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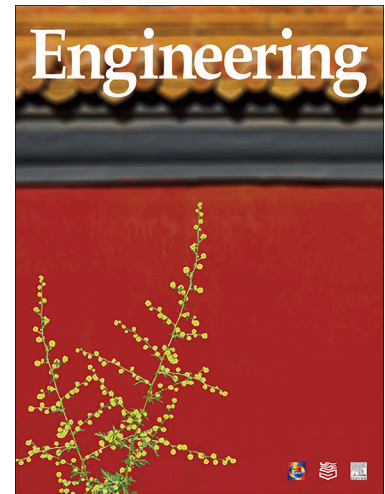
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Research

Sustainable and High-Performance Structural Materials—Article

Technological Approaches to Improve Early-Age Strength of Limestone Calcined Clay Cements

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Abstract

Limestone calcined clay cements (LC³) present a sustainable alternative to traditional Portland cement due to their potential to significantly reduce CO₂ emissions. However, LC³ cements often exhibit slower early-age strength development, which poses a challenge for their broader adoption. This study critically examines various technological approaches to enhance the early-age strength of LC³ cements, focusing on physical, chemical, and hybrid methods. The findings highlight the effectiveness of increased clinker and supplementary cementitious material (SCM) fineness, chemical acceleration using calcium silicate hydrate (C-S-H) seeds and

adn ntal impact of these strategies, evaluating their global warming potential (GWP) in relation to strength performance. The results demonstrate that while these methods effectively improve early-age strength, they may also inadvertently increase late-age strength, necessitating a balanced approach to optimize both performance and sustainability. This research provides a comprehensive framework for advancing LC³ adoption in high early-age demand applications.

1. Introduction

Portland cement (PC) is the binder used to produce concrete which is correspondingly the second most used substance by mankind after water [1]. Due to this enormous utilization, PC is currently responsible for about 8% of manmade CO₂ emissions [2]. Addressing the environmental footprint associated with the cement and concrete industry has become essential in the context of climate change mitigation, but simultaneously this endeavor has proven not trivial considering technological readiness of low-carbon solutions, material availability and performance concerns. Blended cements that incorporate mineral additions (supplementary cementitious materials, SCMs) in combination with cement clinker, enable substantial CO₂ reductions compared to traditional PC [1,3].

Blended cements or composite cements are nowadays more common than PC in many regions of the world. The availability of commonly used SCMs such as fly ash (by-product of coal power plant) and slag (by-product of iron production in blast furnaces) is limited and, especially in the case of fly ash [4], expected to rapidly decrease in the forthcoming decades [5]. In this regard, activated clay (for instance calcined clays) and limestone powder offer a breakthrough opportunity as they are available in virtually unlimited quantities, and can enable a significant worldwide reduction in PC content [1,3,6,7]. Limestone calcined clay cements (LC³) are a family of blended cements that incorporate limestone powder and calcined clays replacing up to 50% or more of clinker. At 50% clinker factor, in general they achieve similar strength to conventional PC from 3–7 d onwards [8,9]. Overall, LC³ cements can save 30%–40% of the CO₂ emissions (50% clinker factor) compared to PC [10]. Recent studies have shown the potential of reducing the clinker factor even further (down to 35%, 25%, and 15% by mass), highlighting the outstanding challenges in terms of strength development and extent of calcined clay reaction [11,12]. In the extreme case, PC clinker can be replaced completely by portlandite in the system with calcined clay and ground granulated blast furnace slag (GGBFS) together with calcium silicate hydrate (C-S-H) seeding [13].

The widespread adoption of blended cements as a primary approach to address the environmental imperatives within the concrete industry, coupled with a concerted focus on cement producers, underscores the imperative to minimize the global warming potential (GWP) of cement. While this metric serves as a valuable optimization tool for refining blend compositions and evaluating production process efficiency, it conceals significant details. Notably, it fails to capture crucial factors such as the actual volume of cement required to achieve desired concrete properties [14]. This is generally a multifaceted consideration that extends beyond cement type, encompassing parameters such as workability requirements (including the use of admixtures), durability specifications, aggregate grading, and intended application scenarios (including placement methods and construction pace constraints). Specifically, early-age performance (understood as rheological properties and development of strength up to 48 h) have emerged as an outstanding challenge for blended cement technologies.

Blended cements, including LC³, exhibit a slower strength gain rate at early-age (< 2 d) compared to PC, explained by the dominance of clinker hydration in the precipitation of hydrates and reduction of porosity over this period [6,15–17]. This may or may not be a problem depending on the intended use. However, it could limit the application of these cements for certain applications and impair the feasibility of further reducing the clinker factor (and consequently, the embodied carbon content), motivating the development of strategies to boost early-age performance.

There are various methods to improve the strength gain rate of mortar or concrete using blended cements. These approaches can be broadly categorized into two main categories: firstly, mixture design choices such

as i v/c
ratio [18]. Secondly, improving the hydration kinetics of the binder. The reaction rate of binders can be enhanced by increasing cement/filler/SCM fineness, curing temperature, or using chemical admixtures.

Recent advancements in enhancing the early strength development of highly substituted blended cements through chemical means involve the use of complexing agents like alkanolamines [19–21] or nanoparticles such as polymer-stabilized C-S-H seeds [12,22,23], or nano-Portlandite [24]. These chemical additives have been found to be able to increase the hydration kinetics of the binder, thereby accelerating the reaction rate and leading to a faster strength development. Most of these approaches have their specific limitations (effects on rheology, compatibility with other admixtures, cost, and availability) which in general hinder their extensive application.

This paper offers a critical comparison of diverse strategies aimed at enhancing the early-age strength of LC³-type cements, characterized by substantial clinker replacement (> 50%), through physical (grinding to increase surface area), chemical (admixtures), or hybrid (surface area + admixtures) approaches. Emphasizing the initial performance until 48 h of hydration, it scrutinizes the environmental impact of each strategy. Additionally, the paper calculates the technological efficiency of these methods, gauged by specific GWP or the GWP-to-strength ratio, thus facilitating a thorough comparison of the proposed solutions.

