



Calcined Marl and Clays as Alternative Materials for Cement Substitution

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Abstract

Transitioning to more sustainable materials than cement is vital for reducing the carbon emissions and ecological footprint associated with cement production. Ternary cement blends, particularly Limestone Calcined Clay Cements (LC3), are gaining attention as sustainable alternatives to Ordinary Portland Cement to reduce clinker content. Three clay samples from the western area of Chania, Crete, Greece, were calcined at 700 °C and reacted with saturated lime to assess their pozzolanic activity as potential cement substitutes. Additionally, a local marl was calcined at 800 °C and then hydrated to evaluate its binding capacity for designing mortars with hydraulic binders. The silica and alumina minerals in the calcined clays and marl, after reacting with lime and undergoing hydration, produced respectively calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H), which contribute to the hardening of plasters and mortars. The study includes Attenuated Total Reflection (ATR-IR) analysis, compression tests on mortar samples aged 1 to 4 months, and workability tests on fresh mortars. The results found that calcined clays, particularly metakaolin-rich samples, reacted more significantly with lime compared to those with high calcite content and low kaolinite. Mortars containing clays and lime required a similar water-to-binder ratio to achieve workability comparable to cement-based mortars. Compressive strength showed that the portlandite produced from the hydration of the marl was insufficient to fully react with calcined clay and cement to form C-S-H. This paves the way for ongoing studies to identify the minimum and optimal lime content required to effectively promote the hydrolysis reaction forming C-S-H, in accordance with LC3 principles.

Keywords Calcined marl · Calcined clay · Pozzolanic activity · Hydration · Cement substitution

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Introduction

The construction sector is poised to play a pivotal role in the global transition to more sustainable development practices. At present, the industry is responsible for roughly 50% of all materials consumed worldwide, 40% of energy use and total solid waste generation, 12% of potable water consumption, and accounts for 5 to 8% of total anthropogenic CO₂ emissions [1]. Achieving efficiency improvements and optimising resource use across the entire value chain will be essential to decoupling the construction sector's economic growth from significant environmental impacts and unsustainable depletion of natural resources.

Efforts to advance sustainable binders are especially urgent due to the significant environmental impact associated with the production of Ordinary Portland Cement (OPC). In recent years, global cement production has surged, making it the third-largest source of anthropogenic carbon dioxide emissions, after fossil fuel consumption and land-use changes [2, 3]. Supplementary cementitious materials (SCMs) are effective for partially replacing clinker in cement production, providing economic and environmental benefits without compromising performance. Common SCMs include coal fly ash, slags, and limestone powder [4–6]. The use of SCMs has steadily increased, lowering the clinker factor from 0.84 in 1990 to 0.77 in 2010 [7]. However, since the early 2010 s, the clinker factor has stagnated around 0.75 due to SCMs reaching their incorporation limits, either because of lower reactivity or supply constraints, such as limited availability of metallurgical slags [7].

To address these limitations and further reduce the clinker content in cementitious materials, ternary cement blends have garnered significant attention. Limestone Calcined Clay Cements (LC3) have emerged as sustainable alternatives to Ordinary Portland Cement, where clinker is partially substituted by calcined clay (CC) and finely ground limestone powder (LP, i.e., calcium carbonate). When combined, the pozzolanic activity of CC and the filler effect of LP are enhanced by synergistic reactions, forming carboaluminate phases [8].

Clays are abundant materials found worldwide. Clays with a significant kaolinite content have shown to possess excellent pozzolanic properties when calcined at temperatures ranging from 700 to 850 °C [9]. Furthermore, various studies have investigated the influence of calcination temperature [10], clay mineralogy [11], and particle size [12] on the performance of calcined clays as pozzolans, showing that these factors play a crucial role in optimizing their reactivity and the overall sustainability of cementitious materials.

For many years, a highly reactive mineral additive called “metakaolin” has been produced through the calcination of high purity kaolinitic clays [13].

Pozzolans are siliceous and aluminous materials that can react with lime (CH) at ambient temperatures to form hydrated calcium silicates (C-S-H) and aluminates (C-A-H), resulting in suitable mechanical strengths for mortar production [14]. Natural pozzolans include volcanic materials, zeolite deposits, diatomaceous earth, opaline cherts, shales, and tuffs. Artificial pozzolans can be produced through heat treatment of clays, earths, and shales, or as industrial by-products such as fly ash, silica fume from silicon smelting, and burned organic materials rich in silica, like rice husk ash [15]. These pozzolanic additions enhance durability and compressive strength by refining pore size distribution and structure through the formation of hydraulic C-S-H and C-A-H products, which harden the mortar. The extent of C-S-H and C-A-H formation depends on several factors, including the quality and quantity of active phases in the pozzolan, the type of thermal treatment, the Si/Al molar ratio, the

lime-to-pozzolana ratio in the mix, the water-to-binder ratio, curing conditions, and specific surface area [16].

