

Article

Calcium-Based Wastes as Additives or Binder Substitutes in Mortars: Experimental Research with Oyster Shells or Lime Kiln Dust, Quicklime and a Modified Vinegar Solution

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Abstract

Lime kiln dust (LKD), a by-product of the paper industry, generates about 100 tonnes of waste per 400,000 tonnes of kraft paper produced, while global aquaculture yields more than 16 million tonnes of oysters annually, 65–90% of which is made up of shells. This study explores their valorisation in the production of more eco-friendly mortars by partially replacing hydrated lime with LKD and oyster shell powder (OSP). In addition, a vinegar solution (VS), prepared by reacting oyster shells with white vinegar (~5% acetic acid), was used as an alternative mixing liquid instead of water. The LKD and OSP were tested at different substitution levels, showing promising mechanical performance, supporting their use as sustainable alternatives in mortar production. Replacement levels of 25%, 50% and 90% achieved compressive strengths ≥ 0.4 MPa at 28 days. At 28 days, the reference lime mortar prepared with water reached 0.83 MPa, while the use of the vinegar solution increased the compressive strength to 1.86 MPa, representing an improvement of approximately 124%. Regarding binder replacement by wastes, the most efficient mechanical performance was obtained for mixtures with 50% LKD substitution, reaching 2.04 MPa at 28 days and 3.11 MPa at 60 days, increasing by 10% and 43%, respectively, while mixtures incorporating oyster shell powder showed more stable mechanical behaviour across substitution levels. Using a hot-mixing process with quicklime in the presence of the vinegar-based solution and sand may account for the higher strengths, due to the heat/steam generated during lime hydration prior to moulding and verified by microscopy. In addition, VS-containing mixes showed higher aragonite contents and detectable phosphorus-bearing compounds, which may further contribute to matrix densification and strengthening. Overall, the results indicate that the combined use of uncalcined calcium-based wastes and a vinegar-based solution can contribute to the development of calcium-based mortars with good mechanical performance, supporting circular economy strategies and the reduction in calcined-binder use in construction materials.



Received: 24 October 2025

Revised: 13 January 2026

Accepted: 27 January 2026

Published: 10 February 2026

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Keywords: vinegar-based solution; eco-efficient binders; hot lime mortars; lime kiln dust; oyster shells; circular and blue economy

1. Introduction

Lime-based mortars have been widely used in construction for centuries due to their workability, breathability and compatibility with historic structures. However, the production of lime, particularly quicklime (CaO), involves calcination processes that contribute

to carbon dioxide (CO₂) emissions and energy consumption. The calcination of limestone (CaCO₃) to produce lime releases up to 1.33 tons of CO₂ emitted per ton of lime produced (primarily due to the decomposition of calcium carbonate and the high energy demand of the process, which varies depending on the energy source [1]). This highlights the need for sustainable alternatives to reduce the environmental impact of lime-based materials, even though a large part of the carbon can be recaptured during the long process of mortar carbonation throughout its useful life. The adsorbed CO₂ amount may be 0.79 t of CO₂, based on the chemical reaction [1].

In recent years, to reduce the carbon footprint of lime mortars the research has focused on the following approaches:

(i) The use of pozzolanic materials, such as metakaolin, fly ash and ground granulated blast-furnace slag (GGBS), which react with lime to form additional calcium silicate hydrates (C-S-H), improving the mortar's performance [2–4] and reducing the amount of lime; (ii) the use of more sustainable energy sources; (iii) new calcination processes; (iv) the use of calcium-based residues, such as eggshell [5] powder and oyster shell [6,7] powder incorporated into lime mortars (as binder replacement or aggregate), providing a sustainable source of calcium carbonate and reducing the demand for virgin raw materials [5–7]; and (v) the use of bio-based additives, such as cellulose fibres and starch derivatives, has been explored to enhance the workability and water retention properties of lime mortars, further contributing to their sustainability [4]. Within this framework, oyster shell residues and lime kiln dust (LKD) represent materials with high sustainability potential in construction, as they are mainly composed of calcium carbonate. However, their valorisation in lime-based mortars remains limited by the industrial difficulty of shell calcination, due to the reduced shell size compared to limestone, the lack of noncalcination processing routes and the limited recovery pathways for lime kiln dust generated by the paper industry.

In this context, the main objective of this research is to develop eco-efficient, lime-based mortars with a reduced content of calcined binders through the valorisation of calcium-rich industrial and biogenic residues. Specifically, this study investigates the combined use of lime kiln dust from the paper industry (LKD) and uncalcined oyster shell powder, together with a vinegar-based calcium solution (VS), obtained by reacting oyster shells with commercial white vinegar, as an alternative mixing liquid to enhance system reactivity without thermal treatment.

