

3D printing of limestone-calcined clay cement: A review of its potential implementation in the construction industry

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ABSTRACT

The rapid development in 3D printing applications requires exploring a sustainable printable mixture to decrease the environmental impact induced by the existing Ordinary Portland Cement (OPC) mixtures and enable 3D printing technology to reach its peak efficiency. The high-volume substitution of OPC with supplementary cementitious materials (SCMs) is of significant interest as a promising solution for developing low-carbon feedstock for 3D printing. Yet, those materials share the problem of limited availability. The combination of limestone and calcined clay could be a promising alternative, offering various benefits, including replacing OPC in high ratios. This paper reviews 3D printable limestone calcined clay cement (LC3) mixtures, compositions, and chemical behaviour. The effect of different sand-to-binder ratios, additives content, OPC replacement levels, clay grade and calcination, and admixtures on the fresh, hardened and printing properties of the 3D printed mixtures are critically discussed. The environmental impact and production cost of the LC3 system compared to OPC and other systems are also critically evaluated along with the applications, future directions and research gaps in this field. The findings of this review show that 3D printed LC3 has a similar hardened performance and better microstructure than OPC system. Moreover, cast LC3 system has 30–50% lower environmental impacts depending on the replacement level and better economic feasibility than OPC. Therefore, making it a suitable feedstock for the innovative manufacturing technology of 3D printing.

1. Introduction

The construction industry could experience an evolutionary development through the implementation of 3D printing technology. The first 3D printing application in the construction sector was in 1997 when various hollow concrete structures were produced [1]. The 3D printing process of concrete elements or components starts with their mix design, followed by their deposition through a pumping system and multi-dimensional movement of a robotic arm or a gantry system in sequential layers [2]. Despite the apparent ease of the printing procedures, this technology requires a printable concrete mixture that does not harden immediately after deposition to avoid cold joints. Hence, the most appropriate mix for the 3D printing method should be extruded smoothly and provide shape stability by holding the consequent layers'

weight. Concrete 3D printing has gained significant interest due to its environmental benefits, lower cost, high efficiency, architectural design flexibility, and safer working conditions compared to the traditional construction method [3–8].

Most of the proposed printable cementitious materials have a high content of ordinary Portland cement (OPC) to meet the requirements of printability, workability and buildability, which decreases its environmental credentials due to the high energy consumption associated with OPC production and the release of CO₂ emissions which reach 900 kg/ton and account for around 8% of total global CO₂ emissions. Around 40–50% of the emissions are generated from the calcination process and the remaining emissions are generated from the decarbonisation process of the decomposition of calcium carbonate into calcium oxide [9]. The high OPC content in 3D printable concrete mixtures is related to the absence of coarse aggregate, because of limited nozzle diameter and low

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Abbreviations

OPC	Ordinary Portland cement
SCMs	Supplementary cementitious materials
LC3	Limestone-calcined clay cement
CH	Portlandite/calcium hydroxide
C-A-S-H	Calcium aluminosilicate hydrate
C-S-H	Calcium silicate hydrate
VMA	Viscosity modifying agent
LP	Limestone
CC	Calcined clay
Mk	Metakaolin
HGCC	High-grade calcined clay
MCC	Medium-grade calcined clay
LGCC	Low-grade calcined clay
PCE	Polycarboxylate
HRWRA	High-range water-reducing agent
WFT	Water film thickness
SSA	Specific surface area
LCA	Life cycle assessment
PPC	Pozzolanic Portland cement

fine aggregate to binder ratio [10]. Increasing aggregate content could lead to lower printability and blockage of the nozzle and the hose of the printer.

Researchers have focused on reducing OPC content in the mixture

through the partial replacement of OPC with supplementary cementitious materials (SCMs). During the last decades, many studies have investigated the efficiency of partially replacing OPC with common SCMs (i.e., fly ash, silica fume, and ground granulated furnace blast slag) in both cast and 3D printed mixtures [11–17]. Although promising results were obtained when incorporating these materials, there are still problems with their limited availability, which led to researchers seeking alternative materials [5,18,19]. The high availability, reactive components and the chemical composition of calcined clay and limestone attracted researchers' interest, as it showed potential as an alternative for common SCMs to produce a ternary blended cement called limestone calcined clay cement (LC3). Nevertheless, one of the main constraints faces clay is that despite its worldwide availability, not all clays are suitable for use as a cementitious material. Some standards require clays to meet a minimum chemical composition (e.g. ASTM C-618 [20]) in order to be counted as an SCM. In addition, it is hard to find clay with high kaolinite content. Kaolinite is the most reactive clay mineral and requires lower calcination temperatures than other types of minerals. Although the calcination temperature is half that of OPC, clay needs to be calcined at elevated temperatures for different durations, depending on the type of clay used, which is considered an energy-intensive process.

Over the last few years, LC3 experienced a fast development due to the ability of limestone and calcined clay combination to replace high OPC percentage (more than 50%) [21,22], generate low CO₂ emissions, enhance the resistance to chemical attacks, and produce mixtures with comparable mechanical performance to conventional OPC after 7 days [23–26]. Due to those various advantages, LC3 was employed in traditional construction application in many developed countries, where



Fig. 1. Constructed LC3 buildings (a) Model house in Jhansi, India, (b) Model house in Santa Clara and (c) building at the Swiss embassy in Delhi, India [27].

more than 25 buildings were built with LC3, some of which can be seen in Fig. 1. In India, the most prominent project is the model Jhansi. This house is made of 98% LC3, which used 26.6 tonnes of industrial waste (192 kg/m^2) and saved 15.5 tonnes of CO_2 (114 kg/m^2). These CO_2 savings are similar to the emissions of 10 passengers travelling by plane from Switzerland to South Africa. The Swiss embassy in Delhi was also built with an LC3 blend. Other than India, LC3 was employed in Latin America, mainly in Cuba [27]. The use of LC3 blend in real-life applications presented a turning point to meeting the global goals and vision for sustainable development. The future directions are moving toward sustainability by combining the benefits of 3D printing technology and LC3 blend to lower environmental impact, waste production, and consumption of limited natural resources to manufacture cement.

Despite the evident advantages of LC3, its implementation in 3D printing applications is still new. In the last five years, several studies investigated the employment of LC3 in 3D printing technology to reduce its reliance on OPC as a binder and to enhance mixtures' properties. However, many research gaps need to be fulfilled to allow 3D printing LC3 on large-scale. The focus on combining limestone and calcined clay being spotlight is due to the various benefits that offers, which include enhanced durability, economic value, environmental impact during manufacturing, and similar strength behaviour to OPC, this paper focused on reviewing different properties of the 3D-printed LC3 mixtures. To the best of the authors' knowledge, a comprehensive review of using LC3 mixtures in the 3D printing application has not been discussed before. The constituents and chemical behaviour of the LC3 system, OPC substitution level, reinforcing and rheology modifier admixtures, and limestone-to-calcined clay ratio, are thoroughly discussed in this review. In addition, the effect of different OPC replacement levels with limestone-calcined clay, clay minerals content (clay grade), sand ratio, and admixtures types and ratios on the fresh and hardened properties of 3D-printed LC3 mixtures are reviewed. The economic and environmental feasibility of LC3 mixtures employing 3D printing technology is also discussed and compared to conventional materials and production methods.

2. Limestone calcined clay cement (LC3)

Several studies were conducted to develop 3D printable mixtures, where the binder was prepared using OPC and common SCMs [15,28]. Even though SCMs could replace high OPC percentages, their low availability restricted their consideration as a main ingredient in 3D

printing applications [29,30]. The abundance of clay and limestone (See Fig. 2) and the benefits of their combination received significant interest in developing the so-called LC3 mixture. The binder of the LC3 system is mainly composed of clinker, calcined clay, limestone, and gypsum. The LC3 binder is obtained by either co-grinding the components or blending them together until achieving a homogeneous blend.

Researchers, on the one hand, have shown that replacing OPC with calcined clay alone produced mixtures with better printability, strength, and shape stability compared to fly ash [31]. In addition, calcined clay was noticed to enhance the cohesion, apparent viscosity, static and dynamic yield stresses, and thixotropy of mixtures [32]. On the other hand, it has been reported that substituting OPC with more than 10% of limestone alone would weaken the strength of the mixture and increase its water absorption [30]. However, the combination of calcined clay and limestone produces mixtures with enhanced mechanical and physical properties and allows the higher OPC substitution than their incorporation individually. The highest compressive strength performance within the first 28 days of curing could be obtained using a 1:2 ratio of limestone to calcined clay [23,24].

