplies soluble sodium and carbonate ions (Na^+, $CO_3{}^{2-}$), which increase pore solution pH, accelerate aluminosilicate dissolution from calcined clay, and promote carboaluminate precipitation [12,13].

2.2.6. Limestone Powder

Fine limestone powder ($CaCO_3$, 98% purity, molecular weight 100.09 g/mol, Fisher Scientific) with a median particle size $d_{50} \approx 10$ µm was used in the production of LC3 mixes. Limestone powder serves a dual role in LC3: it acts as a micro-filler providing heterogeneous nucleation sites for C-S-H growth, and reacts chemically with the alumina released from calcined clay to form stable carboaluminate phases (hemicarboaluminate and monocarboaluminate), preventing the formation of less stable monosulfoaluminate [14,25].

2.2.7. Gypsum

Calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$, 99% purity, molecular weight 172.16 g/mol, Fisher Scientific) was incorporated in LC3 mixes. Gypsum is essential in low-clinker LC3 systems to supply soluble sulfate ($SO_4{}^{2-}$), preventing uncontrolled early C_3A and aluminate flash reactions, ensuring setting regulation, and optimizing the sulfate-to-aluminate ratio necessary for maximum carboaluminate and ettringite stability [14,17].

2.2.8. Admixtures

Two commercial liquid chemical admixtures were utilized in this study. A polycarboxylate ether (PCE)-based high-range water-reducing admixture (Sika® ViscoCrete) which was supplied by Sika Limited, Welwyn Garden City, UK, conforming to BS EN 934-2 [29] was used to regulate mortar workability. ViscoCrete is a chloride-free aqueous solution with a density of ~1.08 kg/L and a mildly alkaline pH. In addition, a chloride-free commercial hardening accelerator (SikaRapid®-1) was employed. SikaRapid®-1 has a density of ~1.17 kg/L and is formulated to accelerate the early dissolution and hydration kinetics of cement clinker phases (C_3S and C_3A), promoting early-age strength gain and rapid setting.

2.3. Mixing Proportions

The mix proportions were designed in accordance with standard mortar formulation principles to achieve structural-grade performance. Table 4 presents the batch weights used to prepare nine standard prisms with dimensions of 40 × 40 × 160 mm per mix batch in accordance with BS EN 196-1 [30]. The water-to-binder (w/b) ratio was maintained at a constant 0.50 across all mixes, and the binder-to-sand ratio was fixed at 1:2.55. As shown in Table 4, the dosage of the PCE water-reducing admixture varied from 15 g to 60 g across the mixes. This variation was systematically implemented to achieve a uniform target fresh mortar workability (flow table spread of 165 ± 10 mm measured according to BS EN

1015-3 [31]). Calcined clay has an irregular, porous morphology and a high specific surface area, which significantly increases water demand. Furthermore, the addition of sodium carbonate introduces dissolved Na^+ and CO_3^{2-} ions into the pore fluid, which alters the ionic strength, increases mix viscosity, and accelerates initial stiffening. Adjusting the superplasticizer dosage ensured proper compaction, consolidated density, and void-free specimens without introducing compaction-induced scatter or rheological bias into the mechanical strength results.

Table 4. Weight of mixing constituents in gm.

Mix	Cement	Sand	Water	Calcined Clay	Limestone	Gypsum	Sodium Carbonate	Accelerator	Water Admixture
CEM II-Control	1500	3825	750	0	0	0	0	0	15
LC3-Control	750	3825	750	450	225	75	0	0	15
C50-S1-D	750	3825	750	450	225	75	15	0	30
C50-S1-A3-D	750	3825	750	450	225	75	15	45	30
C50-S1.5-D	750	3825	750	450	225	75	22.5	0	30
C50-S1-A1.5-D	750	3825	750	450	225	75	15	22.5	30
C50-S1-W	750	3825	750	450	225	75	15	0	30
C50-A1.5-D	750	3825	750	450	225	75	0	22.5	15
C50-S2-D	750	3825	750	450	225	75	30	0	40
C50-S3-D	750	3825	750	450	225	75	45	0	60
C70-D	1050	3825	750	270	135	45	0	0	15

2.4. Specimen Preparation and Testing Set up

All mortar specimens were prepared, cast, cured, and tested at 3, 7, and 28 days in strict accordance with BS EN 196-1 [30]. The dry constituents were homogenized in a standard mortar mixer from the UK. Water and admixtures were added, and mixing proceeded according to the standard EN 196-1 [30] cycle. The fresh mortar was placed into three-gang steel moulds (40 × 40 × 160 mm) and compacted using a standard jolting apparatus (60 jolts per layer). Specimens were stored in the moulds in a curing room at 20 ± 2 °C and >90% relative humidity for 24 h, then demoulded and submerged in water storage tanks maintained at 20 ± 2 °C until their respective testing ages. For flexural performance, three standard prisms (40 × 40 × 160 mm, n = 3) were tested at each age using a three-point loading test rig mounted on an Instron universal testing machine (150 kN capacity) at a controlled loading rate of 50 ± 10 N/s (corresponding to a displacement rate of ~1 mm/min), with a support span L = 100 mm, as illustrated in Figure 1. The flexural strength (Rf, in MPa) was calculated from the peak flexural failure load (Ff, in N) using the standard EN 196-1 [30] equation: $Rf = (1.5 \cdot Ff \cdot L)/b^3$, where b = d = 40 mm. Both the recorded peak flexural load (kN) and calculated flexural strength (MPa) are reported.

Figure 1. Flexure strength test setup.

Flexural strength was evaluated on three standard 40 × 40 × 160 mm mortar prisms per testing age (9 prisms total per mix). Following flexure testing, compressive strength was evaluated on the resulting prism halves (n = 6 tested specimens per testing age, totaling 18 halves per mix across 3, 7, and 28 days) in accordance with BS EN 196-1 [30]. The test was performed using standard 40 × 40 mm auxiliary compression platens (loading contact area of 1600 mm^2) on the same Instron testing machine at a constant loading rate of 2400 ± 200 N/s. The compressive strength was determined as the maximum failure load divided by the cross-sectional area (1600 mm^2). Experimental results are reported as the mean value ± standard deviation (SD). All compressive and flexural strength measurements exhibited low experimental dispersion, with coefficients of variation (CV) consistently below 5.5% and 6.8%, respectively, meeting the repeatability criteria of BS EN 196-1 [30].

To elucidate the hydration mechanisms and phase assemblage responsible for the observed mechanical strength development, Fourier Transform Infrared (FTIR) spectroscopy was performed on selected representative mixes at 28 days of curing. Six mixes were strategically chosen for FTIR analysis based on clear selection criteria: CEM II-Control (standard 100% cement reference), LC3-Control (unactivated baseline 50% cement system), C70-D (to isolate the effect of clinker content at 70% cement), C50-S2-D (to evaluate optimal 2% sodium carbonate activation), C50-A1.5-D (to assess chemical acceleration alone), and C50-S1-A1.5-D (to investigate synergistic/combined activation). FTIR measurements were carried out using a PerkinElmer Spectrum from the UK, Two FTIR spectrometer equipped with an Attenuated Total Reflectance (ATR) module featuring a single-reflection diamond crystal. Mortar fragments were carefully sampled from the core of the crushed prisms, gently ground with an agate mortar and pestle to pass a 75 µm sieve, and dried in a vacuum oven at a controlled mild temperature of 40 °C for 24 h. This mild drying protocol was chosen specifically to remove free evaporable capillary water while strictly preventing the thermal dehydration and decomposition of temperature-sensitive hydration phases, such as ettringite, carboaluminates, and C-S-H gel [32,33]. FTIR spectra were collected in absorbance mode across the wavenumber range of 4000 to 600 cm^{-1} at a spectral resolution of 4 cm^{-1}, averaging 32 co-added scans per sample with automated background subtraction against the clean diamond crystal.