The originality of this work lies in the simultaneous integration of three underexplored strategies: (i) the use of LKD from the paper industry as a partial substitute for quicklime in mortars, (ii) the valorisation of uncalcined oyster shells as a calcium source, and (iii) the application of a vinegar-based solution as a low-energy chemical activation route. To the authors' knowledge, this is the first study to combine calcium-based wastes and vinegar activated by the calcium of oyster shells in lime-based mortars, addressing a clear research gap in the development of low-carbon, calcium-based construction materials.

1.1. Oyster Shell and Related Studies

Global oyster production reaches approximately 6.1 million tons annually [8,9], between 65% and 90% of which is made up of shells, depending on the species [9]. It is estimated that around 5 million tons of related waste are illegally disposed of worldwide each year [10–12]. Primarily composed of up to 96% calcium carbonate (CaCO₃), according to Bellei et al. (2023), oyster shell residues are mainly used in their natural crushed form (74.5%, uncalcined, as aggregate) or in powder form (68%, usually calcined, as binder-filler), depending on the processing route and application [10]. Their application as a partial substitute for Portland cement has been extensively studied, with documented use

in concrete [13], bricks [14], hot-mix asphalt [15], soil mixtures [16], artificial stone [17], drainage layers, magnesium phosphate cement, and residential finishes [18], demonstrating their potential to reduce carbon emissions and enhance construction sustainability. However, these are still applications that use calcination.

To better understand the metrics of scientific studies, exclusively in the field of lime, lime production or lime mortars using similar sources of calcium of biological origin (animal shells), a SCOPUS search and analysis (excluding review articles) was conducted between 5 September 2025, and 18 December 2025, using the following keywords (searching abstracts, titles and keywords): “bivalve shells lime”; “mollusk shells lime”; “oyster shells lime”; “sea shells”; “eggshells lime”, “snail shells”. Excluding articles outside the topic, 469 articles were found, as shown in Figure 1. This shows that since 2007, research into the use of animal shells for the manufacture of lime or for use with lime has increased.

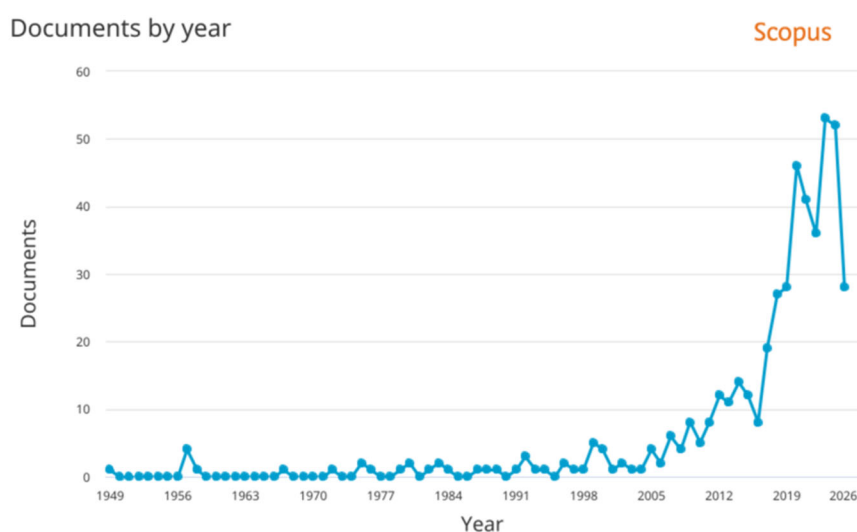


Figure 1. Number of documents indexed in Scopus related to the use of calcium sources of biological origin (animal shells) for lime production and lime-based materials. Reproduced from Scopus®, with permission from Elsevier B.V, Copyright 2025.

Using the same method, a search was conducted relating the use of this type of shell with the use of quicklime, using the same keywords but with “quicklime” instead of “lime”. Only 16 results were found related to the use or production of quicklime from these calcium sources, showing an increase in articles since 2016. However, among these, there are no studies focused on mortars, but instead on the use of lime for other applications, as shown in Table 1.

Table 1. Number of documents referring to the use or production of quicklime with shells of biological origin (SCOPUS research).

Applications/ Materials	Bio-Calcium for Feed	Soil Stabilisation	Contaminated Soils	Lime in General	As Aggregate in Concrete	Lime for Building
Chicken eggshell	1	5	1	3	1	1
Oyster shell		1		1		
Seashell				1		
Sea snail				1		

In order to obtain results on lime-based mortars using seashells, a new search was conducted using the following keywords: “bivalve shells lime mortar”; “mollusk shells

lime mortar”; “oyster shells lime mortar”; and “sea shells lime mortar”. Excluding some results that were out of context, such as applications for agriculture, seventeen results were obtained, as shown in Table 2.

Table 2. Number of documents focused on lime-based mortars with seashells. (SCOPUS research).