Clay is categorised depending on the packing of its octahedral (O) and tetrahedral (T) sheets and their arrangement and ratio in clay layers. Fig. 3 illustrates the structure and chemical formulation of the most common clay minerals like kaolinite (1:1-type clay), montmorillonite (2:1-type clay), and illite (2:1-type clay). Kaolinite was used in most studies due to its higher pozzolanic reactivity than other clay minerals and the easier removal of water molecules in kaolinitic clays [33]. More details concerning different types of minerals can be found in the following reference [34]. Prior to the partial substitution of OPC, clays should be activated. Several techniques for clay activation were reported in the literature, including thermal [35], mechanical [36,37] and chemical activation [38]. Thermal activation is the most used technique, by calcining (burning) clay at elevated temperatures between 600 and 900 °C for adequate time to remove water molecules from their structure in a phenomenon known as dihydroxylation [33,39]. Owing to the clay chemical composition, mainly alumina and silica, clay gains a pozzolanic reactivity when burnt at elevated temperatures by destroying the crystalline network, leaving silica and alumina in a disordered, amorphous and unstable state. It is worth noting that calcination does not affect quartz and other anhydrous minerals. Thus, the pozzolanic reactivity mainly depends on the thermal treatment condition and content of clay minerals [33,40,41]. Clay's reactivity decreases when increasing the temperature above 900 °C due to the sintering effect in the first place

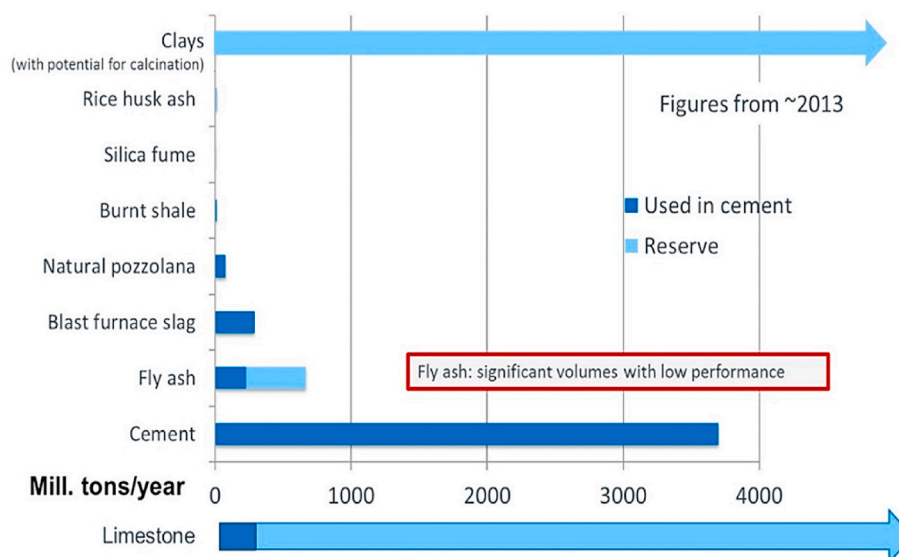


Fig. 2. Supplementary cementitious materials availability [30].

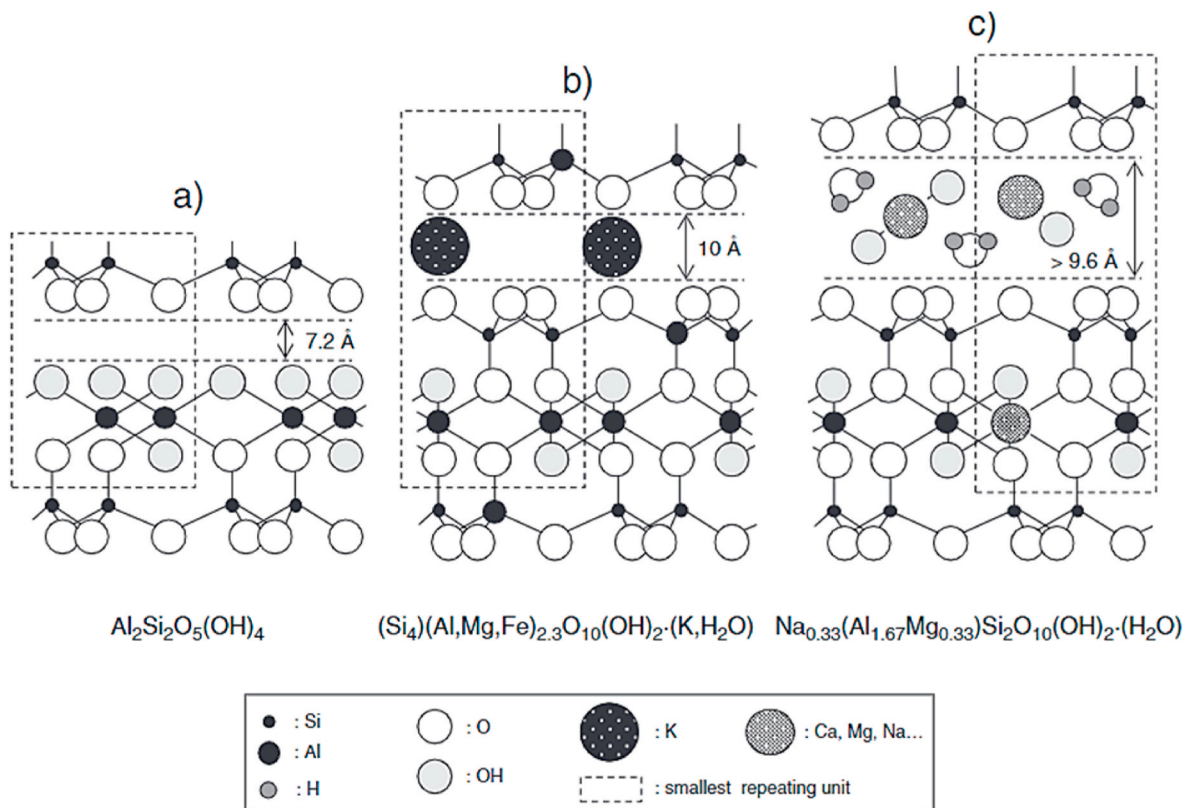


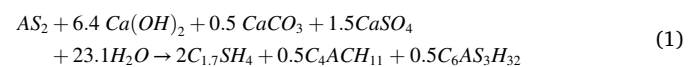
Fig. 3. Chemical formula and structure of (a) kaolinite, (b) illite and (c) montmorillonite [33].

and then its recrystallisation into mullite, spinel and cristobalite [40]. The clay calcination efficacy can be measured by characterisation techniques (e.g., X-ray diffraction (XRD)) or reactivity measurements to ensure proper activation without recrystallisation. There are different techniques for measuring the reactivity of calcined clay that provide reliable results, including a new rapid, relevant and reliable (R3) method based on the correlation between chemical activity and the compressive strength in blended cement systems [24] and lime reactivity test [42]. However, more suitable approaches to measuring the calcination quality should be developed since these methods are time-consuming.

Calcined clay's chemical and mineralogical compositions and physical properties (i.e., fineness and morphology) may differ when obtained from different suppliers or origins [4,24]. Those differences can occur depending on the type of raw clay, purity of the clay, temperature profile, and calcination conditions, and they may substantially influence the fresh and hardened properties of the LC3 mixture [43–45]. There are several noticeable advantages of using calcined clay in concrete, especially low-grade kaolinite clays. These are (1) low CO_2 emissions released during the calcination process (approximately 0.3 kg CO_2/kg) [30], (2) similar strength behaviour to conventional OPC at an early age [46,47], (3) abundance and ease of obtaining [23,48], (4) lower cost [49,50] and (5) further refinement of mixtures' capillary pores [24,51]. According to Muzenda et al. [39], calcined clay is the main factor in the LC3 system that improves its static and dynamic yield stress, cohesion, adhesion, and plastic viscosity. In contrast, the limestone powder can diminish these characteristics, thus, enabling tailoring the flowability of LC3. According to Tironi et al. [52], when raw clay contains more than 50% kaolinite, the pozzolanic activity of kaolinitic calcined clays appears to depend more on the raw kaolinite crystalline order than on kaolinite content.

2.1. Chemical reactions and pozzolanic reactivity

Portland cement is mainly composed of 55–65% alite ($3\text{CaO} \cdot \text{SiO}_2$), known as C_3S , 15–25% belite ($2\text{CaO} \cdot \text{SiO}_2$), known as C_2S , 8–14% aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$), known as C_3A , and 8–12% ferrite or brownmillerite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$), known as C_4AF . These phases, in the presence of water, react to produce hydration products that include calcium silicate hydrate (C–S–H), portlandite (CH), ettringite, monosulfate and monocarbonate. During the first few days of hydration, alite is the first silicate phase to react, contributing majorly to strength development during the first 28 days. However, belite is responsible for strength development after 28 days due to its slower reaction rate. Ettringites are formed from the reaction between aluminate, gypsum and water, which further reacts with the remaining aluminate phases forming calcium monosulfaluminate. The reaction of limestone-calcined clay consisting of calcined clay, like metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, abbreviated as AS_2), with limestone (CaCO_3) and $\text{Ca}(\text{OH})_2$ forms similar reaction products, as shown in the following equation:



The presence of portlandite (CH) is vital to complete this reaction [23]. Hence, the amount of calcined clay that can react is affected by the amount of belite and alite found in the clinker [23]. Moreover, the reactivity of calcined clay at later ages is affected by the internal relative humidity of the material, where it declines with the decrease in humidity [53]. Low internal humidity would reduce the pore solution in capillary pores in the LC3 system, which limits the growth and development of hydration products to small-size saturated pores. Thus, limiting the space in which the hydration occurs.

It has been suggested that alumina dissolution and reaction depend on the available sulphates, unlike silicate reaction, which depends on available CH in the system. The rate of reaction and hydration was

shown to be affected by the presence of alkalis, especially at early ages [54]. The hydration product, calcium aluminosilicate hydrate (C-A-S-H), is formed from the reaction between silicate in calcined clay and portlandite, which mainly depends on the hydration temperature and kaolinite content in the clay [26,55]. Along with the pozzolanic reactivity of calcined clay and the filler effect of limestone, the alumina in calcined clay reacts with carbonate in limestone, producing synergy between the materials and resulting in a mixture with superior performance than OPC [23]. Moreover, calcined clays produce an additional amount of hemi-carboaluminate and monocarboaluminate (AFm phases) in the presence of limestone [23,56].

The reaction behaviour of LC3 compared to OPC was investigated in different studies by conducting isothermal calorimetry to observe the heat evolved during hydration [57,58]. Incorporating limestone-calcined clay to replace OPC would reduce the main hydration peak intensity, at the same time, the total heat released tends to increase at low replacement levels of OPC, which is expected due to the combined energy release from the hydration of OPC along with the pozzolanic reaction from limestone-calcined clay with the calcium hydroxide (CH) produced from OPC reaction. On the other hand, increasing OPC replacement level with limestone-calcined clay decreases the total energy released, due to the reduction in OPC particles, which reduces the amount of available CH for reacting with the pozzolanic materials.