2. Materials and methodological approach

Two CEM I 42.5N (cem_b and cem_e) and one CEM I 52.5R (cem_b2) cement were used in the testing. Here, “CEM I” represents common Portland cement. The numbers “42.5” and “52.5” indicate the standard values of the compressive strength (in MPa) of the cement at the specified age (usually 28 d). “N” stands for “normal”, which means that the properties of this cement meet the standard’s conventional requirements, and its early strength development is relatively moderate. “R” represents “rapid-hardening,” indicating that this cement can achieve a higher strength in a relatively short period. “cem” represents cement. These three cements covered wide range of strength as is shown by the dashed line in Figs. 1 (a)–(c): low (cem_b), moderate (cem_e), and high strength (cem_b2). Two industrial grade calcined clays (CC_b and CC_e) were used. Here, CC represents calcined clay. Characteristics of these two calcined clays were given in Table 1. The strength data of the LC³ with cem_b and CC_b was previously published in Refs. [12,21]. LC³ with cem_e and CC_e data can be found in Ref. [11]. A commercial synthetic C-S-H (HyCon[®] S 7042 F; BASF Construction Additives GmbH, Germany) was used as the C-S-H seeding material. This powder product is an alkaline- and nitrate-free product containing C-S-H particles stabilized by polycarboxylates ether (PCE). This seeding product was always used together with a 0.1 wt% defoamer (Vinapor[®] DF 9010F; BASF Construction Additives GmbH, Germany). Melflux[®] 2500 L (BASF Construction Additives GmbH) liquid additive, a PCE based superplasticizer, with 45 wt% solid content was used as the dispersant.

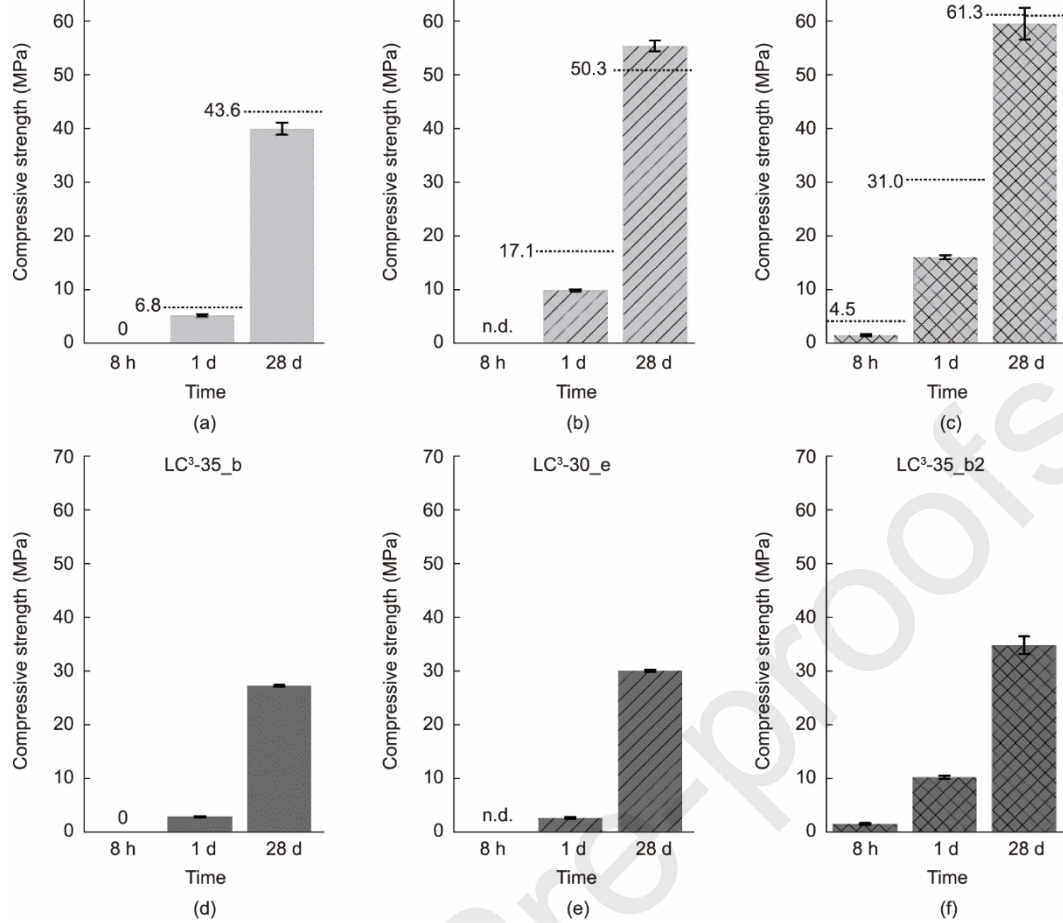


Fig. 1. Compressive strength of the LC³ cement with different amount of PC (expressed as wt% following LC³, e.g., 30, 35, and 50). (a, d) LC³ cement with CEM I 42.5N cem_b and CC_b; (b, e) LC³ cement made with cem_e CEM I 42.5N and CC_e; (c, f) LC³ cement made with cem_b2 CEM I 52.5R and CC_b. “0” label in the strength values refers to strength less than 0.3 MPa which is the detecting limit of the compressive strength machine, “n.d.” refers to not determined data points. Dashed lines with labelled strength value in the top row plots refer the strength of the neat PC reference.

Table 1

Characteristics of the calcined clay—mineral phase composition, chemical composition, physical properties, and American Society for Testing and Materials (ASTM) C1897-20 (R3) reactivity.