Previous studies have examined calcined clay/saturated CH mixtures to assess lime reactivity over time. The results indicated that lime was consumed within up to 30 days, but at varying rates [17]. The metakaolinite-rich clays fully reacted with lime within one week, while the other clay required a month. The lime reactivity was influenced by the clay's chemical and mineralogical composition, particularly its low calcite content and significant kaolinite presence. Additionally, the calcined marl developed hydraulic properties after one month of slaking, suggesting its potential as a natural hydraulic lime binder [17].

Building on previous studies, this research examines local clays and a marl sourced from natural deposits in the western region of Crete, Greece, which were calcined at temperatures of 700 °C and 800 °C, respectively. Specifically, we aim to determine whether the silica and alumina minerals in calcined clays and marl can effectively react with lime, produced from cement through hydrolysis, to form calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H). This reaction is crucial, as the formation of the hydrates is directly linked to the strength and durability of concrete.

Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) was performed on pastes made with CEM, CH and each type of calcined clays, and analysed at 1 month to assess pozzolanic activity in early stage. This technique was used to examine the surface composition of the materials, allowing for the identification of chemical bonds and functional groups present in the samples. Similarly, mortar samples were prepared, and their workability in the fresh state was assessed, followed by an analysis of mechanical properties, such as compressive strength, after 84 days.

Materials and Methodology

Mix Details

As a binder, in combination with commercial CEM I 42.5R, several materials have been evaluated as potential substitutes for cement to enhance sustainability.

As represented in Fig. 1, three clay samples were collected from various locations in the western region of Chania, Crete: Church of Vouves (CB), Metohi (ME), and Giamlidika (GM), while the marl is collected in Alonia (AL). The sampling areas were selected due to the traditional use of local clays in kilns for producing domestic ceramic vessels. The sampling areas, chosen for their historical use of local clays in traditional kilns to produce domestic ceramic vessels, are characterized by clay formations with uniform color. After collection, the clay samples were ground to a particle size smaller than 63 µm. The three clays - CB, ME, and GM - were selected for their high pozzolanic activity, as determined by the Luxán method [4] and highlighted in previous research [5], and were heated to 700 °C. In addition, the marl, AL, was heated to 800 °C. The heating process was conducted in a box kiln with a controlled heating rate of 10 °C per minute.

The studied clays (CB, ME, GM) consisted mainly of quartz, illite, calcite, plagioclase, while in two clays (CB and GM) kaolinite was also identified [18].

Previous studies have reported that the chemical analysis of clays revealed a CaO content not exceeding 6% (w/w), with SiO₂ ranging from 76 to 82%, and aluminum and iron oxides

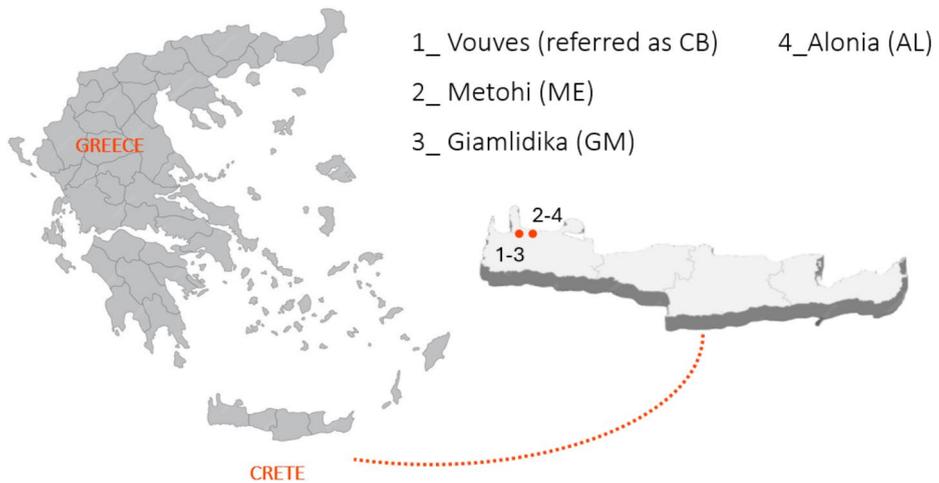


Fig. 1 Raw material locations in the western region of Chania, Crete: Vouves (CB), Metohi (ME), Giamlidika (GM), and Alonia (AL)