3. 3D printed LC3: fresh and hardened properties

Different factors can affect the fresh and hardened properties of the LC3 system, including OPC replacement level, clay type and mineralogical composition, calcination temperature, calcination period, and water-to-binder ratio. The effect of incorporating higher replacement levels of limestone-calcined clay, various clay grade levels, adding other SCMs to the LC3 mixture, different sand-to-binder ratios and different sand gradation on the fresh and hardened properties of 3D printed LC3 mixture was studied by various researchers, as shown in Table 1. The effect of using admixtures (i.e., superplasticiser and viscosity modifying

agents (VMA)) and incorporating different ratios to obtain optimum dosages that can improve 3D printing properties were also investigated. It can be observed that all studies on 3D printing LC3 used a limestone-to-calcined clay ratio of 1:2. Adjusting the above-mentioned parameters affected the fresh and hardened performance of the LC3 mixture, as will be discussed in this section.

3.1. Fresh properties of 3D printed LC3

The fresh state properties of 3D printable LC3 mixtures are considered the main defining parameters for successful 3D printing. These parameters include pumpability, extrudability, printability window (i.e., open time), and buildability [12,62,63]. Table 2 presents the fresh properties of the optimum mix design and the effect of changing some parameters on 3D printing as reported in the literature.

3.1.1. Rheological parameters

Yield shear stress, plastic viscosity, and thixotropy are the main rheological parameters investigated by researchers. Yield shear stress can be divided into static and dynamic yield shear stresses, where static yield stress is the stress needed to start the system flow, while dynamic stress is the needed stress to keep the flow [64]. After removing the stress or pressure applied, the flow stops, and thixotropy happens. Thixotropy is the restoration of the mixture's static yield stress by initiating the flocculation of particles due to inter-particle interaction [65].

The different behaviour of fresh mixtures under static and dynamic stresses could be due to mixtures' rheology and thixotropy, which depend mainly on the mix design. That is related to the binder composition, particle shape, water percentage, and aggregate gradation and content. Long et al. [59] showed that incorporating limestone-calcined clay increases the static yield stress by 7 and 15 times when replacing 40% and 50% of OPC, respectively. Moreover, the incorporation of 5% and 10% silica fume (SF) into the mixture containing 50% limestone-calcined clay resulted in around 75 and 86 times higher static yield stress, respectively. That is due to the higher water absorption and

Table 1
Mix formulations of 3D printed LC3 materials obtained from different studies.

Binder				LP:CC ratio	Sand/binder ratio	Sand size	W/b ratio	Admixtures (%-wt.)	Ref
OPC	Limestone (LP)	Calcined clay (CC)	Others						
10–100%	0–30%	0–60% (about 50% metakaolin (MK))	0.3%-wt. Gypsum	1:2	1.5	0.125 – 2 mm	0.3	Hydroxypropyl methylcellulose (HPMC)-based VMA 0.24%-wt. of binder Polycarboxylate ether (PCE)-based superplasticiser 1.5–2%wt. of binder methylcellulose-based VMA 0.24%-wt. Superplasticizer 2%-wt. polycarboxylate (PCE)	[57]
40%	20% 60% for the reference mix	0–20% High-grade CC (HGCC) (95% MK) 20–40% Low-grade CC (LGCC) (50% MK)	–	1:2	1.5	<2 mm	0.3	0.24%-wt. Superplasticizer 2%-wt. polycarboxylate (PCE)	[18]
35–100%	13.3%, 16.7%	26.7%, 33.3%	5–15% silica fume	1:2	1–4	–	0.48–0.5 0.48	Polycarboxylate-based, high-range, water-reducing admixture (HRWRA) 0.4%-wt. Superplasticizer 0.15–0.7% 0.22%-wt. VMA 0.1%-wt. VMA	[59]
80% 55%	– 15%	– 30%	20% FA –	1:2	1.5	Uniformly-graded <2 mm Well-graded <4.75 mm	0.32 (reference) 0.4	Superplasticizer 0.15–0.7% 0.22%-wt. VMA 0.1%-wt. VMA	[60]
40%	20%	40% Low-grade (40–50% MK)	–	1:2	1.5	<2 mm	0.3	2% Superplasticizer 0.14, 0.24, 0.48% VMA	[5]
40%	20%	40% Low-grade (40% MK)	–	1:2	1.5	<2 mm	0.3	2%-wt. Superplasticizer 0.14, 0.24, 0.48%-wt. VMA	[61]
40% 40%	60% 20%	– 20–40% LGCC, 0–20% HGCC	–	1:2	1.5	>2 mm	0.3	2%-wt. Superplasticizer (PCE) 0.24%-wt. VMA	[46]
40%	20%	30% low-grade, 10% high-grade	–	1:2	1.5	>2 mm	0.3	2% superplasticiser 0.24% VMA	[4]

Table 2
Fresh properties of 3D printed LC3 mixtures.

Mix formulation	Extrudability	Open time	Rheological properties	Buildability	Ref
10% OPC, 60% CC, 30% LP, 1.5 wt% superplasticizer, 0.24 wt% VMA	-Increasing the replacement level of OPC with limestone-calcined clay resulted in a quick loss of workability over time, where mixtures prepared with 75% and 90% limestone-calcined clay replacement levels had an extrudability window of 15 min. - The extrudability window increased with increasing superplasticiser content from 1.5% to 2% by 20 min for high replacement levels.	-Increasing OPC replacement level with limestone-calcined clay by more than 45% decreased the open time from 120 min to 45 and 25 min for 75% and 90% substitution levels, respectively. -The open time was prolonged by 50 min when increasing the superplasticiser percentage by 0.5%	-	-Mixture prepared with a 90% replacement level of OPC with limestone-calcined clay and 1.5 wt % superplasticisers had the highest buildability, reaching more than 20 layers. The test was terminated due to insufficient material in the hopper. -Increasing the superplasticiser content weakened the buildability behaviour of the LC3 mixture.	[57]
40% OPC, 20% HGCC, 20% LGCC, 20% LP	-Increasing HGCC content increased the flowability of the mixture.	-Increasing the HGCC content decreased the open time of the mixture. -Mixture with 20% HGCC content had an open time of 30 min, while for 10% and 0%, the open time was 70 and 80 min, respectively.	-Mixture with the highest HGCC content had the highest shear yield stress.	-For a rectangle opening nozzle, increasing HGCC content enhanced the buildability of the mixture, where the mixture containing 20% HGCC is the only mixture that successfully printed a wall of 21 layers without collapsing. - The round opening nozzle showed fewer differences between the theoretical and measured heights of the printed objects and had more stable boundary conditions between the layers than the rectangle opening nozzle. -Only HGCC successfully achieved the designated number of layers (i. e., 18 layers)	[18]
45% OPC, 33.33% CC, 16.67% LP, 5% SF, and 2.5 S/b ratio	-Increasing the sand-to-binder ratio decreased the quality of the extruded filaments, showing voids and discontinuity. -Increasing limestone-calcined clay content to 50% and silica fume to 10% resulted in minor defects on the surface, while other mix formulations were extruded smoothly.	-	-Using limestone-calcined clay to replace 40% and 50% of OPC increased static yield stress by 7 and 15 times, respectively. -Incorporating 5% and 10% silica fume in mixes containing 50% limestone-calcined clay resulted in almost 75- and 86-times higher yield stress, respectively. -Adding limestone-calcined clay and silica fume increased dynamic yield stress, plastic viscosity and structural recovery.	-Reference mixture was un-buildable compared to the mixtures containing SCMs. Incorporating limestone-calcined clay to replace OPC successfully printed the cylinder. However, it did not maintain its shape. -The combination of limestone-calcined clay and silica fume jointly improved the buildability of the mixture. -Increasing the sand-to-binder ratio improved shape retention of the mixture but, at the same time, induced extrusion problems.	[59]
LC3-well-graded sand 0.6% superplasticiser	-Cracks were observed in the LC3 mixture prepared with well-graded sand after a few minutes of printing due to a significant loss of workability. -Increasing the superplasticiser content enhanced the workability of the mixture and increased the spread diameter. -Using 0.6% superplasticiser for LC3 prepared with uniformly-graded sand enhanced the extrusion quality, where no cracks were observed during printing.	-LC3 prepared with well-graded sand prepared with 0.6% superplasticiser had an open time of 80 min, whereas the reference had 240 min.	- Rheology resistance under compression load was higher for the LC3 mixture compared to the reference. -Increasing superplasticiser content significantly decreased the rheological properties under compression load of the LC3 mixture. -Elongational viscosity was much higher for the LC3 mixture than the reference mixture and decreased with increasing superplasticiser ratio. -The LC3 system showed higher yield stress in the penetration test than the reference mixture, having a penetration resistance of 0.5, 4.5, and 7 MPa for reference, LC3 with uniformly-graded sand, and LC3 with well-graded sand mixtures, respectively.	-A maximum of five layers were printed using the reference mixture. -LC3 prepared with uniformly-graded sand with 0.4% superplasticiser was successfully used to print a 300 mm height cylinder. While adding 0.6% superplasticiser to the LC3 prepared with well-graded sand resulted in similar flowability to the reference mix but increased the buildability to 210 mm before collapsing. -LC3 with well-graded sand containing 0.6% superplasticiser was printed with 76 layers and 1.14 m height.	[60]
LC3-0.24% VMA	-Increasing VMA dosage increased the required pressure for extrusion.	-Increasing VMA dosage from 1.2% to 2% and 4% reduced the open time of the mixture from 90 min to 70 and 50 min, respectively.	-	-Increasing VMA dosage improved the shape stability of the mixture. -Mixture prepared with 0.12% VMA dosage exhibited severe layer deformation and had the worst buildability.	[5]