Characteristic of the calcined clay		CC_b	CC_e
Phase composition (%)	Quartz	1.5	7.5
	Calcite	—	0.9
	Lime	—	—
	Hematite	1.4	1.7
	Magnetite		1.2

	Mullite	9.6	6.9
	Anatase	2	3.7
	Illite	4.4	6.4
	Kaolinite	9.5	1.1
	Rutile	0.5	—
	Amorphous	71.1	70.6
Chemical composition (%)	SO ₃	0.07	0.04
	CaO	0.27	0.2
	K ₂ O	0.06	0.09
	Na ₂ O	0.2	0.26
	SiO ₂	48.26	49.74
	Fe ₂ O ₃	2.34	2.32
	Al ₂ O ₃	41.08	41.78
	TiO ₂	3.42	3.42
	MgO	0.13	0.11
	Loss on ignition (LOI)	2.37	1.85
Physical property	10% percentile diameter (d_{v10}) (μm)	0.73	1.21
	50% percentile diameter (d_{v50}) (μm)	5.55	8.44
	90% percentile diameter (d_{v90}) (μm)	68.56	44.69
	Specific surface area (SSA, $\text{m}^2 \cdot \text{g}^{-1}$)	12.2	9.64
	Density ($\text{g} \cdot \text{cm}^{-3}$)	2.65	2.66

Reactivity ($\text{J}\cdot\text{g}^{-1}\text{ SCM}$) according to ASTM C1897-20 (R3)	1 d	459.1	424.1
	3 d	597.3	528.9
	7 d	640	562.6

EN 196-1 standard mortar tests were used for the compressive strength. Samples for compressive strength testing for LC³ made with cem_b and cem_b2 were cast with one-time-use polystyrene molds with lids (according to German standard DIN 1164) and cured under water at 23 °C after demolding. For blended cement using cem_e, testing conditions defined by EN 196-1 are strictly followed.

A modified, miniaturized version of an L-box was used to analyze the flowability of mortar. The base size of the L-box chimney was 10 cm × 10 cm. One liter of mortar was filled into the L-box reservoir. Upon opening the closing lid, the mortar flowed into the base of the L-box. The flow speed was analyzed using a camera by observing the movement of the mortar front ledge.

The environmental impact of the mortar based on the “Cradle to Gate” GWP (in the unit of $\text{kg CO}_2\text{eq}\cdot\text{t}^{-1}$) were evaluated according to EN 15804. In the case of calcined clay, a long-term scenario with a GWP of 200 $\text{kg CO}_2\text{eq}\cdot\text{t}^{-1}$ was used for the main evaluation [1]. Performance based specific GWP (in the unit of $\text{kg CO}_2\text{eq}\cdot\text{MPa}^{-1}\cdot\text{t}^{-1}$ dry mortar) were used to consider the performance of the mortar while taking into consideration of the GWP simulations. GWP inventory is listed in

Table 2. The calculation of the specific GWP were described in Ref. [13].

Table 2

“Cradle-to-Gate” GWP of the raw materials and additives.

Material	GWP (A1–A3) $\text{kg CO}_2\text{eq}\cdot\text{t}^{-1}$ product	Source
Ordinary Portland cement (OPC, CEM I)	819	Assume 5% limestone in CEM I based on data from Ref. [1]
Calcined clay	200	Long-term and short-term scenario from Refs. [1,25]
GGBFS	67	Matthes et al. [26]
Portlandite	940	Laveglia et al. [27]
Anhydrite	92	Modelled with Simapro in Ref. [28]
Limestone powder (d_{v50} 15 μm)	35	Habert et al [29]

Dispersant: Melflux® 2500 L (liquid product with 45.1 wt% solid)	900	Cradle-to-gate product carbon footprint (PCF) of BASF as of Aug 2023 [13]
C-S-H seeding: HyCon® S 7042 F (powder product)	3200	PCF of BASF as of Aug 2023 [13]

3. Early-age strength development of LC³ cements

Undoubtedly, maximizing early-age strength development stands out as a paramount challenge in advancing the deployment of blended cements with a clinker factor of 50% or lower in real-world applications. While the industry conventionally relies on the 28 d strength as a benchmark for assessing concrete mixtures and structural design, the performance achieved during the initial day of hydration significantly influences the feasibility of various applications, dictating the pace of construction. Some standards, such as the European EN 197-1 standard for cements and the ASTM C595 standard for blended cements, prescribe requirements of two- and three-days strength respectively for most of the cement types they cover. In many application-orientated tests such as precast concrete and certain dry mortar applications, few hours and one-day strength are often required. As such, understanding and enhancing early-age strength development is crucial for expanding the utilization of blended cements and optimizing construction timelines.

Depending on the use intended and/or the technological approach for casting, the definition of what is *early-age* can vary significantly. Within the scope of this article, two different categories of *early-age* strength are defined based on typical applications and their inherent requirements for performance:

- **Very early-age** (≤ 12 h of hydration, equivalent approximately to induction, acceleration period up to the maximum of the Alite peak in LC³ [16,30]): Critical period for some application such as precast (8–12 h), fast drying (shotcrete); 8 h for construction pace to enable a three-shift work routine; bridges, pavement casting, and fast repair mortars (< 8 h).
- **(Normal) early-age** (1–3 d of hydration): Cement certification per standard requirements; ready mix concrete quality control/assurance (QC/QA) (approximately two days); formwork removal in conventional construction.

Fig. 1 shows the strength development of LC³ cements with 50% or lower clinker contents, with emphasis on early-age strength. As seen, the strength of LC³-50 is considerably lower than the PC reference at 8 h and one day. Within the time scope of very early-age and early-age strength development of LC³ cements, clinker hydration dominates the formation of hydration products and consequently, the development of mechanical properties [15,16,31]. The pozzolanic reaction of metakaolin in calcined clay, while not negligible during this period [22], mostly becomes significant from a strength development perspective after two or three days (depending on metakaolin content of calcined clay and sulfation of the system) of hydration when the precipitation of carboaluminates accelerates [16] and the formation of calcium aluminate silicate hydrate (C-(A)-S-H) due to calcined clay reaction. Carboaluminates precipitate in relatively large capillary pores and are effective to reduce porosity and increase strength [15]. However, precipitation of carboaluminates can only occur after ettringite precipitation stops, which in LC³ cements is determined by the sulfate content of the system [9,16].