Table 1 Mix composition ratios (per weight) for pastes (P) and mortars (M)

Sample designation	Paste: P Mortar: M	CEM	Clays			Marl		Sand/binder	CH	W/B
			CB	ME	GM	AL				
CEM (reference)	P	1	-	-	-	-	-	-	0.35	
	M	1	-	-	-	-	3	-	0.60	
CEM_CB	P	1	0.60	-	-	-	-	0.3	0.40	
	M	1	0.54	-	-	0.27	3	-	0.65	
CEM_ME	P	1	-	0.60	-	-	-	0.3	0.42	
	M	1	-	0.54	-	0.27	3	-	0.63	
CEM_GM	P	1	-	-	0.60	-	-	0.3	0.41	
	M	1	-	-	0.54	0.27	3	-	0.63	
CEM_CH	P	1	-	-	-	-	-	1	0.48	
	M	-	-	-	-	-	-	-	-	

making up less than 9%. The marl (AL) primarily consists of 67% calcite and 20% silicon dioxide [17], which can be considered as a source of low feebly hydraulic lime.

Standard quarried sand was used with grains ranging from 0 to 4 mm from Crete. The mix proportions and water-to-binder ratios for pastes (P) and mortars (M) are summarised in Table 1, the same mixing and casting protocol were used throughout the duration of the experimental programme. In Fig. 2 the raw materials are depicted, including cement, clays (CB, ME and GB) and marl (AL).

For the mortars preparation: the dry materials (cement, clays, marl, fine sand) were mixed by hand for 30 s, the water was added as described in “Workability Test” section. It is important to note that slight adjustments to the water-to-binder ratios were made to achieve the desired workability (16 ± 1 cm) in accordance with EN1015 - 3 [19]. The 40 mm square moulds were filled in two layers and gently tapped to level the surface and remove any trapped air bubbles. For 2 days after casting the samples were kept in the moulds in extrac-

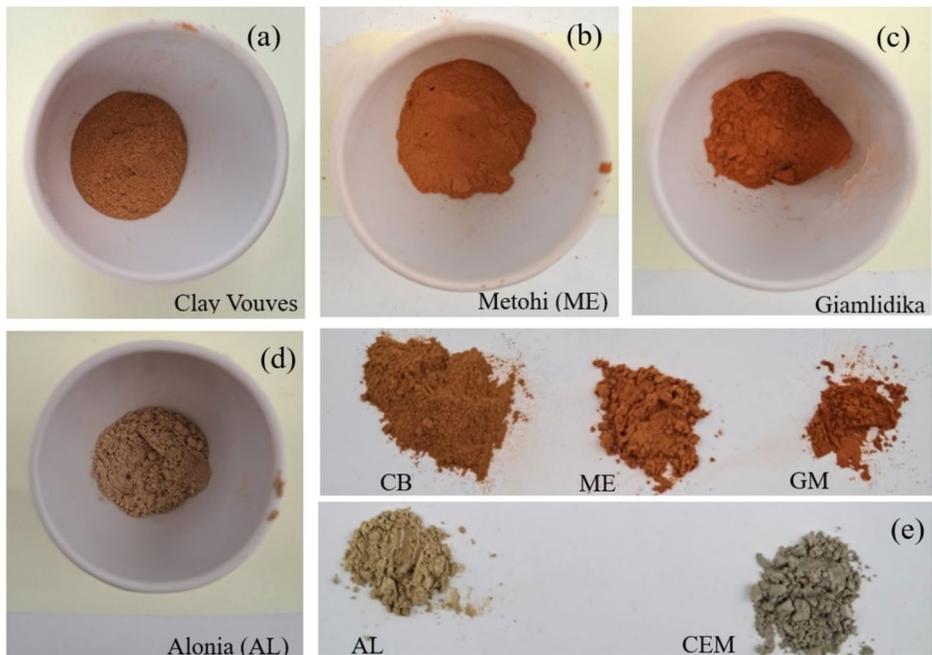


Fig. 2 Raw materials: clay CB (a), clay ME (b), clay GM (c), limestone AL (d), CEM (e)

tion hood ($20\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$, $\text{RH} \sim 65\%$); after this, samples were demoulded and placed in a container with controlled environmental conditions ($20\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$, $\text{RH} \sim 65\%$) for 23 days.

A different approach was taken for pastes' preparation, as the goal was to detect the pozzolanic reaction between calcined clays and lime in the presence of cement. Therefore, in each paste cement, lime and calcined clay were mixed and kept in the same conditions as the designed mortars. Assessing pozzolanic activity after one month was crucial to gaining insights into the early-stage performance of mortars with cement substitution.