3. Test Results and Discussion

The results are discussed with emphasis on distinguishing early-age activation mechanisms from long-term hydration effects in low-clinker LC3 systems. Particular attention is given to differences between compressive and flexural responses, as flexural behavior is more sensitive to microstructural homogeneity, crack initiation, and interfacial bonding. A comprehensive summary of all compressive and flexural strength results (Mean ± SD) across 3, 7, and 28 days of curing is presented in Table 5.

Table 5. Compressive and flexural strength results (Mean ± SD) of mortar mixes at 3, 7, and 28 days.

Mix	Compressive Strength (MPa)			Flexural Strength (MPa)		
	3-Day	7-Day	28-Day	3-Day	7-Day	28-Day
CEM II-Control	12.3 ± 0.5	15.8 ± 0.6	21.4 ± 0.8	4.57 ± 0.19	6.68 ± 0.26	6.09 ± 0.28
LC3-Control	3.6 ± 0.2	6.8 ± 0.3	18.2 ± 0.7	1.52 ± 0.09	2.46 ± 0.12	5.86 ± 0.23
C50-S1-D	4.1 ± 0.2	6.8 ± 0.3	18.9 ± 0.8	1.69 ± 0.09	2.58 ± 0.12	5.86 ± 0.23
C50-S1-A3-D	4.2 ± 0.2	8.2 ± 0.4	18.5 ± 0.7	1.76 ± 0.09	2.91 ± 0.12	5.91 ± 0.23
C50-S1.5-D	4.2 ± 0.2	8.3 ± 0.4	20.1 ± 0.8	1.78 ± 0.09	2.81 ± 0.12	6.33 ± 0.26
C50-S1-A1.5-D	4.5 ± 0.2	9.4 ± 0.4	19.0 ± 0.7	1.99 ± 0.12	3.30 ± 0.14	6.09 ± 0.23
C50-S1-W	3.6 ± 0.2	5.5 ± 0.3	18.0 ± 0.7	1.41 ± 0.07	2.23 ± 0.09	6.21 ± 0.26
C50-A1.5-D	3.6 ± 0.2	6.6 ± 0.3	17.8 ± 0.7	1.59 ± 0.09	2.86 ± 0.12	5.74 ± 0.23
C50-S2-D	4.3 ± 0.2	8.8 ± 0.4	22.2 ± 0.9	1.88 ± 0.09	3.00 ± 0.14	6.68 ± 0.26
C50-S3-D	4.4 ± 0.2	9.1 ± 0.4	22.5 ± 0.9	1.83 ± 0.09	2.93 ± 0.12	6.68 ± 0.26
C70-D	5.7 ± 0.3	9.9 ± 0.4	19.6 ± 0.8	1.99 ± 0.12	3.28 ± 0.14	6.21 ± 0.26

3.1. Effect of Cement Content

The influence of cement and clinker content on the compressive strength of LC3 mortars is illustrated in Figure 2 and summarized in Table 5. A substantial reduction in early-age strength was observed when the cement content was reduced from 100% (CEM II-Control, clinker content ~85.0%) to 50% (LC3-Control, clinker content ~42.5%). At 3 days, the LC3-Control mix achieved a compressive strength of 3.6 MPa, corresponding to approximately 29% of the CEM II-Control reference strength (12.3 MPa). Furthermore, the 7- and 28-day compressive strengths of LC3-Control reached 6.8 MPa (43% of CEM II-Control) and 18.2 MPa (85% of CEM II-Control), respectively. This early-age strength deficit is directly attributed to the lower clinker fraction available for rapid alite (C_3S) hydration and the sluggish early dissolution kinetics of calcined clay at room temperature.

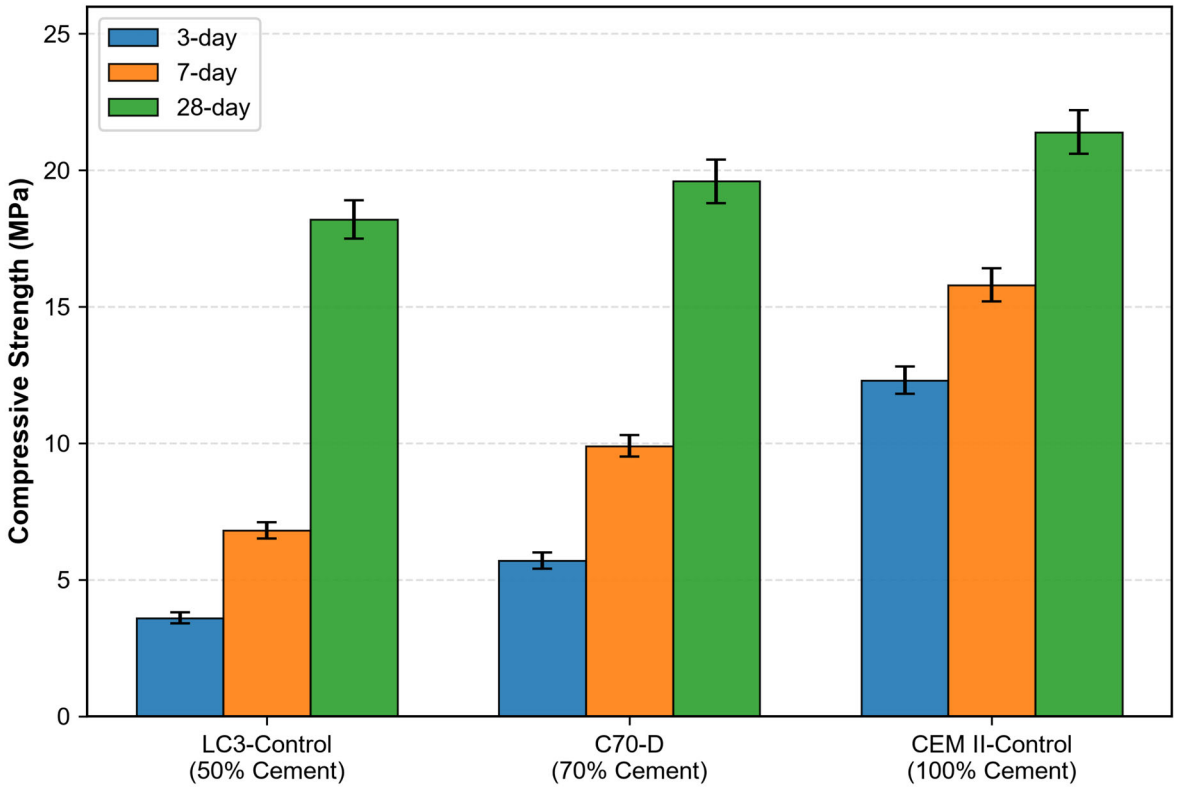

Figure 2. Effect of cement content on compressive strength.

Increasing the cement content to 70% (C70-D, clinker content ~59.5%) significantly improved compressive strength across all testing ages, reaching 5.7 MPa at 3 days (a 58% increase over LC3-Control), 9.9 MPa at 7 days (a 46% increase), and 19.6 MPa at 28 days (an 8% increase over LC3-Control and 92% of CEM II-Control, Table 5). The higher clinker fraction in C70-D provides greater quantities of C_3S and C_2S for early C-S-H nucleation, while the remaining 30% LC3 blend contributes sustained pozzolanic reactivity and carboaluminate precipitation at later ages. These findings confirm that low-clinker LC3 systems are primarily constrained by early-age hydration kinetics rather than long-term reaction potential.