Considering the relatively high reactivity of calcined clays compared to other SCMs [32], it has been hypothesized that availability of portlandite at early-age could impose a kinetic limitation to the reaction of metakaolin. This idea has been proven incorrect in several recent studies [11,12,15], where portlandite (except nano-portlandite seeds) has been shown to impose a limitation mostly at later ages (> 7 d) and only in systems with low-clinker contents (< 50 %). A recent study showed that the incorporation of an external source of portlandite has no effect on the development of mechanical properties at early-age in these low-clinker systems [11,12], but contributes mainly to the late strength after 28 d when portlandite become a limiting factor for further pozzolanic reaction. As such, it appears that the kinetics of the early age metakaolin reaction are driven by other factors (likely dissolution rate) rather than availability of a reactive calcium source. This can also be

As previously discussed, the (very) early-age strength development of LC³ cements depends mostly on the hydration extent (kinetics and overall amount) of the clinker fraction present in the blend. Consequently, boosting the reaction of clinker is the key to maximize the early-age strength of these cements. Several approaches such as additional grinding of the clinker fraction [33], chemical acceleration with alkalis [34,35], and the use of C-S-H seeds [12,36] have proven effective to accomplish this task with pros and cons that are specific to each technological approach.

However, the strategies employed to enhance early-age performance may inadvertently result in an undesired increase/decrease of later-age strength [12], which can be deemed unnecessary or even counterproductive (for example, increasing shrinkage, creep, and cracking). From a mechanistic standpoint, it appears improbable to effectively decouple these two aspects—enhancing early and late-age strength—if the focus of strategies used is circumscribed to the reaction of alite and subsequent precipitation of C-(A)-S-H, as is typically pursued in the strategies mentioned above. Concurrently, devising solutions that facilitate a balance between early and late-age strength enhancements becomes significant. Such solutions are instrumental in fostering the widespread adoption of low-carbon cements across various applications, while mitigating the risk of inadvertently increasing their carbon footprint through (unnecessary) overdesign.

4. Strategies to boost early-age strength development of LC³ cements.

4.1. Increase of the fineness of clinker and/or SCMs

A common approach to enhance the hydration of clinker is to rely in the so-called filler effect. The filler effect has an accelerating mechanism on the C-S-H reaction due to higher shear forces (friction between particles during mixing), and a seeding effect on surfaces where the surfaces of the SCMs (inert or pozzolanic) act as additional sites for heterogeneous nucleation of hydrates, increasing the rate of reaction during the first hours of hydration [37,38]. As previously mentioned, additional grinding of clinker is another effective pathway to achieve a faster reaction rate at early-age [39].

Fig. 2 underscores the critical role of cement fineness in the early-age strength development of LC³-50 cements. At 8 h, the cement produced with 52.5R (cem_b2, 52.5R; Blaine 5201 cm²·g⁻¹, d_{v50} 7.2 μm) exhibits greater compressive strength relative to the cement produced with 42.5N (cem_b, 42.5 N; Blaine 3075 cm²·g⁻¹, d_{v50} 19.2 μm). At one day, this trend persists, with the 52.5R cement continuing to show enhanced strength development. The finer particle size of the 52.5R cement contributes to its increased reactivity and hydration rate, resulting in improved early-age strength performance. It is noteworthy that preparing the mortar with finer cement necessitates a higher dispersant dosage to achieve comparable workability to that of the coarser cement (42.5N).

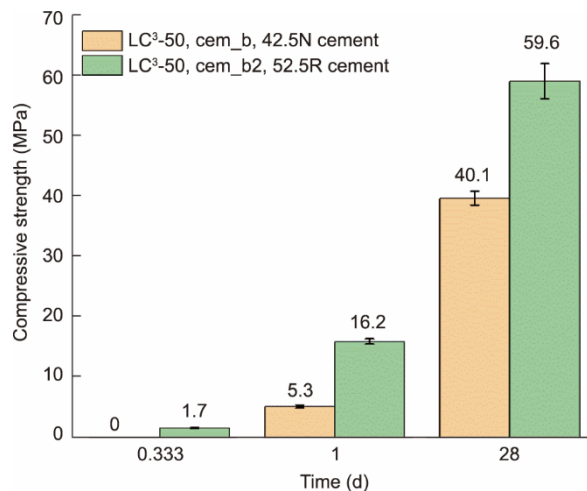


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 strength class (42.5N vs 52.5R). 8 h strength, one-day strength and 28 d strength are shown. “0” label in the strength values refers to strength less than 0.3 MPa which is the detecting limit of the compressive strength machine, 0.333 d converts to 8 h. Water-to-binder (w/b) ratio is 0.5 according to EN 196-1.

However, this approach is restricted to industrial setups where separate grinding of PC, limestone, and clay is conducted [33], given the challenges associated with the different grindabilities of LC^3 constituents [20,40,41]. It has been observed that co-grinding of LC^3 constituents can lead to overground limestone and clay (workability issue) and coarse clinker (reactivity issue) if adequate grinding control measures are not taken [33]. In the case of calcined clay, surface area is poorly correlated with the particle size as most of it comes from the inter-layer space (microstructural stacking) in metakaolin particles [42,43].

Thus, using finer limestone appears as an interesting approach to enhance the early hydration of LC^3 through a smaller particle size (i.e., higher surface area). Fig. 3 shows the compressive strength of LC^3 -50 mortars prepared with three different limestone sizes (coarse: $1.13 \text{ m}^2 \cdot \text{g}^{-1}$, normal: $3.60 \text{ m}^2 \cdot \text{g}^{-1}$, fine: $8.96 \text{ m}^2 \cdot \text{g}^{-1}$). The finer the limestone, the higher the overall strength at all ages for the same calcined clay grade (metakaolin content). At 24 h, an increase of strength of about 20% is observed when comparing the coarsest limestone with the finest one. Cost aside, a main drawback of this approach is the negative effect of finer limestone in the overall workability of the system which is already challenged with the presence of calcined clay. This increase in water demand may require the use of higher dosages of superplasticizer, which in turn increase cost and may also induce retardation of the alite reaction [44], offsetting part of all of the improvement originally obtained.