(continued on next page)

Table 2 (continued)

Mix formulation	Extrudability	Open time	Rheological properties	Buildability	Ref
40% OPC, 20% LP, 40% low-grade CC	-The mixture prepared with the highest VMA dosage had better cohesion during the visual inspection of the extruded materials. -Increasing VMA dosage increased the extrusion pressure.	-	-Increasing VMA dosage increased the elongational yield stress and shear yield stress.	-Increasing VMA dosage increased the green strength of the mixtures, where 0.48% VMA achieved high values up to 2.5 h. -Increasing VMA dosage enhanced the shape retention in the first 2 h. -A stable shape could be found immediately after extrusion for 0.48% VMA. However, using 0.14% and 0.24% VMA produced a stable shape after 25 min and 60 min, respectively.	[61]
40% OPC, 20% low-grade, 20% high-grade and 20% LP	-Increasing calcined clay grade (MK content) showed a higher extrusion pressure growth rate with time. - After reaching the initial setting time, mixtures prepared with medium and high-grade clay showed significantly high extrusion pressure -Using high-grade calcined clay increased the extrusion pressure, which may bring extruding difficulties.	-Using high-grade calcined clay increased the extrusion shear strength, reducing the mixture's open time.		-The incorporation of high-grade calcined clay enhanced the green strength of the mixtures, which improved the buildability of the fresh mixture in the 3DCP process.	[46]

flocculation induced after adding limestone-calcined clay and SCMs can increase the static yield stress of the mixture [31]. The static yield stress increases due to limestone-calcined clay particles that possess angular geometry, which can increase inter-particle locking [49,66]. Besides the replacement level, adding high-grade calcined clay increases the shear yield stress of the mixtures due to the inclusion of more reactive calcined clay [18,67,68]. For instance, Chen et al. [18] found that increasing metakaolin content in calcined clay increased the shear yield stress. Moreover, incorporating limestone-calcined clay and SF also increase the dynamic yield stress, plastic viscosity, and thixotropy of mixtures [59].

Replacing OPC with 40% and 50% limestone-calcined clay exhibited a thixotropy recovery of 96% and 67% in the mixture, respectively, compared to 62% in OPC [59]. The better thixotropic behaviour when incorporating limestone-calcined clay is due to the particle flocculation because of its morphological structure, which also increases the yield stress [69,70]. The improvement in the thixotropic behaviour of the mixture could be due to the nature of calcined clay that exhibits a shear-thinning behaviour, which induces a flocculation structure and absorbs a high quantity of free water. After removing the load or shear stress, it can rebuild the intermolecular forces and flocculation structure [39,44]. That is because clay particles are heavily charged, where the faces possess negative charges and the edges positive charges, allowing them to produce scaffolding structures with the hydroxide and calcium ions produced from OPC reaction with water. That, in turn, influences clay particle flocculation behaviour and enhances the thixotropy recovery of the mixture [71]. It is noteworthy that fresh cementitious materials require a high thixotropy in 3D printing for the deposited layers to have enough yield stress to withstand the gradually increasing load induced by the succeeding deposited layers' weight [72]. However, the high thixotropy may result in weak interface adhesion [73,74].

Moreover, increasing the aggregate/binder ratio in the mixture induces a higher static yield stress due to the higher packing density and solid-to-solid contact because of the smaller spacing in the presence of more sand. Increasing the sand percentage in the mixture increases the dynamic yield stress and plastic viscosity but decreases the structural recovery (thixotropy). This is due to the low binder content, which reduces the flocculation and the formation of hydrates, thus, reducing the structural recovery [59]. Shantanu et al. [60] argued that the impact of sand type and gradation is not significant in the first few minutes, indicating that the rheology effect of the binder is dominant. The

authors stated that using well-graded and uniformly graded sand did not exhibit any differences at the first few minutes, whereas LC3 prepared with well-graded sand exhibited significantly higher yield shear stress and viscosity than the uniformly graded sand after 30 min.

The most effective way to enhance the workability and adjust the rheological parameters of a printable mixture could be by incorporating admixtures [61,75,76]. Most of the work on 3D printing LC3 has incorporated additives such as viscosity modifying agents (VMA) and superplasticisers, as shown in Table 1. Superplasticiser addition reduces viscosity and yield stress, which reduces the required extrusion pressure [60]. On the other hand, VMA incorporation improves the rheological parameters and the needed pressure for the extrusion process [5].

3.1.2. Extrudability and pumpability

Extrudability is the ability to smoothly extrude the printable mixture under pressure from the nozzle without any discontinuity or breakage. On the other hand, pumpability is the transporting process of the mixture under pressure from the reservoir to the nozzle through a pipe without affecting the mixture's properties (i.e., workability and rheological properties). Extrudability and pumpability mainly depend on the mixtures' rheological behaviour (i.e., static yield stress and plastic viscosity). Depending on the type of printer used and if there is no additional pressure, extrudability and pumpability can be considered similar processes. Hence, pumpability and extrudability, in this review paper, were considered to be one process defining one material property due to the fact that recent studies employed printers without any additional pressure input. This property was defined as the ability to print material in a continuous filament and acceptable quality [12,77,78]. The incorporation of limestone-calcined clay mainly lowers the mixture's workability, decreasing the mixture's extrudability. Hence, LC3 printability depends mainly on the replacement ratio. For instance, Chen et al. [57] found that increasing OPC replacement level with limestone-calcined clay up to 90% decreased the mixtures' flow rate due to different rheological performance, where rapid stiffness was observed with increasing limestone-calcined clay content, reducing the workability of the mixture and thus the extrudability. According to the authors, increasing the superplasticiser content can enhance the extrudability of the mixture even at high OPC substitution levels. However, it lowers the mechanical performance of the mixtures.

The rheology, flowability and fresh cementitious mixture strength are strongly related to the corresponding water film thickness (WFT)

[79–84] as it could be formed from excessive water on the particles' surface to reduce friction between particles [80]. Incorporating limestone-calcined clay could increase the physical properties of the mixture, including total specific surface area (SSA) and solid friction, which in turn affects WFT. It was reported that packing density was not affected by replacing OPC with limestone-calcined clay, where a slight decrement was observed when incorporating it in a high percentage (i. e., 90% limestone-calcined clay) [57]. In contrast, the SSA of dry binder increased with increasing limestone-calcined clay content, possibly due to the high SSA of calcined clay. Moreover, the higher SSA of LC3 mixes reduced the WFT. According to Chen et al. [57], the most significant factor affecting fresh properties is the WFT of pastes as a basic indicator incorporating various physical characteristics, i.e., water content, packing density, and SSA.

The grade of calcined clay (i.e., MK content presented in the clay) can also affect the printability and extrudability of the mixture. Increasing the calcined clay grade increases the extrusion pressure growth rate over time. Increasing the MK content, present in the clay, would accelerate the cement particles' phase change from flocculation to structuration [46]. At an early age, most SCMs (including MK) act as fillers, as indicated by Lothenbach et al. [85], since the pozzolanic reaction is generally dependent on the hydrated cement products. One of the main effective properties of fillers is their fineness, which could offer additional surfaces for the nucleation sites for the hydration products.

Increasing the solid percentage (sand content) could lower the quality of the printed mixture, producing more defects in the samples due to the high friction between the solid particles and the low binder volume present in the composite. Long et al. [59] investigated the effect of incorporating different percentages of limestone-calcined clay, silica fume, and sand on the extrudability of the mixture. They found that increasing the sand content in the mixture produced voids and discontinuity in the extruded filament, as shown in Fig. 4. Moreover, it was found that incorporating high percentages of limestone-calcined clay along with silica fume could result in minor defects on the surface of the extruded filament. Superplasticisers were used in most of the proposed LC3 printable mixtures to enhance their extrudability and flowability by reducing viscosity and yield stresses [4,5,18,46,59–61].

3.1.3. Open time and setting time

Open time, also known as the printability window, is the period at which the mixture can be printed with acceptable quality through the nozzle without any cracks [86]. The open time and setting time are directly related to the workability and rheological properties of the

mixture. Using a pump in the 3D printing process induces high friction, which increases the mixture temperature and results in a faster loss of workability [57]. Pumpability and buildability are significantly affected by the open time, where the mix with low open time may face difficulties during the extrusion process due to the rapid development of yield stress over time. In contrast, mixtures with long open time may limit the structure's buildability while printing due to the low structuration rate.

The setting and open time mainly depend on clay mineral content and OPC replacement level. Incorporating calcined clay containing a high percentage of kaolinite (high-grade clay) decreases the setting time of the mixtures. Chen et al. [46] found that the initial setting time decreased with the higher MK content in the calcined clay, which could be due to the acceleration effect that MK induces in the matrix. The authors showed that the mixture prepared with low-grade calcined clay (40–50% MK) had an initial setting time of 147 min compared to those of medium (around 62.5% MK) and high-grade (about 75%) mixtures of 78 and 52 min, respectively. Thus, using high-grade calcined clay shorten the open time of the composite. As explained in Section 4.1.2, that could be due to the acceleration effect in the presence of more MK. Due to clay's porous nature and limestone's high fineness, increasing OPC substitution ratio lowers the workability of the composite [57]. That will decline the flowability and narrow the printability window of the composite.

A suitable way to extend the open time of the mixture is by increasing the superplasticiser content [57]. It has been reported that increasing the replacement ratio of OPC with limestone-calcined clay reduces the open time of the mixture, whereas incorporating higher superplasticiser dosages prolongs it [57]. Another way to extend the open time is by subjecting the mixture to continuous mixing and pumping [60]. On the other hand, incorporating VMA admixture can shorten the open time of mixtures, as shown in Fig. 5 [5]. Although the open time of the investigated mixtures is long enough, more studies concerning the influence of changing the retarder content and aggregate/binder ratio and incorporating other SCMs and admixtures on the open time of the LC3 mixture are needed.