In addition to compressive strength, cement content had a pronounced influence on the flexural strength of the mortars, as illustrated in Figure 3 and Table 5. Standard flexural strengths (Rf) were determined per BS EN 196-1 [30]. The LC3-Control mix exhibited flexural strengths of 1.52 MPa at 3 days, 2.46 MPa at 7 days, and 5.86 MPa at 28 days, achieving 33%, 37%, and 96% of the CEM II-Control flexural capacity at 3, 7, and 28 days, respectively (Table 5). Interestingly, for CEM II-Control, the flexural strengths at 7 days (6.68

MPa) and 28 days (6.09 MPa) showed very close values, with no further increase between 7 and 28 days. In cementitious mortars, flexural and tensile strengths are highly sensitive to microstructural flaw size, interface transition zone (ITZ) microcracking, and local tensile stress concentrations. In CEM II reference systems, rapid early hydration densifies the paste–aggregate ITZ within the first 7 days, causing the flexural failure threshold to stabilize early. Subsequent hydration from 7 to 28 days continues to refine gel micropores and boost compressive resistance, but has limited impact on the critical flaw size governing tensile/flexural fracture. In contrast, for the LC3-Control mix, flexural strength continued to increase substantially from 7 days (2.46 MPa) to 28 days (5.86 MPa, an increase of 138%), demonstrating that prolonged pozzolanic reaction and carboaluminate crystallization progressively bridge microcracks and refine the ITZ in low-clinker LC3 systems.

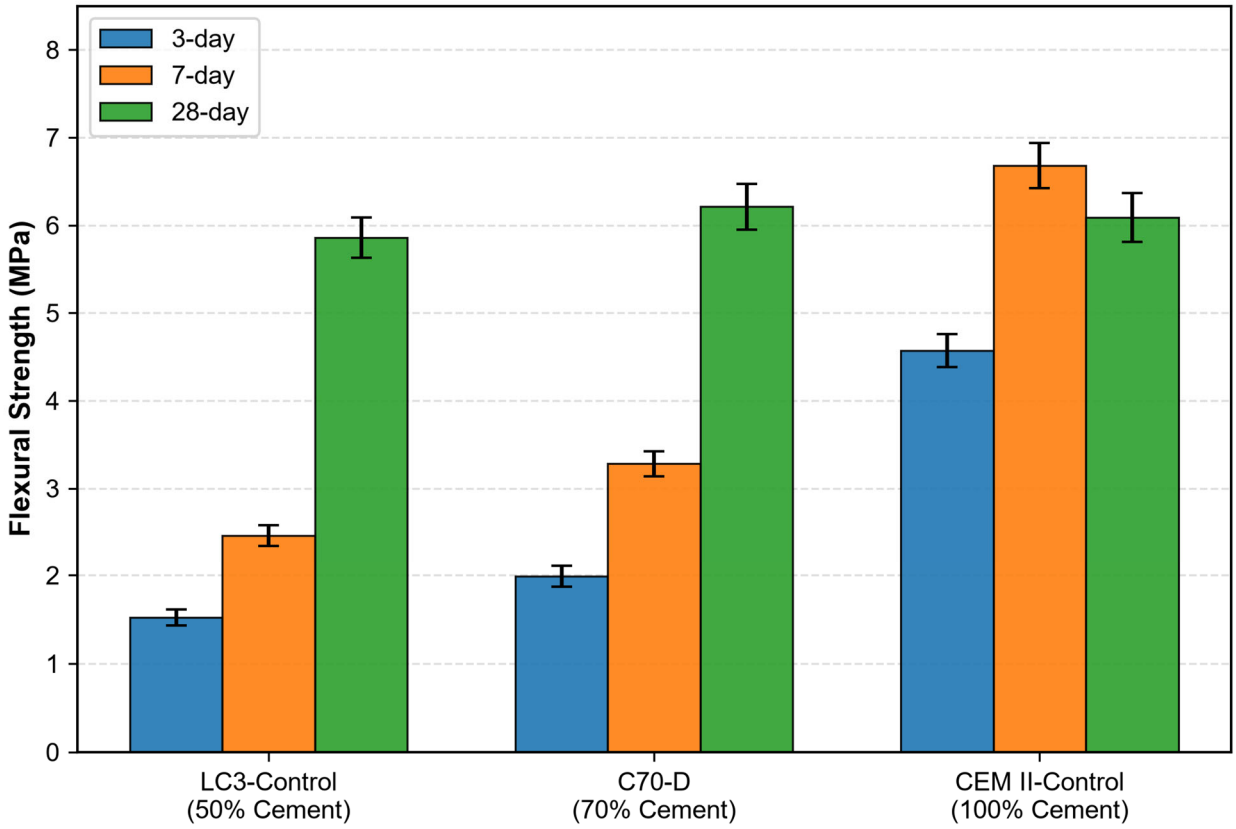

Figure 3. Effect of cement content on flexural strength.

Increasing the cement content to 70% (C70-D) resulted in flexural strengths of 1.99 MPa at 3 days, 3.28 MPa at 7 days, and 6.21 MPa at 28 days (Table 5). At 28 days, the flexural strength of LC3-Control (5.86 MPa) reached 94% of C70-D and 96% of CEM II-Control, confirming that low-clinker LC3 mortars achieve robust long-term crack resistance. These experimental observations align well with the findings of Zunino et al. [14] and Sun et al. [13], demonstrating that low-clinker LC3 mortars are structurally viable once early-age activation strategies are applied.

3.2. Effect of Sodium Carbonate

The effect of sodium carbonate (Na_2CO_3) dosage on the compressive strength of low-clinker LC3 mortars is shown in Figure 4 and Table 5. Incorporation of 1% sodium carbonate (C50-S1-D) increased the 3-day compressive strength from 3.6 MPa to 4.1 MPa (a 14% improvement), while the 7-day strength remained unchanged at 6.8 MPa. Increasing the dosage to 1.5% (C50-S1.5-D) enhanced the 7-day strength to 8.3 MPa (a 22% improve-

ment over LC3-Control). Increasing the dosage further to 2% (C50-S2-D) resulted in marked improvements across all testing ages: 3-day strength increased to 4.3 MPa (19% increase), 7-day strength reached 8.8 MPa (~29% increase over LC3-Control), and 28-day strength reached 22.2 MPa (~22% increase over LC3-Control and 4% higher than CEM II-Control, Table 5). When the sodium carbonate content was raised to 3% (C50-S3-D), the 7-day compressive strength reached 9.1 MPa, representing a 34% increase over LC3-Control. However, the incremental strength gain obtained when increasing the dosage from 2% to 3% was only 0.3 MPa (~3%), compared to the substantial 2.0 MPa (~29%) gain achieved from 0% to 2%. In addition, Table 4 shows that the 3% mix required 50% more superplasticizer (60 g vs. 40 g) to maintain target workability, due to accelerated stiffening. Therefore, based on a multi-criteria evaluation of strength enhancement efficiency, superplasticizer demand, workability retention, and chemical economy, 2% sodium carbonate is identified as the optimum dosage for low-clinker LC3 mortars. Similar activation trends were reported by Zhou et al. [12] and Dai et al. [34].