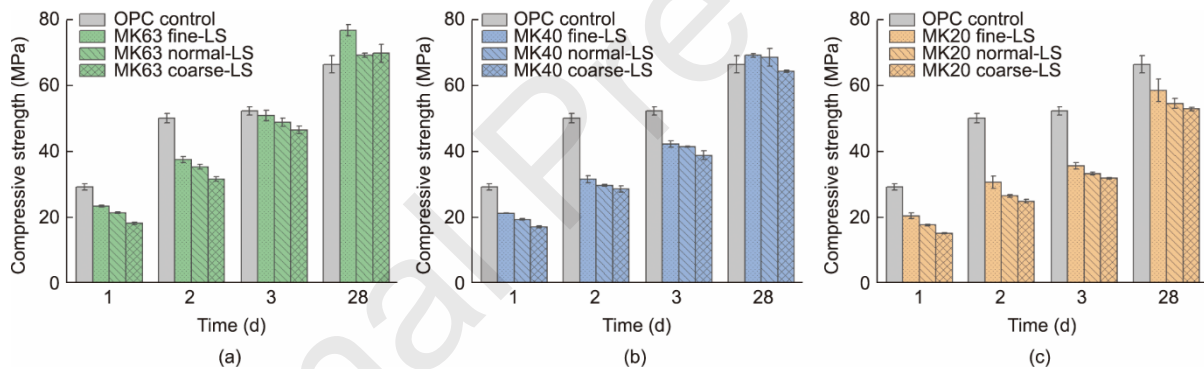


Fig. 3. Compressive strength of LC^3 -50 (30% CC, 15% limestone) mortars with different clay qualities (metakaolin content: 63%, 40%, and 20%, labelled as MK63, MK40, and MK20, respectively) incorporating coarse ($SSA 1.13 \text{ m}^2 \cdot \text{g}^{-1}$, labelled as coarse-LS), normal ($SSA 3.60 \text{ m}^2 \cdot \text{g}^{-1}$, labelled as normal-LS), or fine ($SSA 8.96 \text{ m}^2 \cdot \text{g}^{-1}$, labelled as fine-LS) limestone. LS: limestone; MK: metakaolin. Reproduced with data from Ref. [6].

4.2. Reduce the water-to-cement (w/c) or water-to-binder (w/b) ratio

Reducing the w/c ratio is the most effective way to increase the strength of construction materials [45]. This reduction influences (reduces) the porosity of the final hydrated cement paste, resulting in higher strength. Fig. 4 illustrates the impact of a reduction in w/b on the strength profile of a mortar. Decreasing the w/b from 0.5 to 0.38 leads to a strength enhancement of more than 100% and more than 60% at 8 h and one day, respectively. The combination of reducing w/b ratio and using C-S-H seeds showed significant enhancement of the strength across all the tested ages. In some cases, this final strength increase may be unnecessary and exceed the building's needs.

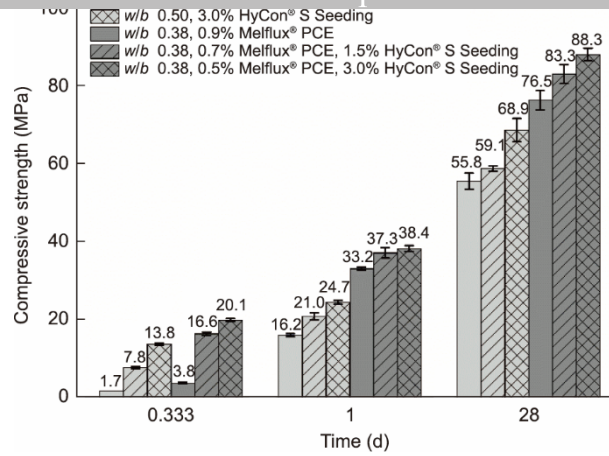


Fig. 4. Mortar compressive strength of LC³-50 cement made with CEM I 52.5R with different w/b ratios (0.38 and 0.5, Melflux[®] dispersant amount was adjusted for a proper spread of the mortar), 0.333 d converts to 8 h.

Conversely, reducing water content is linked to a decrease in workability, especially in highly blended cements that already exhibit poor rheology. A dispersant can be utilized to partially offset the reduction in workability by decreasing the yield stress of the paste. Nonetheless, lowering water content also results in increased plastic viscosity, which craftsmen often describe as making the concrete “sticky” or “heavy,” leading to poor flowability. A significantly higher amount of dispersant is required for casting the mortar sample at w/b 0.38 compared to those at w/b 0.5 (Fig. 4).

To illustrate the effect of w/c ratio on the rheology, a LC³-50 made with 50% cem_b2, 30% metakaolin, 15% limestone powder, and 5% anhydrite was used. The mortar is a special mortar for rheology test with sand/cement ratio of 2.2.

The results presented in Table 3 show that lowering the w/b ratio boosts compressive strength. When the w/b ratio is reduced from 0.6 to 0.5, there is a notable increase in compressive strength across all tested periods (1, 7, and 28 d). Increasing the percentage of Melflux[®] dispersant from 0.18% to 0.25% is essential to maintain workability with the decreased w/b ratio. Fig. 5 illustrates how reducing the w/b ratio affects mortar flowability based on L-box flowability test. Although workability (Table 3) can be modified by using more dispersant to achieve similar flow/slump values (which correspond to yield stress), the flow speed (related to plastic viscosity) in an L-box decreases significantly. Poor flowability can lead to insufficient mold filling, which may cause serious defects when casting highly reinforced structures.

Table 3

Special mortar strength of the LC³-50 made with metakaolin, comparing two w/b ratios.