3.1.4. Buildability

Buildability is the ability of the printed mixture to retain its geometry under the loads brought from the upper layers [87]. Buildability mainly depends on the static yield stress [14], which is affected by OPC replacement level, water content, and calcined clay grade. Mixtures that show rapid growth in static yield stress immediately after extrusion have the least deformation during printing successive layers, allowing for

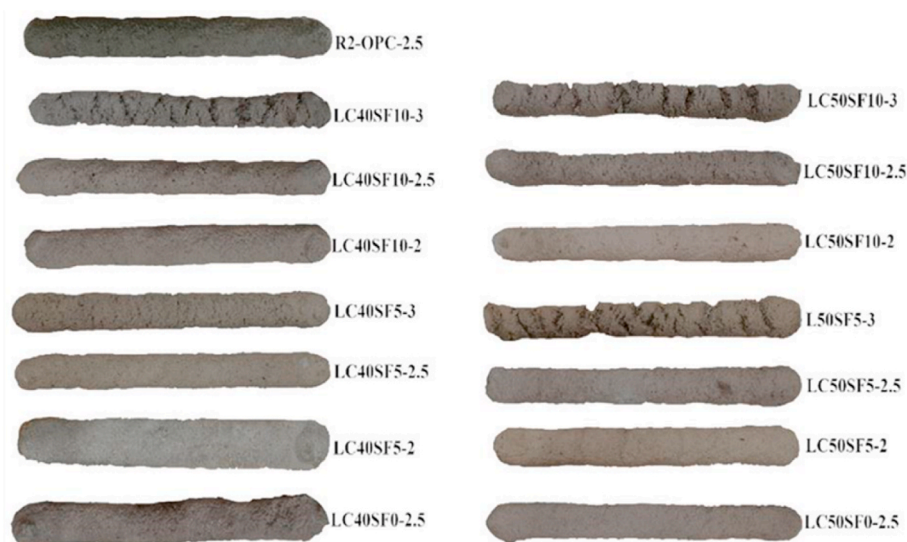


Fig. 4. Extrudability of LC3 mixtures with different limestone-calcined clay, SF and sand contents [59].

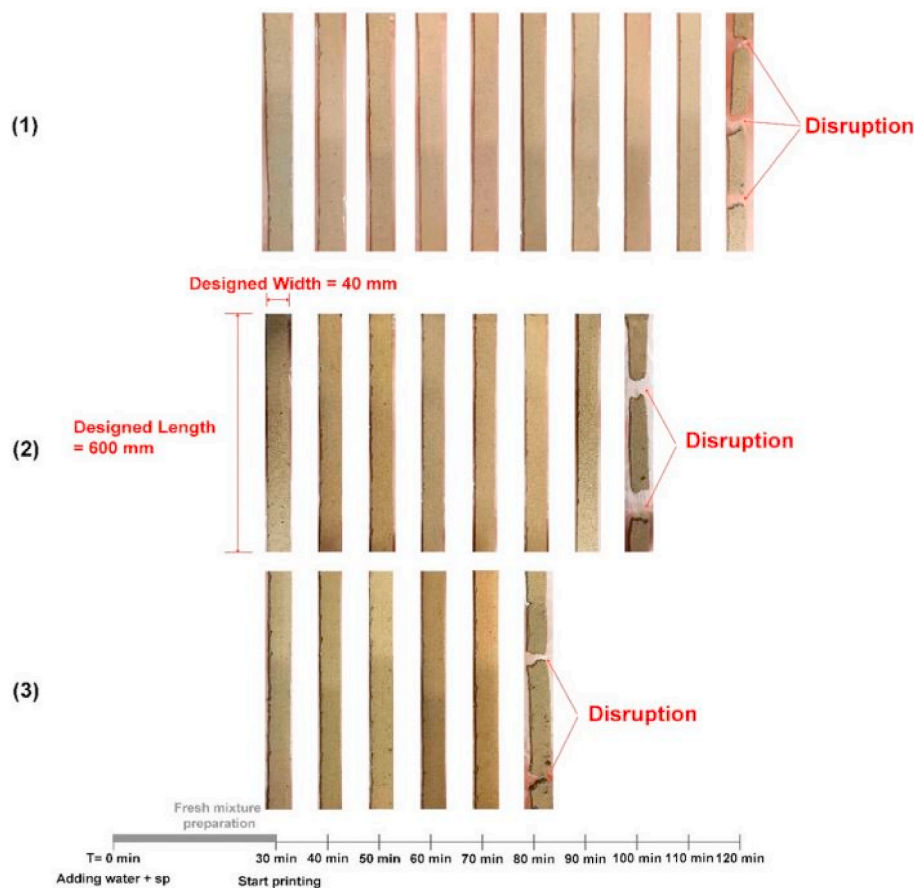


Fig. 5. Open time of LC3 mixtures containing (1) 0.14%, (2) 0.24%, and (3) 0.48% VMA [5].

better buildability. In addition, buildability is affected by geometrical and material properties. Chen et al. [18] investigated the effect of using two different nozzle openings and heights on the buildability of LC3 mixtures prepared with different calcined clay grades. The first nozzle had a rectangular opening with a height of nozzle opening of 13.5 mm, and the second had a round opening with an 8.5 mm height. The round opening nozzle showed fewer differences between the measured and theoretical height and had more stable layers than the rectangle opening. The authors found that the mixture prepared with the highest content of high-grade calcined clay achieved good buildability in both nozzle shapes. Increasing the substitution level of cement with limestone-calcined clay decreased the workability, which in turn increased the shape stability of the mixture, thus, resulting in a better buildability performance [18]. In another study, Chen et al. [57] investigated the effect of replacing up to 90% of OPC with limestone-calcined clay on the buildability behaviour of the mixture. The authors found that the mixture with the highest replacement level (90%) exhibited the highest buildability performance, reaching more than 20 layers. While mixes with lower replacement levels collapsed due to mix instability induced by plastic deformation in the bottom layers. Increasing the number of printed layers increases the self-weight load on the bottom layers, resulting in their compaction and a decrease in their theoretical height, which increases the designated standoff distance and causes instability when printing the succeeding layers. According to Chen et al. [57], structural instability occurs due to the plastic deformation induced by the self-weight of successive layers, which increases the standoff distance, as illustrated in Fig. 6. In addition, the authors employed a down-flow nozzle in their study that prints the succeeding layers by a squeezed forming process, increasing the load the bottom layers should withstand. These forces compacted the bottom layers and increased their width, causing a decrement in the contact area between

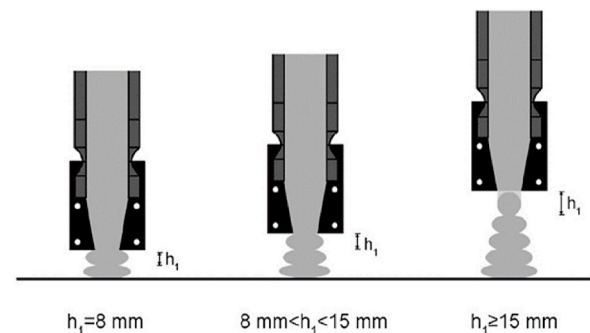


Fig. 6. Illustration of the increased standoff distance with the more compaction induced from the weight of the top layers [57].

layers and resulting in structural instability.

Buildability is also affected by the sand-to-binder ratio used in the composite. Sand content in the mixture affects the static yield stress, where the higher the sand percentage, the higher the static yield stress, thus, the better the buildability of the mix. Long et al. [59] showed that increasing the OPC replacement level with limestone-calcined clay from 40% to 50% improved the buildability of the LC3 mixture and allowed for more layers to be printed, but that was not sufficient to maintain its shape and presented large deformations. The authors found that the hybrid incorporation of LC3 and SF can effectively improve the mixture buildability and retain the object shape, as shown in Fig. 7. Although increasing the sand content can improve the buildability and shape retention of the mixture due to the better static yield stress, extrusion problems (e.g., blockage in nozzle or poor-quality filaments) occur when



Fig. 7. Buildability and shape retention of the object using different LC3 mix formulations [59].

exceeding certain sand content. The buildability and shape stability of the printed filaments can be improved by incorporating additives like VMA to adjust the mixture's rheological properties. According to Refs. [75,78,88], a small dosage is sufficient to improve buildability.

3.2. Hardened properties of 3D-printed LC3

3.2.1. Compressive strength of cast and 3D printed LC3

The effect of different mix formulations on the compressive strength is presented in Table 3. One of the main advantages of limestone-calcined clay is its ability to replace a high amount of OPC, around 40–50%, without having a remarkable reduction in compressive strength. The mechanical performance of LC3 mixtures mainly depends on the OPC replacement level and clay grade. In a study by Chen et al. [46], the strength development rate and green strength significantly increased with increasing the MK content in the calcined clay. At later ages, the compressive strength of cast specimens was found to be more dependent on the MK content in the calcined clay. The authors concluded that increasing the MK ratio could significantly accelerate the initial cement hydration, which results in higher mechanical performance. Moreover, Avet et al. [24] stated that the compressive strength of the LC3 mixture mainly depends on MK content, regardless of the calcined clay's fineness, compositions, and secondary phases. Although calcined clay with high MK content could improve the mechanical performance of mould-cast cementitious mixtures at an early age, using high-grade calcined clay in 3D printing could lower the mechanical performance of the printed samples due to the increased thixotropy that results in forming cold joints. Chen et al. [18] investigated the effect of different grades of calcined clay on the mechanical properties of 3D-printed LC3 and found that LC3 prepared with medium-grade clays (around 70% MK) showed the highest compressive strength performance. The low mechanical performance when incorporating high-grade clays could be due to the high thixotropy that can allow for the easy formation of weaker interfaces and cold joints [73,74]. In 3D printed cementitious materials, it is typical to find a high amount of air voids between two layers with a weak adhesion in the interface that could be due to the high structuration rate [7,89,90]. According to Avet et al. [25], porosity refinement when incorporating clay with kaolinite

content above 65% results in reaching a critical pore entry radius that slows the reaction and restrains hydrated phase participation, which limits the strength at later ages (28 days). Another critical role that can influence the compression performance of the LC3 system is the OPC replacement level. Various studies have shown that replacing OPC with up to 50% limestone-calcined clay can achieve similar mechanical performance. Nevertheless, increasing the OPC substitution ratio declines the compressive performance of the mixture [57,58]. According to Zhou et al. [91], increasing the substitution level of OPC results in forming fewer hydration products (i.e., C–S–H) due to the less OPC presented, thus, reducing compressive strength.