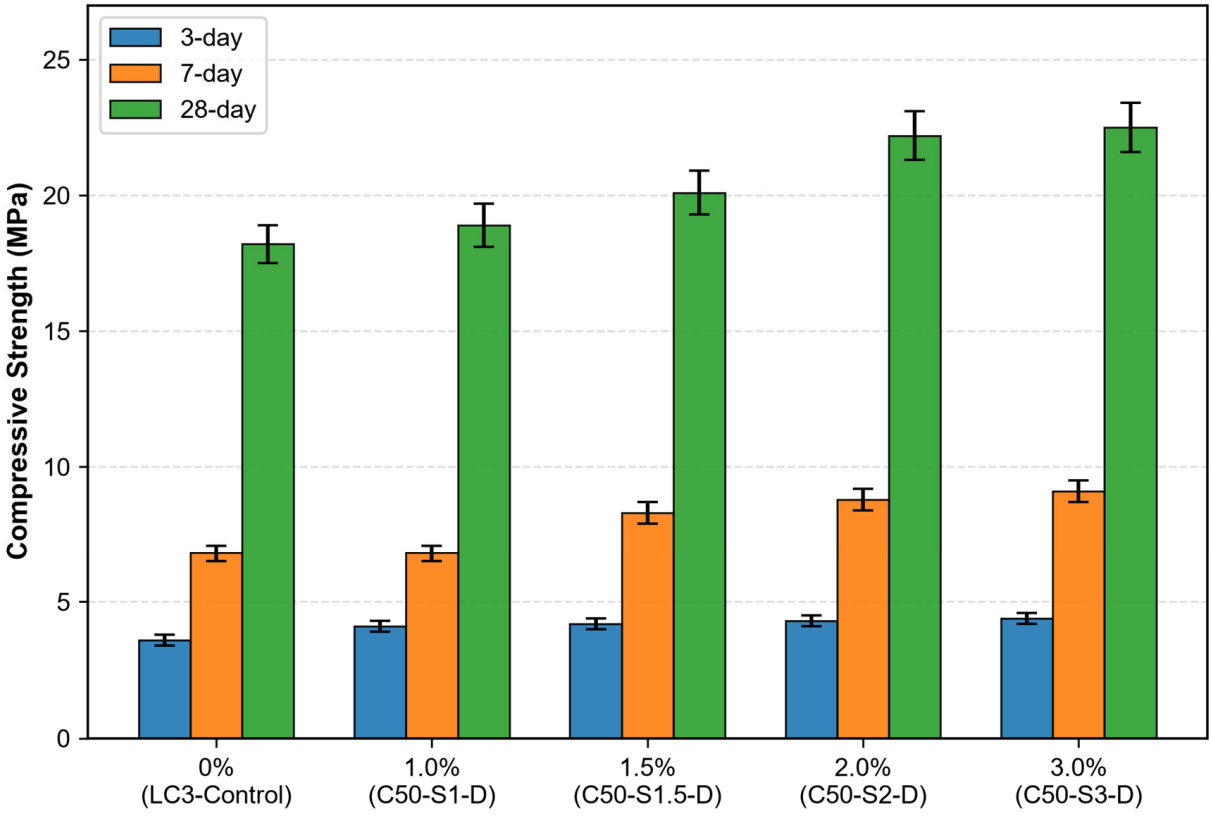

Figure 4. Effect of sodium carbonate percentage on compressive strength.

The influence of sodium carbonate on flexural performance is illustrated in Figure 5 and Table 5. The addition of sodium carbonate produced noticeable improvements in flexural strength. The 2% and 3% mixes achieved 7-day flexural strengths of 3.00 MPa and 2.93 MPa, respectively, representing a 22% and 19% improvement over LC3-Control (2.46 MPa) and reaching ~45% of CEM II-Control at 7 days. At 28 days, both the 2% and 3% mixes achieved flexural strengths of 6.68 MPa (Table 5), exceeding LC3-Control (5.86 MPa) by 14% and matching or exceeding the 28-day performance of CEM II-Control (6.09 MPa). The enhanced flexural strength is attributed to accelerated dissolution of alumina from metakaolin and the precipitation of carboaluminate phases, which densify the paste matrix and reinforce aggregate bond interfaces.

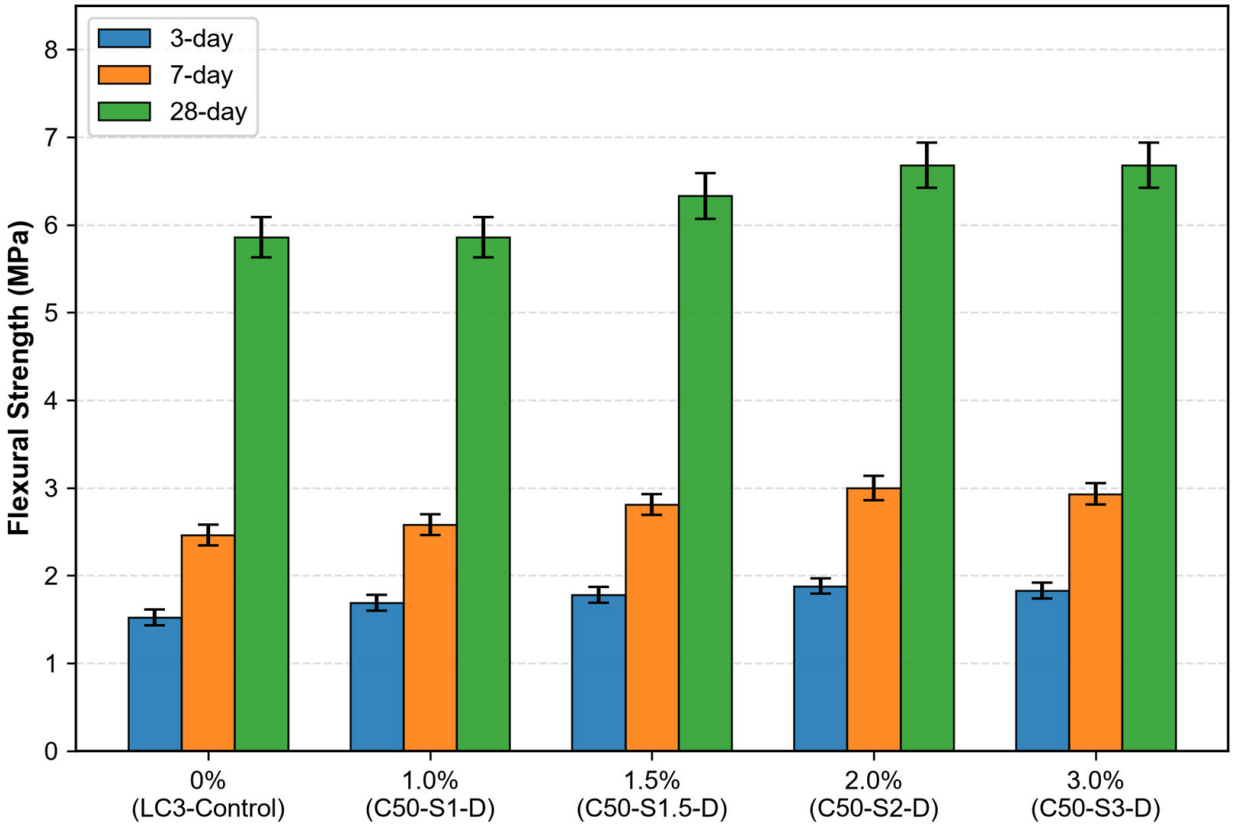

Figure 5. Effect of sodium carbonate percentage on flexural strength.

3.3. Effect of Accelerator

The influence of the commercial chemical accelerator (SikaRapid®-1) on compressive strength is presented in Figure 6 and Table 5. When used alone at 1.5% dosage (C50-A1.5-D), the accelerator provided only marginal effects on compressive strength, yielding 3.6 MPa at 3 days and 6.6 MPa at 7 days (comparable to LC3-Control). However, when 1.5% accelerator was combined with 1% sodium carbonate (C50-S1-A1.5-D), a pronounced synergistic activation effect was observed. The 7-day compressive strength increased significantly to 9.4 MPa, representing a 38% increase over LC3-Control and achieving ~59% of CEM II-Control. Furthermore, the 28-day compressive strength reached 19.0 MPa (104% of LC3-Control and 89% of CEM II-Control, Table 5). In contrast, increasing the accelerator dosage to 3% in combination with 1% sodium carbonate (C50-S1-A3-D) did not provide further improvement, yielding 8.2 MPa at 7 days. This demonstrates that a 1.5% chemical accelerator combined with 1% sodium carbonate provides an optimal balance for low-clinker LC3 activation.

The effect of the chemical accelerator on flexural performance is presented in Figure 7 and Table 5. When used alone at 1.5% (C50-A1.5-D), the accelerator improved 7-day flexural strength to 2.86 MPa, a 16% increase over LC3-Control (2.46 MPa). When combined with 1% sodium carbonate (C50-S1-A1.5-D), a noticeable improvement was observed: the 7-day flexural strength reached 3.30 MPa, representing a 34% increase relative to LC3-Control and achieving 49% of CEM II-Control. At 28 days, this combined mix achieved a flexural strength of 6.09 MPa, matching CEM II-Control (Table 5).