Melflux [®] dispersant (% by weight of binder)	w/b	Hägermann cone flow (cm)	Compressive strength (MPa)		
			1 d	7 d	28 d
0.18	0.6	22.5	7.9	43.7	51.5
0.25	0.5	23.3	13.4	60.2	66.6

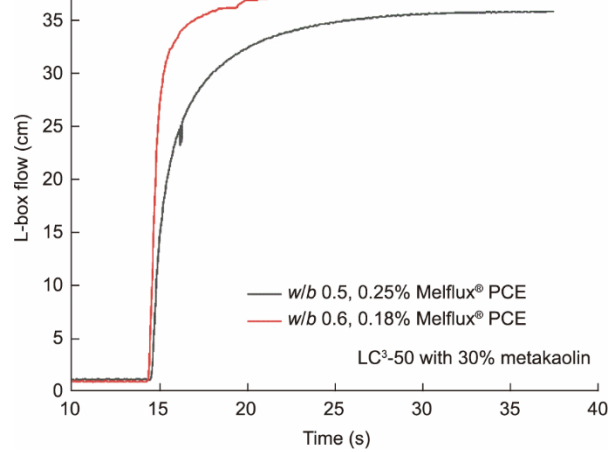


Fig. 5. L-box flow of the LC³ with w/b of 0.5 and 0.6. The graph describes the flow of the mortar over time in the L-box at the same flow adjusted with Melflux[®] superplasticizer.

4.3. C-S-H seeding

Given the considerations of pure physical approaches such as the use of fine limestone fillers, C-S-H seeds have emerged as a potential strategy to tackle the early-age strength challenge of blended cements. C-S-H seed technology rely on the similar principles of the filler effect but introducing a much higher surface area (typical values around $100\text{--}200\text{ m}^2\cdot\text{g}^{-1}$) per unit mass and providing an ideal substrate for additional C-S-H growth. In addition, they act as nuclei for C-S-H growth, reducing the activation energy of the process. Nowadays, there is a variety of commercial products in the market that put this technology at reach for the construction industry.

Fig. 6 shows the strength enhancement achieved on an LC³ system with two dosage levels of C-S-H seeds (1.5% and 3.0%). Fig. 4 presented similar results in LC³ system with different w/b ratio. As observed, C-S-H seeding is effective in boosting very early and early age strength. However, initial setting occurs earlier as the hydration kinetics are accelerated with increasing seed dosages, reducing the open time of the system. The main drawback of this technology is its relatively high cost.

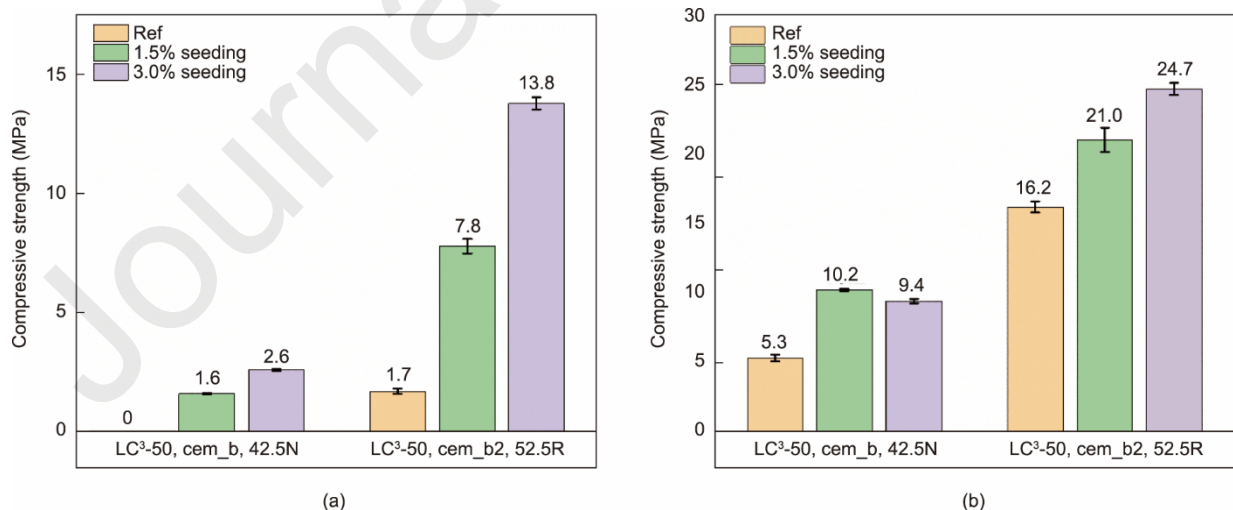


Fig. 6. Impact of the accelerator on the early strength for different LC³-50 cements made from the same calcined clay (CC_b) and two cements with different strength class. (a) 8 h strength; (b) one-day strength. “0” label in the strength values refers to strength less than 0.3 MPa which is the detecting limit of the compressive strength machine. w/b ratio is 0.5 according to EN 196-1. Ref: LC³-50 reference.

Fig. 7 shows the dosage efficiency of C-S-H seeds on one-day strength of LC³ at two different clinker factors (50% and 35%). As observed, there seem to be an optimum for this seed formulation sat about 1.5%

for [redacted] This difference could be related with the extend of hydration and amount of hydration products/space available at one day to continue growing C-S-H. Nevertheless, it highlights the need of optimization of seeding dosage for every cement formulation for an efficient and effective use.

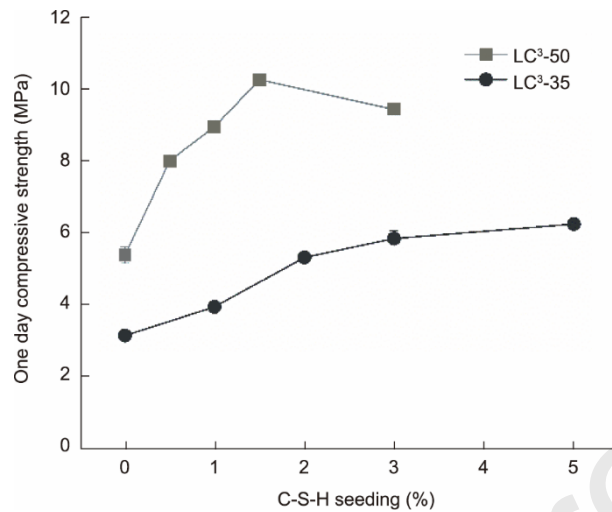


Fig. 7. one-day strength of the LC³ cement with different C-S-H seeding dosages. Reproduced from Fig. 3(a) in Ref. [12].