Unlike cast LC3, 3D printed LC3 had anisotropic properties in compressive strength performance when loads were applied in different directions. Chen et al. [18] found that different LC3 mixtures exhibited the highest compressive strength when loads were applied parallel to the printing direction, as shown in Fig. 8. This anisotropic behaviour could be due to printing quality and weak interface [92]. The better compressive strength performance parallel to the printing path could be due to the more compaction in the printing direction because of movement patterns [92]. In addition, layer weight should be taken into account due to its ability to compact layers and cause variation in compressive performance [7]. Compared to cast specimens, on the one hand, 3D-printed samples have denser microstructure due to intense pressure during printing. On the other hand, 3D-printed specimens and objects have a weaker interface with higher porosity and air content [93, 94], which might lower their performance under compression and causes this anisotropic behaviour.

The gradation and percentage of sand can also influence the compressive strength of mixtures. Shantanu et al. [60] claimed that incorporating well-graded sand enhances the compressive strength of the mixture due to better particle packing compared to uniformly graded sand. Similarly, Long et al. [59] showed that increasing the sand content increases the strength performance of LC3 mixtures due to the better packing density of the mixture. However, increasing sand above a certain level might reduce the binder content that covers aggregates, which decreases compressive performance due to a decline in cohesion.

Superplasticizer was incorporated in different studies to enhance the printability properties of LC3 mixtures. However, its incorporation

Table 3
Compressive strength of 3D-printed LC3 mixtures.

Optimum mix formulation	Compressive strength	Ref
55% OPC, 30% CC, 15% LP, 1.5 wt% superplasticizer, 0.24% VMA	-A significant loss in compressive strength was observed with increasing OPC replacement level with limestone-calcined clay at different test ages. -Increasing the superplasticiser content decreased the compressive strength values.	[57]
40% OPC, 20% HGCC, 20% LGCC, 20% LP	-The LC3 mixture exhibited higher compressive strength values than the reference mixture. -3D printed mixtures exhibited higher strength performance than the cast mixture. -Mixture prepared with 10% HGCC and 30% LGCC had the highest strength values for 3D-printed specimens. 3D-printed specimens containing 20% HGCC achieved lower strength values -The highest compressive strength was obtained when applying load lateral (D2) to the printing direction.	[18]
45% OPC, 33.33% CC, 16.67% LP, 5% SF, and 2.5 S/b ratio	-Increasing limestone-calcined clay content decreased the compressive strength values. -The addition of 5% SF increased the compressive strength. -Mixture prepared with a 2.5 sand-to-binder ratio achieved the highest compressive strength values in all mixtures	[59]
LC3-MS, 0.6% superplasticiser	-Compressive strength results of the LC3 mixture prepared with well-graded sand (MS) were comparable to that of the reference mixture at all test ages. -The LC3 mixture prepared with uniformly-graded quartz sand (QS) had comparable compressive strength to the MS and reference mixtures at 1 day, with lower results at 7 and 28 days.	[60]
LC3 - 0.24%VMA	-Reference cast mixture prepared without VMA exhibited higher compressive strength values than the printed mixtures with different VMA dosages. -Increasing VMA dosage from 0.14% to 0.24% increased the strength performance in all directions. Further increase of the VMA dosage to 0.48% decreased the strength values to a lower level than 0.14%. -All printed specimens exhibited the highest compressive strength when the load was applied parallel to the printing direction.	[5]
40% OPC, 20% low-grade, 20% high-grade and 20% LP	-Compressive strength increased with increasing the MK content in the mixture at all test ages. -All mixtures had higher compressive strength than the reference mixture.	[46]

degrades the early-age mechanical performance of the mixture. According to Ref. [57], increasing the superplasticiser percentage from 1.5% to 2% reduced the compressive strength by around 50% at 1 day, where the effect diminished at later ages beyond 3 days.

3.2.2. Bond strength of 3D-printed LC3

Table 4 presents the impact of different parameters that has been investigated on the bond strength of 3D printed LC3. Interlayer bond strength is believed to be a weakness between two adjacent layers in printed structures [72]. Due to a lack of intermixing between the old and new layers, a weak interlayer adhesion occurs, usually referred to as the cold joint [73,95,96]. Thixotropy dominates the formation of weak

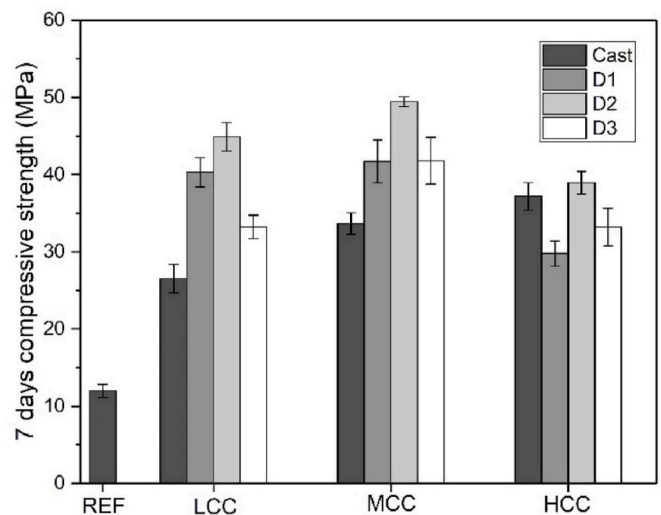


Fig. 8. Compressive strength of cast and 3D-printed LC3 samples at different directions at 7 days (D1: perpendicular, D2: parallel, and D3: lateral to printing path) [18], where LCC is low-grade calcined clay, MCC is medium-grade calcined clay, and HCC is high-grade calcined clay.

Table 4
Impact of different parameters on the bond strength of 3D printed LC3.

Investigated parameters	Bond strength	Ref
Time intervals	-Increasing the time interval decreased the interlayer bond strength.	[5]
-Nozzle standoff distance (0,5 and 10 mm). -Time intervals (20 s, 1 min, and 10 min),	-The bond strength decreased with increasing the time gap. -Using a time gap of 20 s resulted in higher bond strength for the printed specimen than the cast specimen. Increasing the standoff distance up to 10 mm did not induce a critical effect.	[4]
Superplasticiser addition (0.8 and 0.6%)	-A nozzle standoff distance of more than 10 mm resulted in an inaccurate layers' positioning. - Increasing superplasticiser content decreased the 7-day strength results of the cast and 3 d printed samples while slightly affecting the cast's later age bond strength values. - 3D printed specimens with 0.8% exhibited higher strength performance than 0.6% at later ages and were comparable to the cast. - 3D printed specimens exhibited better performance in the lateral direction than in the perpendicular direction.	[97]

interlayer bonds (cold joints) from a material perspective [73]. In addition, bond strength can be affected by the time interval between the succeeding layers and the nozzle standoff distance.

Although, prolonging the time gap between the layers could offer the extruded filaments more time for the evolution of static yield stress, it can lead to decreased bond strength [14,98,99]. There are no specific time intervals, but the printability window (open time) could be a boundary for dividing the time interval length since cement is a time-dependent material. For short time intervals, Tay et al. [89] confirmed that the adhesion between the layers at the interface is affected by the thixotropy behaviour of the deposited mixtures [89]. While for long time intervals, on the one hand, bond strength may be influenced by the printing environment [98,99]. For instance, different studies revealed that the bond strength of deposited layers could exhibit a noticeable reduction under a drying environment [7,90,100]. Sanjayan et al. [101] and Van Der Putten et al. [102] indicated that the

moisture content of the surface of the layer is crucial concerning bond strength. Hence, seeking methods to retain the deposited layers' surface moisture is essential.

On the other hand, the nozzle standoff distance could be changed depending on the change of layers' height since it is challenging to avoid extruded material deformation. Changes in the distance standoff may cause severe or limited effects on the bond strength of the mixture depending on the difference in the contact surface area between the layers. Chen et al. [4] investigated the influence of using three different time gaps (i.e., 20 s, 1 min, and 10 min) and three nozzle standoff distances (i.e., 0, 5, and 10 mm) on the bond strength of 3D printed LC3 mixture and compared it to cast mixture. The authors found that using a time gap of 20 s resulted in around 14% higher tensile strength than the cast mixture. While increasing the time gap to 1 min and 10 min, decreased the tensile strength by 4% and 13%, respectively, compared to the cast specimen. Only a slight decrease in the bond strength resulted from increasing the nozzle standoff distance. The decline in the bond strength with increasing the time gap could be due to the increased local porosity in the interlayer zone, as illustrated in Fig. 9. A stiffer layer surface minimises the deformation in the surface of the bottom layer induced by succeeding layer weight, which could limit the interactive bond space between the layers [89]. That, in turn, increases the unfilled area between layers, causing more macro-pores and increasing the porosity in the interface.