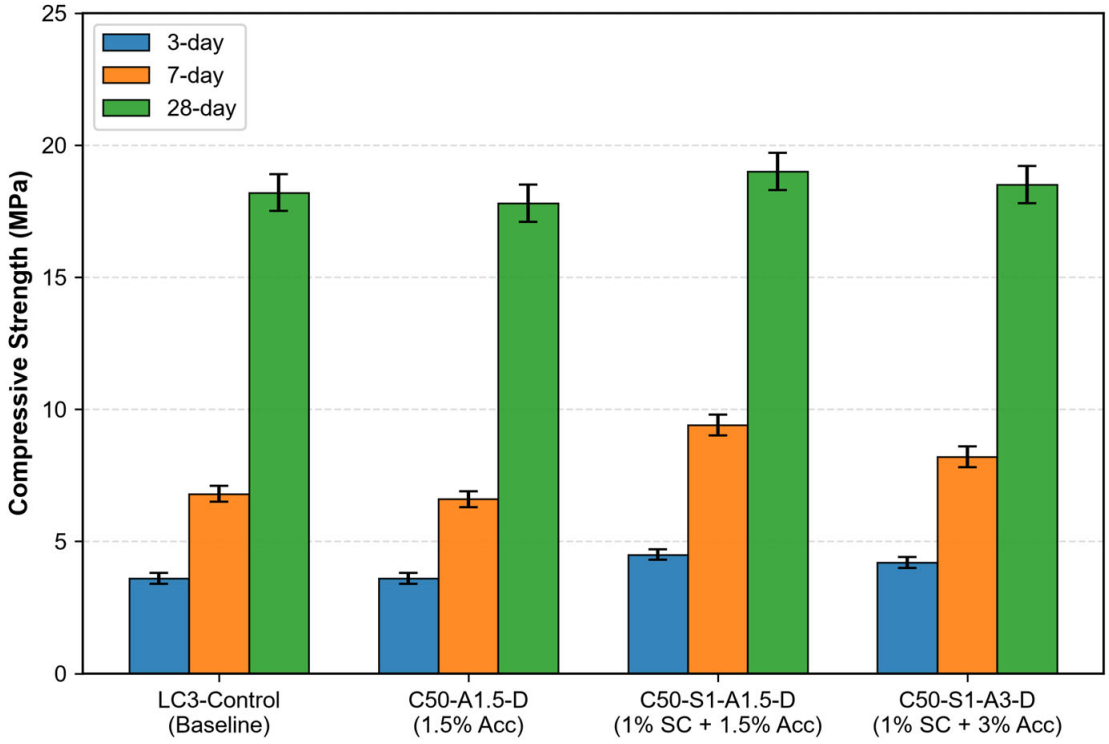

Figure 6. Effect of chemical accelerator percentage on compressive strength.

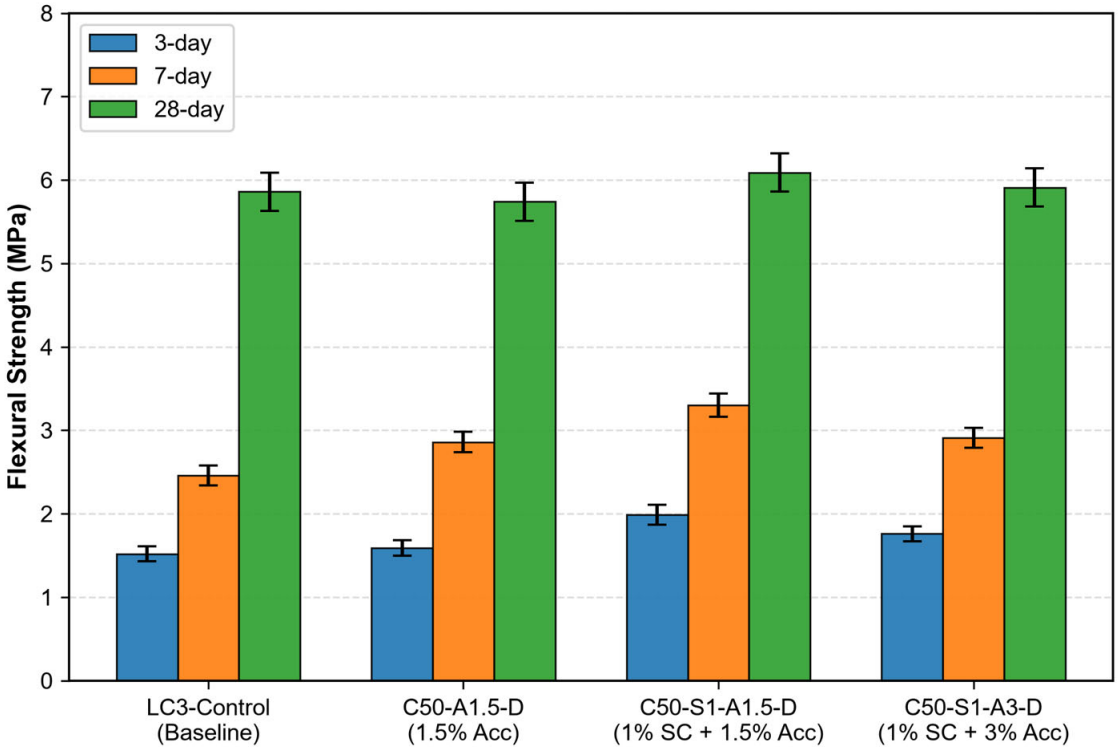

Figure 7. Effect of chemical accelerator percentage on flexural strength.

Increasing the accelerator dosage to 3% (C50-S1-A3-D) resulted in a reduction in 7-day flexural strength to 2.91 MPa (12% lower than C50-S1-A1.5-D at 3.30 MPa, Table 5). This behavior suggests that excessive accelerator dosage causes rapid localized setting and microstructural heterogeneity, which adversely affects tensile crack-bridging resistance. Unlike compressive strength, flexural performance is particularly sensitive to micro-cracking and matrix homogeneity. In the broader cement literature, chemical accelerators are known

to promote clinker dissolution [35,36]. However, systematically coupling sodium carbonate with a commercial accelerator in low-clinker (<50% clinker) LC3 systems represents a novel and practical activation pathway.

The mechanistic basis for this beneficial combined effect lies in complementary chemical reaction pathways: the chemical accelerator promotes rapid early dissolution of alite (C_3S) and tricalcium aluminate (C_3A), releasing abundant Ca^{2+} ions into the pore fluid during the first 24–48 h; simultaneously, sodium carbonate (Na_2CO_3) provides an immediate alkaline buffer and soluble CO_3^{2-} ions, which accelerate the dissolution of reactive alumina from calcined clay. The simultaneous presence of elevated Ca^{2+}, dissolved alumina, and carbonate ions facilitates early carboaluminate (hemicarboaluminate/monocarboaluminate) nucleation alongside rapid C-(A)-S-H gel growth. This dual-action mechanism effectively overcomes the slow early-age reaction kinetics characteristic of low-clinker LC3 systems, as detailed further in Section 3.5.