As previously shown, the use of C-S-H seeds in LC³ are an effective tool to boost very early and early age strength development. The relative increase in strength opens, in turn, a set of technological choices for mixture design and optimization that can be implemented solely or combined depending on the use scenario and the requirements of a specific project:

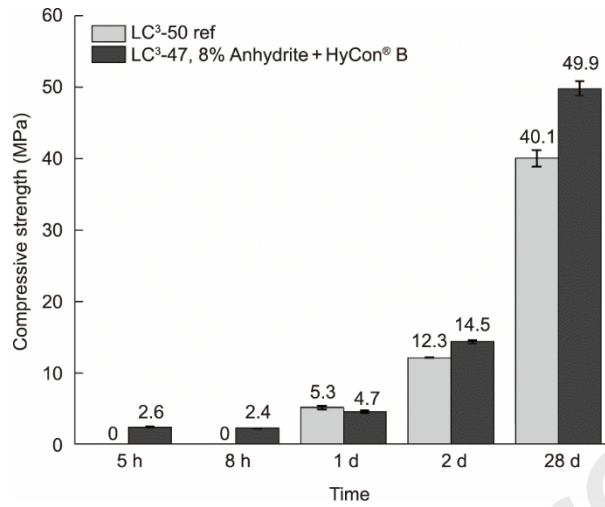
- Use LC³ in high (very) early-age strength applications.
- Further reduction of the clinker factor to go back to unseeded levels of strength [11,12] if the increase in early age performance is needed.
- Use less reactive calcined clays.
- Blend in other less reactive SCMs such as fly ash, natural pozzolan or more limestone to formulate the concrete with better workability [12].

In all cases, a comparison of cost, performance and GWP of each solution is needed to provide a holistic overview and aid in the decision-making process.

4.4. Boosting the aluminate hydration

Unlike the C-S-H seeding approach, the HyCon[®] B additive promotes the ettringite formation by enhancing the ferrite and C₃A reaction, thus providing an instant very early-age strength boost through ettringite precipitation as soon as initial setting takes place [21].

Fi. 8 shows the strength development of an LC³ cement with HyCon[®] B and an 8% addition of anhydrite as source of sulfate to balance the additional alumina dissolved from ferrite and C₃A. The early strength measured at 5 h was 2.6 MPa while the reference LC³ was still soft at this stage. The one-day strength is slightly lower than the LC³ reference, however, the strength quickly catches up at two days and then exceeded the reference at 28 d by about 10 MPa (25% of the reference strength). While the late-age strength of the reference is still exceeded, this approach highlights the potential of engineering the aluminate reaction to



Fi. 8. Early and late strength of LC³ with HyCon® B. “0” refers to values lower than the detecting limit of the machine (0.3 MPa), data reported previously in Ref. [2]. Data at 5 h were added with new batch of cement thus showed slightly higher strength than 8 h. ref: reference.

5. Sustainability considerations

LC³ is a technology that enables substantial GWP reductions while retaining key performance parameters such as 28 d strength and durability. As discussed in this article, this is not necessarily the case of (very) early-age strength, and different strategies available to offset this outstanding challenge have been presented. However, these solutions should also be compared in terms of their inherent impact on the GWP of the cements where they are used. For example, the addition of portlandite to low-clinker LC³ is effective to promote the metakaolin reaction and boost compressive strength from seven days onwards [11]. However, the CO₂ footprint of portlandite (940 kg CO₂eq·t⁻¹ portlandite) [27] is in fact higher that of PC (819 kg CO₂eq·t⁻¹). A similar situation can be extended to C-S-H seeds and other chemical admixture which, while used in small quantities, have high GWP.

Fig. 9 shows a summary of GWP of different LC³ mix design and the different technological solutions presented above, decoupling the contribution of the binder and the additives used. However, the GWP impact of chemical additives should not discourage their use as in most cases they bring performance enhancement to levels that are not achievable without them. Furthermore, they open additional avenues for further optimization that would not be available otherwise.

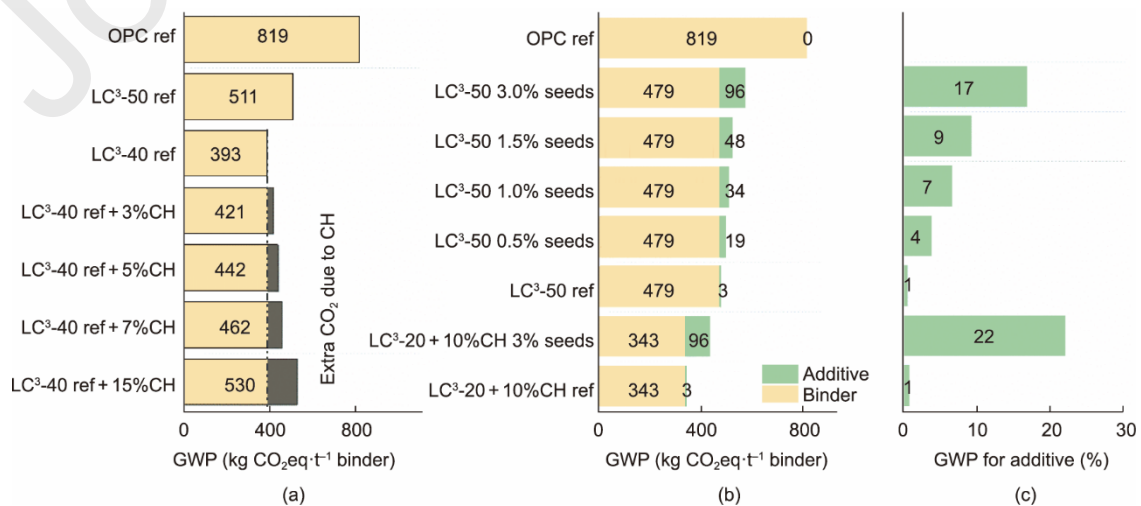


Fig. [11], contribution from portlandite was marked as dark gray; (b) the absolute GWP for LC³ made with cement_b and LC³⁺ where extra portlandite were introduced to the LC³, and (c) the corresponding proportion of the chemical additive parts in percentage of the total formulation. CH: portlandite. ref: reference.