Attenuated Total Reflection (ATR-IR)

Total Reflection (ATR) measurements were conducted using an integrated, all-reflective diamond as the internal reflection element to characterize lime mortar samples aged four months. The chemical structure of the paste and mortar surfaces over time was examined by studying the functional groups, using Attenuated Total Reflection – Fourier-Transform Infrared spectroscopy (ATR-FTIR). Analyses were performed on a Nicolet™ iS50 FTIR Spectrometer equipped with a diamond ATR accessory (Thermo Scientific, USA). Spectra were obtained with Thermo Scientific's OMNIC software. Spectrum acquisition was done after 32 scans for absorbance numbers between 4000 and 400 cm^{-1} , with a scan resolution of 4 cm^{-1} . A background scan was performed at the beginning of each session and repeated after approximately 30 min, to ensure the quality of the acquired spectra.

Workability Test

As is well known, water content is a crucial factor influencing the workability of mortars, as it directly affects initial flow. Given the numerous variables that impact mortar workability—such as the quality and quantity of aggregates and binders—an effective approach to determine the correct water amount is to specify an optimal initial flow. This measurement considers various factors affecting workability, including the porosity, size, and shape of aggregates, the type of binder, and the aggregate-to-binder ratio.

The initial flow was assessed according to EN 1015 - 3 [19]. Each of the five mortars was combined with the appropriate amount of water to achieve three specific initial flow values: 165 mm, in diameter. To measure the initial flow, a truncated cone mold was placed on a flow table and filled with freshly mixed mortar. After removing the mold, the flow table was mechanically raised by 10 mm and then dropped at a rate of once per second for 15 s. This process allowed the mortar to spread outward, progressively increasing the flow diameter. The final diameter of the mortar (initial flow) was then measured in millimeters.

If the flow was too high, the sample was discarded, and mixing commenced again. If the flow was too low, additional water was added, and the batch was mixed for another minute to ensure even distribution of the water (the entire process lasted approximately 1.5 min to prevent significant setting of the lime). The flow test was then repeated.

Compression Test

Uniaxial compressive tests were performed on three 40 mm cubes at 84 days to evaluate the compressive strength. Tests were conducted at a load control rate of 2.4 kN/s using a Digi Max Controls testing machine, in accordance with EN 1015 - 11 [20]. The mean of three readings was taken as the compressive strength and the coefficient of variance calculated.

Results

ATR-IR Spectra Comments

In Fig. 3, the FTIR spectra of the pastes comprising lime, cement and calcined clays after curing for one month (A), along with the mortars with cement substitution with calcined clays and marl after curing for 4 months (B) are illustrated.

In the lime-cement (a) and lime-cement-clay pastes (b), (c) and (d) illustrated in Fig. 3A, calcite is formed as indicated by the double peak at $1400\text{--}1500\text{ cm}^{-1}$ and was also noticed by other authors [21]. Since only a negligible quantity of calcite was found in the unheated sample, it can be inferred that the calcite detected after reaction with lime resulted from the carbonation process of portlandite. However, portlandite still exists as indicated by the peak at 3640 cm^{-1} and is related to the unreacted ingredient of the paste and the neofomed one with the hydration of both cement and the hydraulic components formed from the reaction of calcined clays with lime. Furthermore, the shoulder in the $1100\text{--}950\text{ cm}^{-1}$ range indicates hydraulic component formation in the samples with calcined clays.

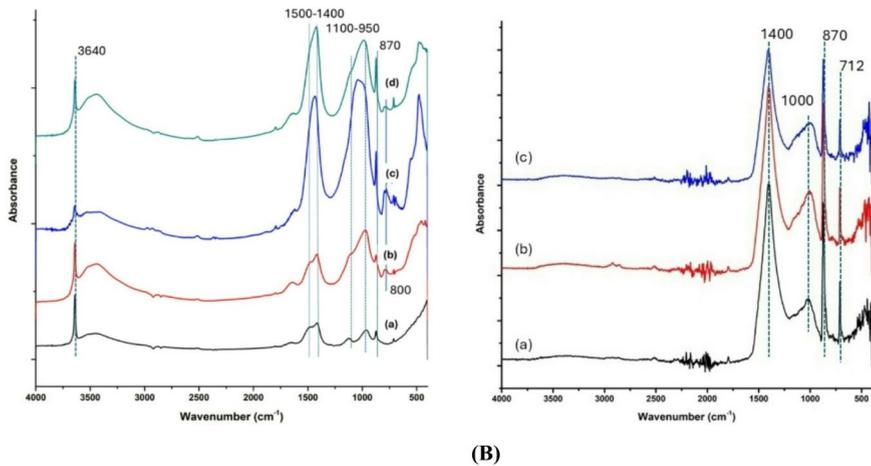


Fig. 3 FTIR spectra of: **(A)**: Pastes of CEM_CH (a), CEM_CB (b), CEM_ME (c), CEM_GM (d) after one month curing and **(B)**: Mortars of CEM_CB (a), CEM_ME (b), CEM_GM (c) after 4 months of curing