To contextualize the performance of the proposed activation strategy, the magnitude of early-age strength enhancement was systematically compared with various acceleration methods reported in the recent literature for LC3 systems. Existing technological approaches can be broadly classified into several categories [36]: (1) Nanomaterials and reactive silica sources (e.g., nano-silica [11] and waste-derived silica minerals [9]), which achieve substantial 1–3 day strength gains of ~25–56% through explosive heterogeneous C-S-H nucleation and rapid pore refinement; however, their extreme cost, high water/superplasticizer demand, and agglomeration risks hinder practical job-site application. (2) Synthetic C-S-H seeds and bio-engineered fillers (e.g., C-S-H seeds [37] and biochar [38]), which provide direct growth templates to bypass the hydration induction barrier, though requiring specialized synthetic preparations. (3) Soluble alkali salts and inorganic activators (e.g., sodium carbonate [12], sodium silicate [34], and dry FGD ash [39]), which elevate pore solution alkalinity, accelerating alumina dissolution from calcined clay and promoting carboaluminate precipitation, typically yielding 15–30% early strength gains (consistent with the ~29% 7-day gain observed here for 2% Na_2CO_3). (4) Commercial chemical accelerators (nitrate/alkanolamine-based [35,36]), which accelerate clinker phase dissolution (C_3S/C_3A) but provide limited benefit when used alone in low-clinker LC3 (<50% clinker) due to the reduced clinker volume. In contrast to single-activator or high-cost nanomaterial approaches, the combined activation strategy in the present study (1% Na_2CO_3 + 1.5% commercial accelerator) achieves a +38% increase in 7-day compressive strength (from 6.8 to 9.4 MPa) and a +34% increase in flexural load in a low-clinker system (~42.5% clinker). This dual mechanism bridges both clinker acceleration (Ca^{2+} release) and metakaolin activation (alumina/carbonate reactivity) simultaneously, delivering a commercially scalable, safe, and cost-effective solution for structural low-clinker LC3 applications.

3.4. Effect of Mixing Method

The effect of the mixing method on the mechanical performance of sodium carbonate-activated LC3 mortars was investigated by comparing dry mixing (D) and wet mixing (W) protocols for mix C50-S1 (50% cement, 1% Na_2CO_3). In the dry mixing protocol, sodium carbonate powder was blended uniformly with the dry binder constituents before water addition. In the wet mixing protocol, sodium carbonate was completely dissolved in the mixing water prior to contact with the solids.

The results shown in Figures 8 and 9, and Table 5 demonstrate that the mixing method has a noticeable influence on early-age strength development. At early ages, the wet-mixed mortar (C50-S1-W) exhibited lower compressive strength by 12% at 3 days (3.6 MPa vs. 4.1 MPa) and by 19% at 7 days (5.5 MPa vs. 6.8 MPa) compared to the dry-mixed mortar

(C50-S1-D). Similarly, 7-day flexural strength was lower in the wet-mixed mortar (2.23 MPa vs. 2.58 MPa, Table 5). This early-age strength deficit in wet mixing is hypothesized to arise from instantaneous dissolution of sodium carbonate in the mixing water: when the highly concentrated alkaline carbonate solution contacts anhydrous cement grains, it induces rapid localized flash precipitation of calcium carbonate and carboaluminate reaction rims directly around clinker particles. These dense initial reaction shells create diffusion barriers that hinder subsequent water ingress and retard the continued hydration of unreacted C_3S and C_3A cores, leading to microstructural heterogeneity and reduced early mechanical strength.

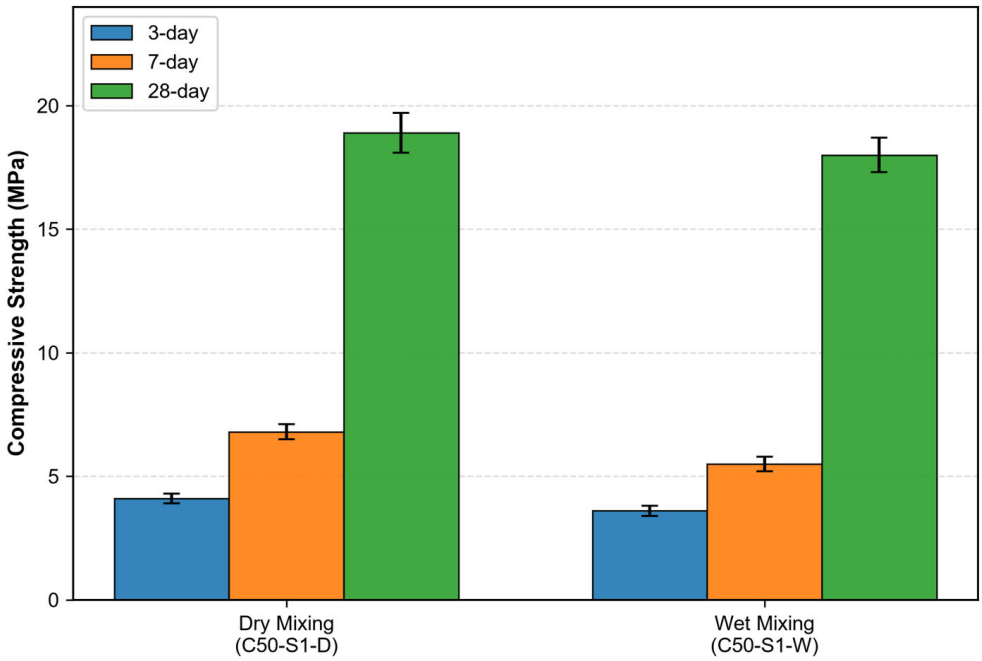

Figure 8. Effect of mixing method on compressive strength.

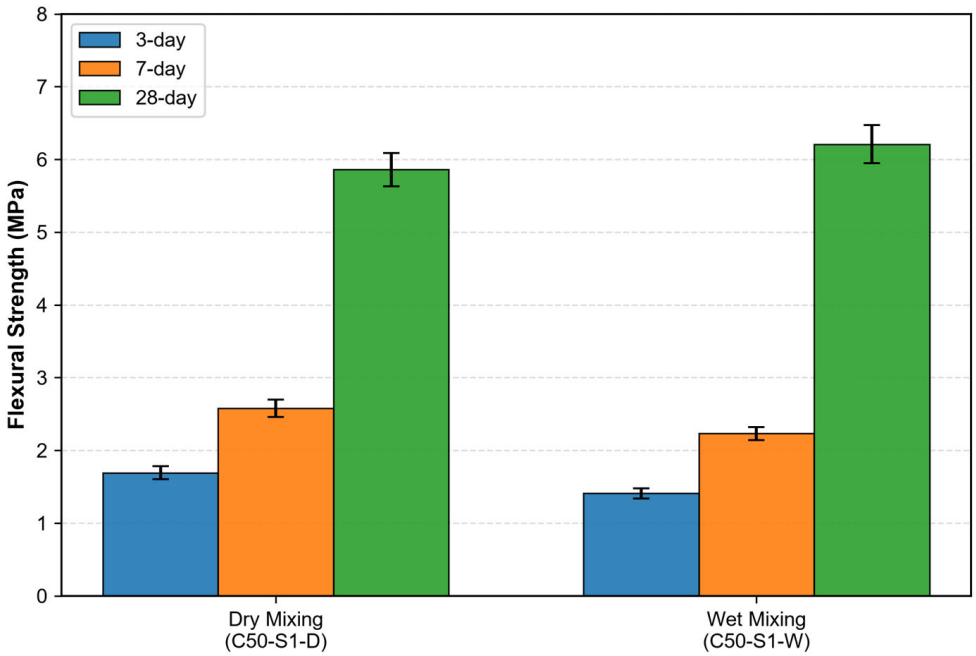

Figure 9. Effect of mixing method on flexural strength.

In contrast, the dry mixing method facilitates a more gradual, controlled dissolution of sodium carbonate as water is absorbed through the pore network. This controlled release avoids localized supersaturation, promoting uniform spatial nucleation of C-(A)-S-H and

carboaluminates throughout the bulk matrix, resulting in superior early strength and higher matrix homogeneity.

At 28 days, the wet-mixed mortar exhibited a compressive strength of 18.0 MPa (comparable to dry-mixed C50-S1-D at 18.9 MPa) and a slightly higher flexural strength (6.21 MPa vs. 5.86 MPa, Table 5). This suggests that the early diffusion barriers formed during wet mixing eventually break down under sustained hydration, allowing prolonged carbonate availability to support continued carboaluminate precipitation and microstructural densification at later ages. Nevertheless, for applications where early-age strength and rapid demoulding are critical, dry mixing is the recommended protocol.