Fig. 10 aims to highlight this fact by comparing the specific GWP (GWP per unit strength) with the overall strength of the system at one day (Fig. 10 (a)) and 28 d (Fig. 10(b)). In this representation, the size of each bubble represents the absolute embodied CO₂ footprint (GWP) of each formulation (also indicated with numbers), while its position within the diagram indicates its efficiency and overall performance. The values for the reference (100% PC) are shown as a general guideline.

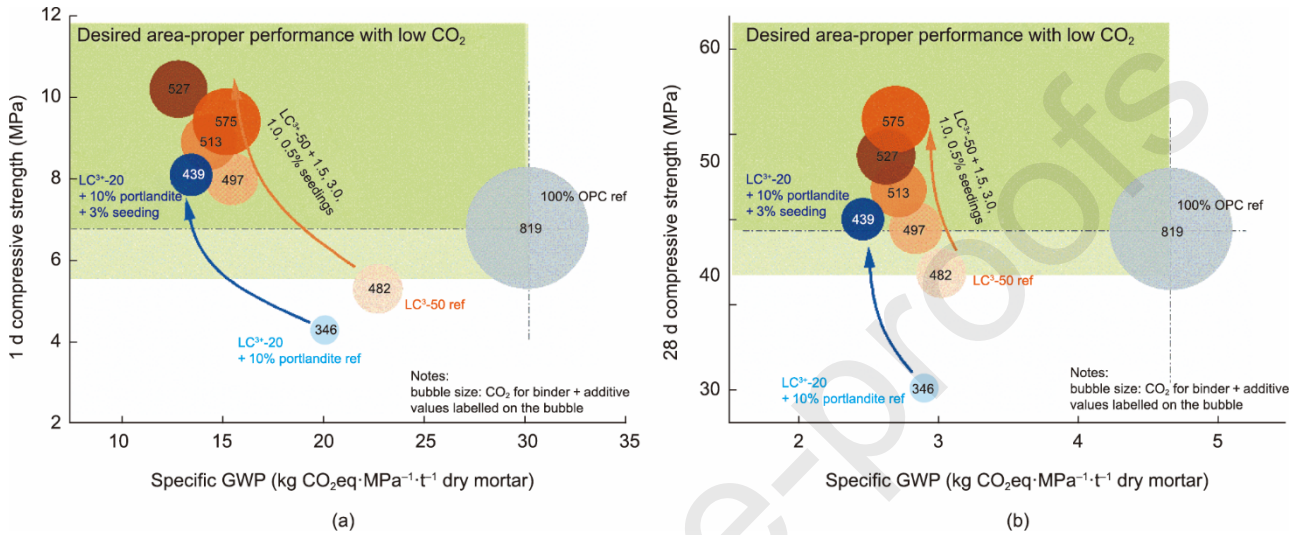


Fig. 10. Plots of compressive strength versus specific emission. Evaluation at (a) one day and (b) 28 d. The bubble sizes (labeled in black numbers) refer to the CO₂ emission of the binder including additives (kg CO₂eq·t⁻¹ binder). The green area corresponds to greater strength, but lower CO₂ emissions compared to the 100% OPC reference. The arrow indicating the impact of using C-S-H seeding (dosages were indicated aside the arrow as 0.5, 1.5 and 3%) on the strength and emission. ref: reference.

At one day, the use of LC³-50 alone significantly reduces the CO₂ footprint but also strength. The use of C-S-H seeds can offset the strength reduction (going even beyond PC), but in turn the GWP increases, though still well below PC levels. However, if the use of seeds and portlandite additions in the LC³⁺ system coupled with GGBFS and calcined clay, it is possible to reduce the clinker factor to 20% while obtaining the same strength performance similar to that of PC at one day and 28 d [12]. This is a significantly better specific emission (efficiency) and an overall lower CO₂ footprint, even compared to the reference LC³-50. While cost has been left out of the discussion here, this overview highlights the potential of engineering combinations of these strategies to smartly improve the performance of LC³ systems and thus produce better and greener cements.

6. Outlook and perspectives

Increasing the fineness of the binder, which includes clinker, SCMs, and fillers, is an effective method to enhance early-age strength. However, this approach has limitations due to reduced grinding efficiency, increased energy consumption, and workability constraints, particularly in systems incorporating calcined clay.

Particle size optimization presents potential for further advancement, but it must consider the variety of materials and particle sizes/surfaces in modern cements. Additionally, the environmental impact of additional emissions from grinding and mixing processes should be considered, as well as the effect of using finer materials on water demand.

at it presents challenges in workability. While increasing the amounts of dispersants can improve workability by reducing the yield point, highly viscous mortar with a low w/b ratio still pose challenges.

The application of C-S-H or other seeding techniques offers new possibilities for enhancing strength. Recent improvements in the quality and effectiveness of commercial seeding formulations have increased the versatility of this method for addressing early-age strength challenges in high-demand (fast setting, high early strength) applications.

Boosting aluminate reaction using HyCon[®] B additive enhances ettringite formation, resulting in early-age strength boost also showed potential for better performance in LC³ cements at very early ages and late ages.

However, the use of performance-enhancing additives like C-S-H seeding incurs extra costs and CO₂ emissions. Nevertheless, the extra CO₂ emissions coming from chemical additive is marginal and can be offset due to the performance enhancement. Still the balance between performance, CO₂ emissions, and the final cost of the application is crucial. Overall, while binder fineness and seeding techniques provide effective solutions for early-age strength enhancement, careful consideration of environmental and economic impacts is essential for sustainable implementation in modern cementitious materials.

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Declaration of interests

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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X. Li and J. Dengler are employees of BASF Construction Additives GmbH as of submission of the work.

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