Incorporating additives and admixtures could also influence the bond strength of 3D-printed LC3. Most recently, Ibrahim et al. [97] reported that early age bond strength of the cast and 3D printed samples decreased with increasing superplasticiser content. In contrast, comparable results were obtained for the different ratios for cast samples at later ages. However, for 3D printed specimens, the mixture prepared with 0.8% exhibited higher strength performance at 7 and 28 days than the mixture with 0.6%, which could be due to the difference in the surface moisture content. Moreover, anisotropic behaviour was observed for bond strength depending on the testing direction, similar to compressive strength. Bond strength exhibited comparable values to cast when tested parallel to the printing direction and higher than the perpendicular direction. According to Ibrahim et al. [97], printing

parameters and the strength development of materials influence bond strength. The hydration product formation and chemical compatibility of materials improved between the deposited layers when incorporating limestone-calcined clay due to their synergistic effect, silicate minerals' stick nature in kaolinitic calcined clay, and chemical admixtures incorporation significantly strengthened the bonding strength.

Studies on the LC3 interlayer bond strength are limited. Further research is required to illustrate the effect of varying the mix design, calcined clay grade, and limestone to calcined clay ratio on the bond strength of 3D-printed LC3 mixtures.

3.2.3. Porosity of 3D printed LC3

One of the main advantages of limestone-calcined clay is microstructural refinement induced by the different products formed from the pozzolanic reaction [23,24,45,103]. In addition, the high fineness of limestone particles allows it to act as a filler and reduce porosity [104, 105]. The porosity is mainly affected by the water-to-binder ratio, where decreasing the ratio decreases the porosity of the mixture [46]. Kaolinite content in calcined clay can also affect the porosity of LC3 mixture at early ages. Avet and Scrivener [25] investigated the porosity of different calcined clays with various kaolinite content in LC3. The porosity was found to be depended on kaolinite content at early ages (3 days), showing lower porosity values and finer pore microstructure when calcined clay contains kaolinite content of less than 65%. At 28 days, LC3 prepared with calcined clay containing less than 50% kaolinite content showed significant pore refinement, having finer pore microstructure than OPC. The authors have shown that all LC3 mixture containing calcined clay with a kaolinite content of 40% or more had similar critical pore entry radius of 3–5 nm. In 3D printing technology, printing parameters, such as time interval and nozzle standoff distance, can affect porosity. Chen et al. [4] investigated the effect of different printing time gaps (20 s, 1 min and 10 min) on LC3 interlayer and local porosity and found that the local porosity increases with increasing time intervals between layers. However, the total porosity of the different mixtures was comparable, except for cast and 10 min time intervals, as shown in Fig. 10a. Extending time gaps between layers could increase the concentration of macropores along the interface (see Fig. 9), which

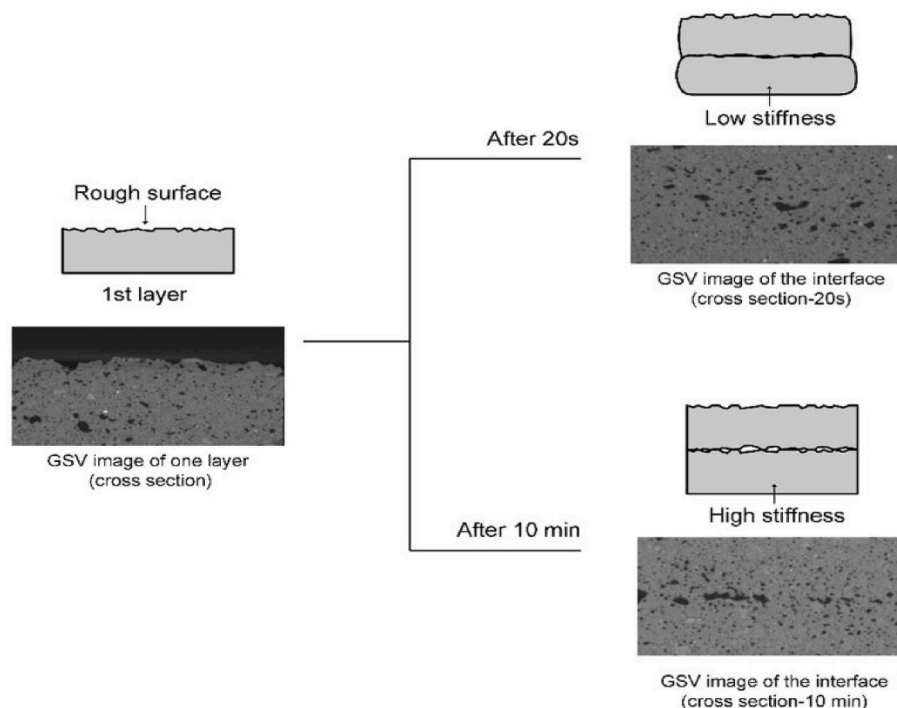


Fig. 9. The influence of different time gap intervals on the interface of the 3D printed specimens [4].

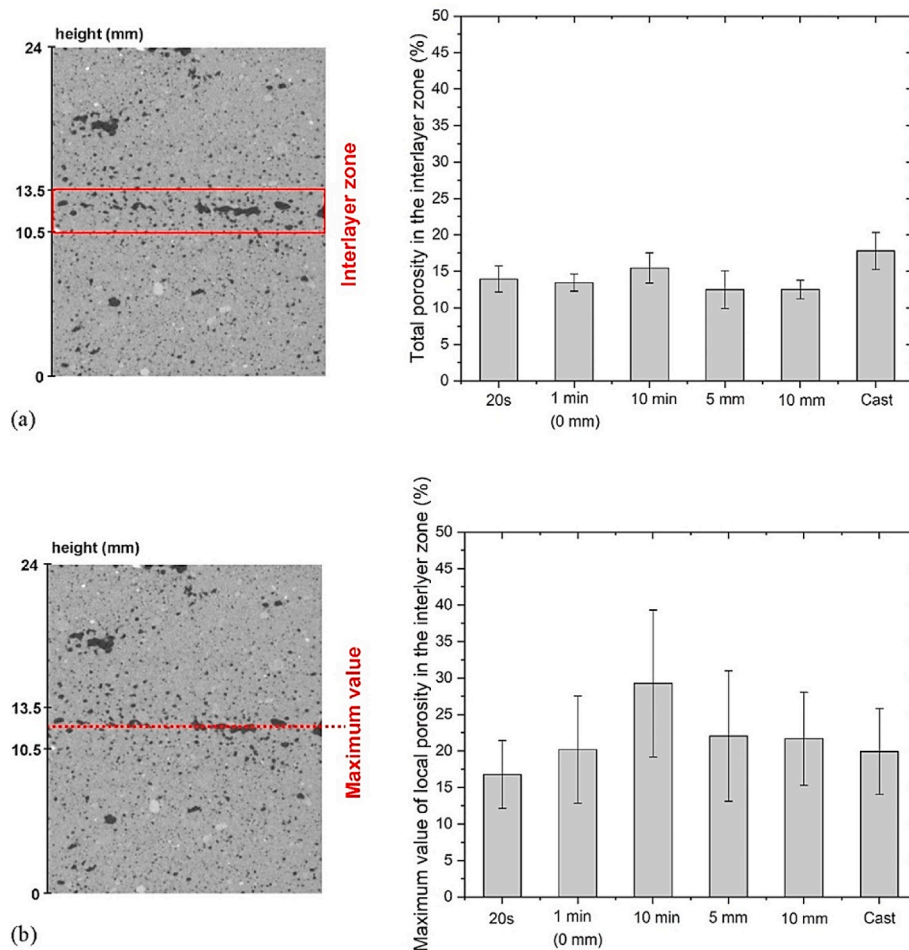


Fig. 10. (a) Total porosity in the interlayer zone and (b) maximum local porosity in the interlayer zone [4].

increases the local porosity value, as shown in Fig. 10b. According to Ref. [89], at short time intervals, the load induced from depositing succeeding layers would rearrange the top surface of the substrate layer, increasing the interacted area between the two layers. However, increasing the interval time would allow more time for the stiffness growth of the substrate layer, which decreases the changes that could occur when depositing the successive layer and, in turn, limits the interacted bond areas between layers and increases macropores formation. In this study, the authors have also studied the effect of different nozzle standoff distances (5 and 10 mm) on LC3 porosity and obtained similar total and local porosity values, as shown in Fig. 10(a and b).

VMA was used in different studies to enhance the various properties of the mixtures. Incorporating VMA increases the porosity of the mixture [61,106]. For instance, Chen et al. [5] investigated the effect of adding different dosages of VMA (i.e., 0.14%, 0.24% and 0.48% by weight of the binder) and found that the optimal dosage of VMA is 0.24%, which achieved the lowest porosity. According to the authors, porosity is affected by the adhesion between the two layers, which is affected by the rheological properties of the lubrication layers. The lubrication layer viscosity should not be too low since it would contain higher water content, thus, increasing the porosity. At the same time, the viscosity should not be too high because it would increase the extrusion pressure and the porous microstructure in the layer and the interface [5]. Therefore, it is preferable to control and optimise the used dosage of VMA to avoid degradation in the other properties. Based on the different studies that investigated the effect of VMA dosage on LC3 properties [5, 57], the optimum dosage of VMA for 3D printing could be recommended as 0.24% by the weight of the binder with considering optimising the

superplasticiser content in the mixture.