Overall, the results demonstrate that the mixing method plays a critical role in controlling the effectiveness of sodium carbonate activation in low-clinker LC3 systems. Dry mixing is more beneficial for enhancing early-age strength, while wet mixing may offer advantages in long-term strength development. These findings highlight the importance of mixing procedures when implementing chemical activation strategies in practical LC3 applications and suggest that optimized mixing protocols should be carefully considered to balance early and long-term performance. It should be emphasized that while these dissolution and diffusion-barrier mechanisms are supported by established cement chemistry principles and literature [12,34], further experimental verification through early-age setting-time measurements, isothermal calorimetry, and in-situ microstructural characterization is recommended for future research to directly capture the initial dissolution–precipitation sequence.

The slightly higher long-term flexural performance observed for the wet-mixed specimens may be attributed to improved ion dispersion and sustained carboaluminate formation, which enhances crack-bridging capacity and stress redistribution under bending, even though early-age strength is compromised.

3.5. FTIR Analysis and Hydration Mechanisms

Fourier Transform Infrared Spectroscopy (FTIR) was conducted on the six selected mixes at 28 days to elucidate the hydration products and phase assemblages associated with the mechanical performance trends. Figure 10 presents the baseline-corrected FTIR spectra for mixes CEM II-Control, LC3-Control, C50-S2-D, C50-S1-A1.5-D, C50-A1.5-D, and C70-D. To facilitate a comprehensive mechanistic understanding, the proposed activation pathways and hydration mechanisms are illustrated schematically in Figure 11.

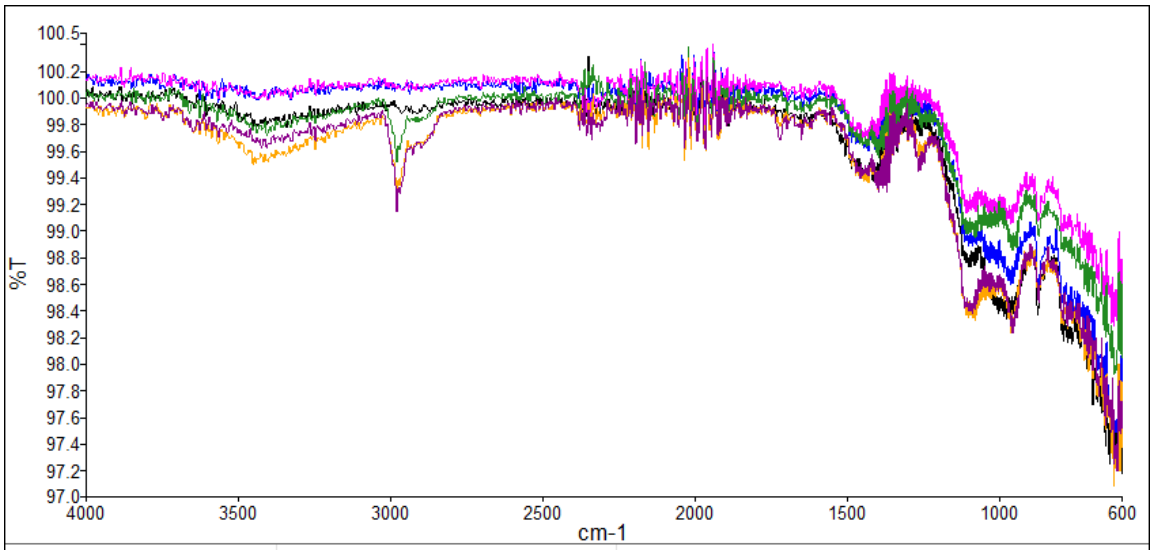

Figure 10. FTIR spectra of investigated mortar mixes at 28 days of curing: Black for CEM II-Control, Blue for LC3-Control, Orange for C50-S2-D, Magenta for C50-S1-A1.5-D, Green for C50-A1.5-D, and Purple for C70-D.

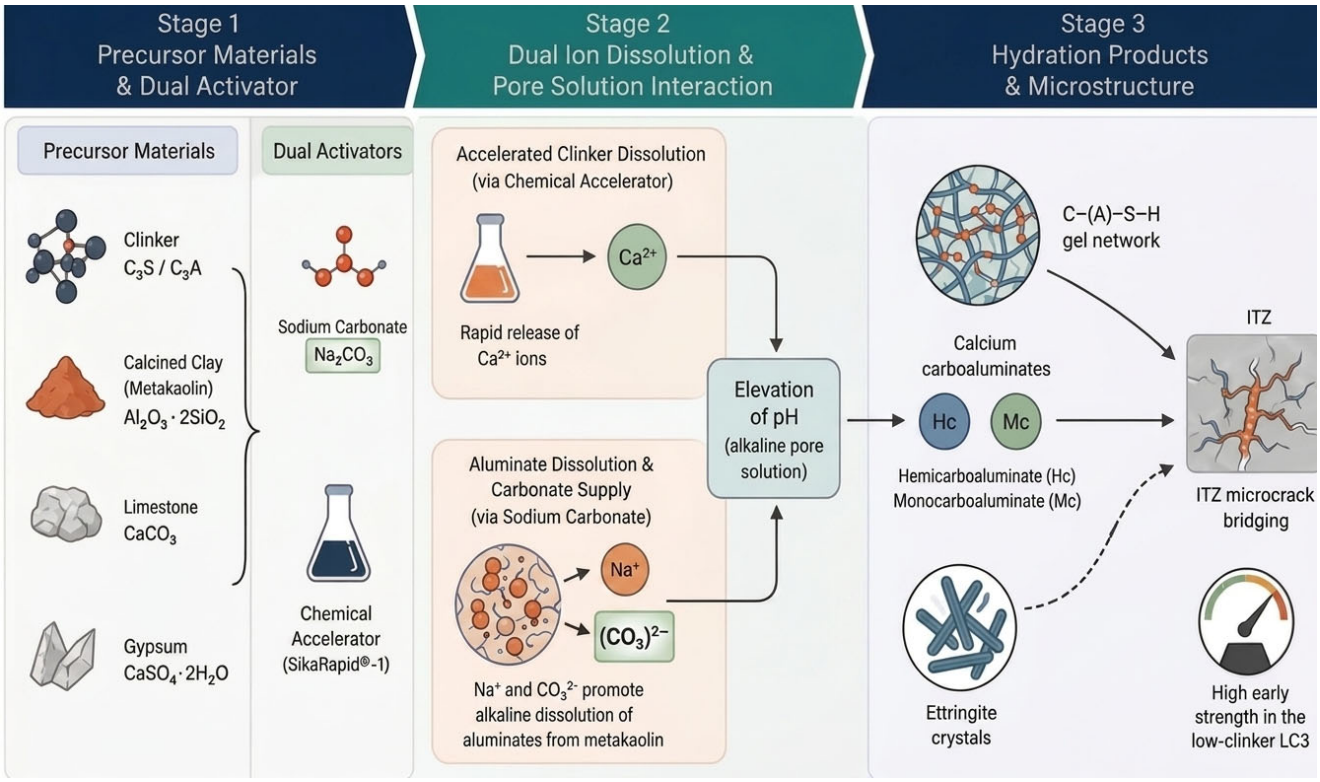

Figure 11. Schematic diagram of the proposed synergistic activation mechanism and hydration pathways in low-clinker LC3 mortars activated with sodium carbonate and chemical accelerator.