Table 2 Workability and compression tests results

Sample designation	Initial flow (mm)	Notes on workability	Compression strength MPa (CoV%)
CEM (reference)	160–165	Good, slightly dry	32.7 (1)
CEM_CB	160–165	Good, easy to work with	14.2 (1)
CEM_ME	160–170	More workable than others	13.6 (2)
CEM_GM	160–165	Good, easy to work with	14.5 (3)

On the other hand, in mortars containing cement, calcined clays, and marl, there is no clear evidence of hydraulic compound formation (Fig. 3B). However, the absence of portlandite in these samples may be attributed to carbonation and pozzolanic reactions.

Workability and Compression Strength

As previously mentioned, workability is often evaluated qualitatively by craftsmen, making it beneficial to describe mortar consistency using verbal descriptions. Table 2 summarised the results of both workability and compression tests.

The entire set of mortars containing clays in conjunction with lime appeared to require a similar water-to-binder ratio to achieve workability levels comparable to those of the cement-based mortar. This consistency in water requirements indicates that the inclusion of clays does not significantly affect the overall hydration behavior necessary for achieving optimal workability. There was a slight tendency towards a drier consistency observed in the CEM_ME mortars. In terms of compression strength values, low coefficients of variation (CoV) indicate that the results are reliable and consistent. As a matter of fact, the mortar composed of clays and marl as substitutes for cement demonstrated a decrease in compres-

sive strength, achieving a maximum value of 14.5 MPa -in the case of CEM_GB- compared to the reference strength of 32.7 MPa. The results aligned with the FTIR analyses, indicating that the portlandite from marl hydration was insufficient to fully react with calcined clay and cement to form C-S-H.

However, it is important to note that the single value tested at 84 days does not accurately reflect the overall mechanical behavior of the mortar. While this initial assessment provides valuable insight, it does not account for the long-term performance that may emerge as the material continues to cure. It is well established that hydraulic binders typically exhibit low curing rates, meaning their strength development can extend well beyond the initial testing period. Therefore, additional evaluations over time are necessary to fully understand the strength characteristics and durability.

Conclusion

In this study, local clays and marl sourced from natural deposits in the western region of Crete, Greece, were calcined at temperatures of 700 °C and 800 °C, respectively, to evaluate their feasibility and performance in combination with commercial CEM I 42.5R (CEM) for enhancing the sustainability of mortars. The sampling areas were selected for their historical significance in utilizing local clays for producing domestic ceramic vessels in traditional kilns. Utilising local clays not only fosters sustainability but also strengthens local economies while preserving traditional practices.

The reaction of calcined clays with lime, as indicated by the study of the reaction with lime in the FTIR, is more pronounced in the samples with metakaolin, such as CB and GM than ME, which contained insignificant kaolinite quantity and the highest calcite quantity. The study found that mortars containing clays and lime require a similar water-to-mortar ratio to achieve workability comparable to cement-based mortars, indicating that the inclusion of clays does not significantly alter hydration behavior. Compression strength values showed low coefficients of variation (CoV), suggesting reliable and consistent results. However, the use of clays and marl as substitutes for cement led to a decrease in compressive strength, with a maximum value of 14.5 MPa for CEM_GB compared to a reference strength of 32.7 MPa. The contribution of calcium carbonate from ME and AL alone is not sufficient to produce portlandite that can react with cement and calcined clays to form calcium silicate hydrate (C-S-H). As a result, the calcined clays act as inert inclusions that do not participate in the hydrolysis reaction, which is essential for gaining strength over time.

Ongoing studies aim to assess the minimum and optimum lime content needed to effectively facilitate the hydrolysis reaction that leads to the formation of calcium silicate hydrate (C-S-H). These studies will examine various boundary conditions, including the specific ratios of calcined clay to lime, as well as the water-to-binder ratios.

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Data Availability The data presented in this study are available on request.

Declarations

Ethics Approval and Consent to Participate Not applicable.

Consent for Publication All authors have read and agreed to the published version of the manuscript.

Conflict of Interest The authors declare no conflicts of interest.

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