4. Environmental sustainability of LC3

A comparison between different construction methods has revealed that 3D concrete printing produced the lowest CO₂ emissions and it can become the most sustainable construction method in near future [107]. However, the concrete mixture used in 3D printing requires higher amounts of OPC binder than the traditional casting method [11], which makes the research on environmentally-friendly alternatives to OPC vital [108]. The impact of replacing OPC with limestone-calcined clay on CO₂ emissions and energy consumption has been studied using life cycle assessment (LCA) [109]. It was found that replacing cement with limestone-calcined clay significantly lowered CO₂ emissions to 610 kgCO₂/tonne of cement and energy consumption to 4850 MJ/tonne of cement compared to that of OPC of 930 kgCO₂/tonne of cement, 5945 MJ/tonne of cement in traditional cast method. LC3 had also lower CO₂ emissions than pozzolanic Portland cement (PPC) prepared with fly ash that exhibited 680 kgCO₂/tonne of cement but with slightly higher energy consumption, in which PPC requires 4690 MJ/tonne of cement.

Common SCMs are derived from industrial applications and activities, such as fly ash [110,111], silica fume [112], and other naturally obtained SCMs like limestone [113–115]. Clay can be considered an environmentally friendly SCM. However, unlike the other common SCMs, clay needs to be processed and calcined to be used. The production of calcined clay requires lower energy and generates fewer CO₂ emissions than OPC, which helps decrease the negative environmental impact by using blended cement containing those SCMs with

maintaining similar performance. The energy required for clay calcination was reported to be around 60% of that to produce OPC [116]. In addition, CO₂ emissions from clay calcination are almost 30% of that from OPC manufacturing. Long et al. [59] selected mixtures having similar properties to the reference mix to allow for a reasonable evaluation of different mixtures' environmental impact. The results showed that the various composites prepared with limestone-calcined clay and silica fume as a replacement to OPC had around 41–50% lower greenhouse gas and 39–45% less energy consumption than the reference mixture. Malacarne et al. [117] investigated the environmental performance of LC3 mixtures prepared with four different types of Brazilian clays compared to OPC and found that LC3 had lower greenhouse gas emissions by around 38% than OPC. According to authors' findings, clay sources did not significantly change the impact on global warming potential (kg of CO₂ produced).

Unlike OPC production, the main causes of greenhouse gas in calcined clay production are clay extraction and processing, followed by calcination. Different studies reported that calcined clay could be responsible for producing CO₂ emissions in the range of 150–300 g/kg [30,118,119]. Berriel et al. [109] compared the environmental impact between OPC, blended cement containing 15% zeolite and LC3 systems under three different technological levels, namely Pilot (no investment), Industrial (low investment), and Best Available Technology (BAT) (massive investment). The authors found that LC3 had the lowest impact whatever the technological level used, as shown in Fig. 11. The reduced emissions of LC3 were not from the calcination process only but also from energy savings from LC3 crushing and grinding due to its softness compared to OPC. Although, LC3 can reduce emissions, the availability of clay sources plays a significant role in LC3 production. Hence, the environmental impact depends on the transportation type and location distance to the plant.

5. Economic feasibility of 3D printed LC3

Using 3D printing technology could provide potential cost savings. Implementing 3D printing offers suitable economical solutions in terms of required manpower, material saving, and energy. That will also be reflected in lowering the number of co-workers for formwork preparation, decreasing the overall cost by around 50% or more [120]. Compared to the different construction methods, the concrete 3D printing system is more economical, where the overall cost in one of the studies was divided into 55% construction cost and 45% material cost [107]. The total cost of construction can be further decreased when employing the 3D printing method by implementing different approaches, including using alkali-activated materials and blended cement

to reduce the cost of printing materials, using 3D printing hollow structures or incorporating industrial by-products and recycled aggregates [121–123]. Moreover, the construction cost could change depending on the printing technique, material delivery systems, and process precision. Hence, the machinery and the cost change depending on the method used. The machinery can be categorised into unconventional construction equipment (UCE) and conventional construction equipment (CCE). Often CCE, such as a piston pump, can deliver the material to the print head. While for extrusion and printing, a print head in new equipment with a multi-functional complex design is needed. Indeed, for a successful industrial implementation, a print head should be fitted with sensors that continuously track the evolution of material properties for data feedback and active rheology control and should be flexible to change in size and shape. With all these advancements, print heads will become a substantial cost factor [3]. It is expected that price of 3D printing technologies fall due to the industrial competition [124]. However, some challenges might face the owner of the printers since its new to the construction industry, including the availability of spare parts and the lack of expertise for maintenance. The operational and maintenance cost of a 3D printer was estimated to be 75\$/h [125,126].

Different studies have confirmed the economic feasibility of cast LC3 in various scenarios [109,127,128]. The economic assessment differs from one country to another depending on the locally used materials since the alternative feasibility must be compared to that of the product that has the potential to replace. Different factors can influence the economic viability of the material, like transportation mode and distance and availability of the material. In addition, since LC3 composes of raw material (i.e., clay) that needs to be calcined and processed, processing plays a significant role. Berriel et al. [109] assessed the economic potential of LC3 prepared using four different types of Cuban calcined clay by performing Capital and Operational Expenditures. The authors indicated that changing technology or fuel type changes production costs. Moreover, depending on the type of transportation used, production cost tends to increase with increasing the transportation distance. Nevertheless, there are limited cost analysis on LC3 compared to other cementitious binders, especially in 3D printing application.

6. Conclusions and future prospects

Utilising limestone calcined clay cement (LC3) in 3D printing technology presents several advantages over traditional concrete systems. This paper focused on reviewing materials properties of cast and 3D printed LC3, the environmental impact and cost assessment of cast LC3. The following conclusions can be drawn from this review.

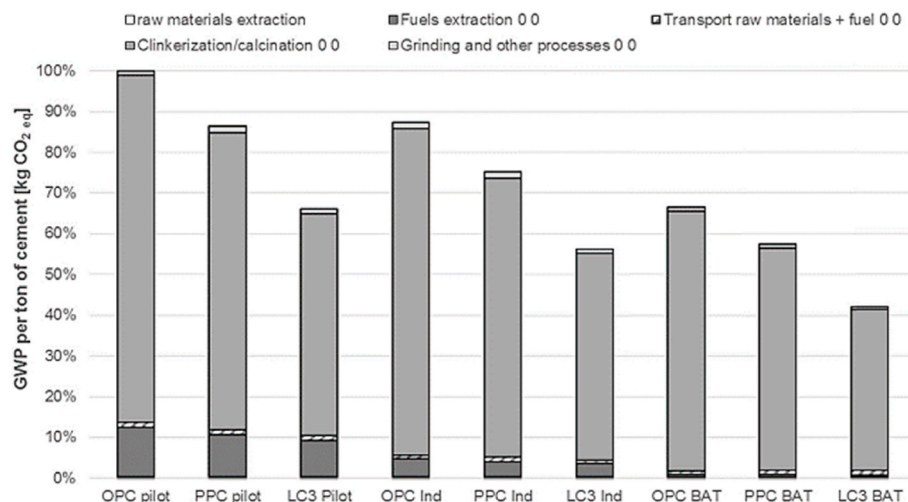


Fig. 11. Global warming's potential impact on different scenarios of cement production in Cuba [109].

- 1 The rheological properties and thixotropy of the mixture increase when incorporating limestone-calcined clay, where using high-grade clays or increasing replacement levels could further modify rheological performance. Nevertheless, a higher replacement level and using high-grade clay content can lower the mixture's flowability, extrudability and open time. Moreover, incorporating additives and admixtures can modify the rheological parameters of LC3, at the same time, influence other printing properties.
- 2 Increasing the replacement level can enhance the buildability of the LC3 mixture. Similarly, using high-grade clay could improve the buildability. In addition, nozzle shape and geometrical properties affect the buildability of the mixture.
- 3 Metakaolin content in calcined clay plays a key role in influencing the cementitious mixture's different properties and in the printable mixtures' performance. Although, incorporating high-grade calcined clay in cast method is preferable and provide better performance, using high-grade calcined could lower the mechanical performance of 3D printed LC3. Moreover, high replacement level can also lower the mechanical performance of both cast and 3D printed LC3.
- 4 Printing parameters (i.e., nozzle standoff distance and time gap intervals), layer surface moisture content and additives incorporation affect the bond strength behaviour of 3D printed LC3 mixture.
- 5 Production of LC3 mixtures can lower economic and environmental impacts compared to that of OPC. However, the economic and environmental feasibility tends to depend on the availability and location of clay sources.

The implementation of LC3 in 3D printing applications is still new. Hence based on the presented review, further research studies are needed to fulfil the research gaps. For example, more studies on different types of additives and admixtures on the printing properties (extrudability, printability, and buildability) are needed. Most studies have reported the impact of different parameters on compressive strength and fresh properties. Hence further research is needed to investigate the effect of different mix designs, additives, admixtures, printing parameters and mixing time on the bond strength and porosity of 3D printed LC3. Moreover, the durability and flexural strength of 3D-printed LC3 mixtures must be investigated since most studies focus on investigating the compressive strength performance of printed mixtures. Although the open time of LC3 mixtures is suitable for 3D printing, more studies should consider the effects of different parameters and admixtures on the large-scale delivery of the material to the extruding nozzle. Moreover, the impact of incorporating different additives and admixtures on the flowability and slump performance of the mixtures should be further investigated since it could indirectly indicate the performance of the printing mixtures. Further studies should be executed on analysing the environmental and economic benefits of LC3 and employment in 3D printing applications compared to other binder systems.

Credit authors statement

Yazeed A. Al-Noaimat: Data curation, Methodology; Validation, Investigation, Writing - Original Draft, Visualization. Mehdi Chougan: Writing - Review & Editing, Data curation. Mazen J Al-Kheetan: Writing - Review & Editing, Validation. Othman Al-Mandhari: Writing - Review & Editing, Validation. Waleed Al-Saidi: Writing - Review & Editing, Validation. Marwan Al-Maqbali: Writing - Review & Editing, Validation. Haitham Al-Hosni: Writing - Review & Editing, Validation. Seyed Hamidreza Ghaffar: Conceptualization, Methodology, Supervision, Writing - review & editing, Resources, Writing - Original Draft, Visualization, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

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