The FTIR spectrum of the reference mix (CEM II-Control) exhibits characteristic vibrational bands typical of hydrated Portland cement. A sharp band at ~874 cm^{-1} is assigned to the out-of-plane bending vibration (ν_2) of carbonate (CO_3^{2-}), while the prominent broad band at ~1425–1450 cm^{-1} corresponds to the asymmetric stretching (ν_3) of CO_3^{2-} in calcite/carbonated phases [32,33]. The prominent absorption band centered around 960–980 cm^{-1} corresponds to the Si–O tetrahedral stretching vibrations (ν_3 SiO_4) characteristic of calcium silicate hydrate (C-S-H) gel [32,40]. Peaks corresponding to ettringite (AFt) are detected at ~1115–1150 cm^{-1} (SO_4^{2-} stretching) and ~620 cm^{-1} [33]. Furthermore, the broad absorption band in the 3400–3600 cm^{-1} region is assigned to the O–H stretching vibrations (ν_1, ν_3 H_2O) of chemically bound and interlayer water in C-S-H gel, AFm/AFt phases, and calcium hydroxide (portlandite), accompanied by the H–O–H bending band at ~1640 cm^{-1} [32,41].

The unactivated low-clinker LC3-Control spectrum shows overall similarity to CEM II-Control, but with a noticeable reduction in the intensity of the primary Si–O stretching band at ~975 cm^{-1}, reflecting a lower quantity of early C-S-H gel formed due to 50% clinker replacement. In addition, the broad O–H region (3400–3600 cm^{-1}) displays lower overall absorption, consistent with the consumption of calcium hydroxide by the pozzolanic reaction of calcined clay to form additional C-(A)-S-H and carboaluminates [14,33]. The C70-D mix (70% cement) exhibits intermediate spectral intensity between CEM II-Control and LC3-Control, with stronger Si–O stretching absorption reflecting higher clinker availability and greater C-S-H formation, corroborating its higher compressive strength.

Incorporation of 2% sodium carbonate (C50-S2-D) produces marked changes in the FTIR spectrum. The intensity of the main Si–O stretching band at ~965 cm^{-1} increases significantly and shifts slightly to lower wavenumbers, indicating enhanced silicate polymerization and greater C-S-H/C-(A)-S-H gel precipitation. Furthermore, the carbonate asymmetric stretching band at ~1420–1460 cm^{-1} and the shoulder at ~1080 cm^{-1} become

more pronounced, which can be attributed to the enhanced formation of calcium carboaluminates (hemicarboaluminate and monocarboaluminate) and carbonated phases resulting from the reaction between dissolved carbonate ions, calcium hydroxide, and alumina released from calcined clay [12,14,34]. The broad O–H band around 3400–3600 cm^{-1} also shows increased intensity, reflecting the higher volume of hydrated reaction products containing structurally bound water.

For the mix containing accelerator alone (C50-A1.5-D), moderate enhancement in the O–H stretching region is observed, indicating accelerated early hydration of clinker phases (C_3S and C_3A). However, the Si–O stretching band at ~970 cm^{-1} remains less intense and broader than in the sodium carbonate-activated mixes. This is consistent with the hypothesis that the accelerator primarily promotes early clinker reaction and pore-solution consumption without providing the alkaline buffering or soluble carbonate ions needed to dissolve metakaolin and precipitate carboaluminates, explaining why the accelerator alone provided limited early-age strength gain.

Combining 1% sodium carbonate with 1.5% accelerator (C50-S1-A1.5-D) results in a distinct, intensified, and sharper Si–O stretching band at ~965 cm^{-1}, coupled with strong carbonate absorption bands at ~1425 cm^{-1} and ~874 cm^{-1}. This spectral signature reflects the combined acceleration of silicate hydration and enhanced carboaluminate precipitation. While 28-day FTIR spectra directly characterize the mature phase assemblage, these spectral features provide strong complementary evidence supporting the proposed synergistic activation mechanism (Figure 11), wherein accelerated clinker dissolution and alkaline aluminate activation operate simultaneously to generate a denser, highly interconnected hydrate matrix.

4. Summary and Conclusions

This study investigated the mechanical performance, early-age strength development, and hydration product evolution of sustainable, low-clinker limestone calcined clay cement (LC^3) mortars formulated with ~42.5% clinker. To overcome the pronounced early-age strength deficit inherent to low-clinker blended systems, chemical activation strategies involving sodium carbonate (Na_2CO_3), a commercial chemical accelerator, and their combined synergistic incorporation were systematically evaluated alongside dry versus wet mixing protocols. The experimental results demonstrate that while single-activator additions provide moderate early strength improvements, the combined activation of 1% Na_2CO_3 and 1.5% chemical accelerator triggers a synergistic acceleration mechanism, enhancing 7-day compressive and flexural strengths by 38% and 34%, respectively, while dry mixing ensures uniform dispersion and prevents localized diffusion barriers. ATR-FTIR spectroscopy corroborated that this dual-activation route promotes enhanced silicate polymerization and calcium carboaluminate precipitation without compromising long-term 28-day matrix integrity. Based on the experimental findings, the main conclusions of this study are summarized as follows:

- Reducing clinker content to ~42.5% in LC3-Control causes a major early-age deficit at 3 days (3.6 MPa compressive strength, 29% of CEM II-Control; 1.52 MPa flexural strength, 33% of CEM II-Control). By 28 days, compressive and flexural strengths recover to 85% and 96% of CEM II-Control (18.2 MPa and 5.86 MPa), respectively.
- An optimum sodium carbonate dosage of 2% increased 7-day compressive strength by ~29% (8.8 vs. 6.8 MPa) and flexural strength by 22% (3.00 vs. 2.46 MPa) over LC3-Control. Increasing dosage to 3% yielded only marginal extra strength (9.1 MPa) while increasing superplasticizer demand by 50%.
- The chemical accelerator alone at 1.5% had minimal effect on compressive strength (6.6 vs. 6.8 MPa at 7 days), but increased 7-day flexural strength by 16% (2.86 vs. 2.46 MPa).

- Combining 1% sodium carbonate with 1.5% accelerator produced a synergistic activation, boosting 7-day compressive strength by 38% (9.4 MPa) and flexural strength by 34% (3.30 MPa), outperforming either activator used alone.
- Dry mixing of sodium carbonate was substantially more effective than wet mixing for early-age performance, yielding 12% and 19% higher compressive strength at 3 and 7 days, respectively.
- ATR-FTIR spectra at 28 days confirmed enhanced Si–O stretching (C-S-H gel) and carbonate bands in activated mixes, supporting increased matrix densification and carboaluminate formation.
- Combined sodium carbonate and chemical accelerator activation offers an efficient, practical route to accelerate early strength gain and facilitate early demoulding in sustainable low-clinker LC3 mortars.

Limitations of the Study: Although this study provides valuable practical insights into the early-age activation of low-clinker LC3 mortars, several limitations should be noted. First, the experimental investigations were conducted on standard mortar prisms under controlled laboratory conditions (20 ± 2 °C); concrete-scale performance with coarse aggregates and field curing conditions were not evaluated. Second, mechanical testing was limited to 3, 7, and 28 days, and long-term durability properties (such as carbonation resistance, chloride ingress, and sulfate attack) were not assessed. Third, FTIR spectroscopy was performed only at 28 days, meaning that early-age reaction kinetics and phase evolution were inferred from mechanical responses and literature rather than in-situ early characterization (e.g., isothermal calorimetry or in-situ XRD).

Future Recommendations: Based on the findings and limitations of this study, future research should focus on: (1) investigating the long-term durability performance of sodium carbonate-activated low-clinker LC3 concrete under aggressive environmental exposures; (2) conducting isothermal calorimetry and in-situ quantitative XRD/TG analyses during the first 72 h of hydration to directly track early reaction kinetics; (3) evaluating the fresh-state rheology, setting times, and slump retention of concrete-scale mixtures; and (4) performing life-cycle cost and carbon footprint assessments for industrial precast applications.

Author Contributions: Conceptualization, A.S. and R.S.; methodology, X.Z.; investigation, K.T.K. and Y.A.A.-N.; writing—original draft preparation, A.S. and R.S.; writing—review and editing, X.Z. and K.T.K.; visualization, A.S.; supervision, X.Z. and R.S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article; further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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