Applications/ Materials	As Aggregate in Mortars	Restoration Mortar Additive	Insulating Filler	Lime Production	Lime for Bricks	Lime for Light Insulating Bricks	Source of Lime/ Characterisation Historical Mortars
Oyster shell or Seashells	5	1	2	1	3	1	6

Considering all the research, here is a summary of some of the most relevant studies found in this field. It is important to note some of the effects of seashells as a binding material (subject to calcination) or aggregate (uncalcined material), even in cement-based mortars.

Marine shell waste (>90% calcium carbonate, CaCO_3), mainly composed of aragonite [19], with species-dependent microstructural characteristics, has been tested as a partial replacement of aggregate in mortars and concretes. Evidence shows that the use of uncalcined shells presents lower compressive strength and increased water absorption, restricting feasible levels to $\leq 20\%$ as aggregate and $\leq 5\text{--}10\%$ as a cement replacement [20,21]. Other experimental results confirm this trend: Kwon and Wang (2024) reported 35–55% reductions in 28-day compressive strength with 15–30% oyster shell powder replacement, confirming its limited reactivity and filler behaviour in cementitious systems [22], whereas Liao et al. (2021) showed that fine particles (<0.6 mm) could even improve strength by 10–15%, while coarse aggregates (>2 mm) reduced workability and decreased compressive strength by up to 25% [23].

Thermal treatment can enhance performance: Liao et al. (2023, Case Studies) reported that oyster shells calcined at 950 °C (8% replacement with metakaolin) increased compressive strength by 12.5% and reduced water absorption and permeability by ~23–24%, although drying shrinkage by 18–23% and the high energy demand (≥ 950 °C) limits sustainability [7].

Considering other properties besides resistance, Martínez-García et al. (2024) showed that the minimum adhesion required for ETICS (External Thermal Insulation Composite System) mortars (≥ 0.08 MPa) is maintained up to 25% substitution of aggregate by mussel shell [24], while Bellei et al. (2025) found that with 30%, oyster shell porosity increases to 27–30% and capillary absorption rises, reducing durability [25].

In addition, Table 3 presents a compilation of the main results of several studies, focusing on the type of seashell and its function in different building materials.

Table 3. Studies with seashell waste in construction materials.

Reference	Shell Type/Function	Application	Main Results	Gaps/Limitations
Ferraz et al., 2019 [26]	Different types of seashell/binder replacement (calcined)	Lime production	Dog cockle classified in the most reactive class (R5); white tonality superior to commercial lime	The lowest reactivity was found for oyster shell
Martinez García et al., 2020 [27]	Crushed mussel shell/Loose-fill insulation material	Walls, roofs and floors (cavity insulation)	$\lambda = 0.12\text{--}0.20$ W/m·K; $R_w = 42$ dB	Not a binder; insulation only

Table 3. Cont.

Reference	Shell Type/Function	Application	Main Results	Gaps/Limitations
Liao et al., 2021 [23]	Shell powder/aggregate replacement (different grain sizes tested)	Cement mortars	<0.6 mm ↑ strength 10–15%; >2 mm ↓ strength up to 25%	No durability
Liao et al., 2023 [7]	Oyster shell/aggregate replacement	Cement mortars	Strength ≈ control with fines; ↓ with coarse; absorption ↑	No chemical activation: no lime used
Zhu et al., 2024 [20] (review paper)	Calcined shell powder for cement replacement /fine or coarse aggregate replacement	Cement and mortars	Feasible ≤ 20% as aggregate, ≤5% as cement; >30% strength loss at higher dosages	High absorption, shrinkage; no chemical activation
Martínez-García et al., 2024 [24]	Crushed mussel shell/aggregate replacement	Lime/cement mortars for ETICS	↑ Breathability; adhesion acceptable ≤ 25% (≥0.08 MPa)	>25%: adhesion and durability ↓
Bellei et al., 2025 [25]	Crushed oyster shell (30%)/aggregate replacement	NHL mortars	Porosity ↑ (27–30%); capillary absorption ↑; density ↓	No strength data; only 30% tested

Note: the arrow ↑ indicates an increase and the arrow ↓ indicates a decrease compared to the reference composition.

In summary, marine shells seem to be studied more in recent years for their potential sustainability and, in some cases, strength. However, their uses are limited by strength losses at high dosages, increased absorption and shrinkage, and reliance on costly treatments, highlighting the need for more efficient alternative approaches.

1.2. Lime Kiln Dust (LKD)

Lime kiln dust (LKD) can be generated in both the lime industry and the pulp and paper industry. In this study, only LKD from the paper industry was used. However, considering the reduced literature about this type of LKD, information about LKD of the lime industry is also presented, given that most of the articles found are from this industry, as well as lime sludge from the paper industry, since some properties are similar.

In the lime industry, LKD is as a fine by-product of high-temperature rotary kilns or vertical kilns, collected through air pollution control systems such as cyclones, bag houses, and electrostatic precipitators [28–30]. After being captured in emission control systems, it has different destinations depending on the plant and the availability of vaporising applications: it can be recirculated as raw material [31], used in works as a stabiliser or in the production of materials [32], or end up in stockpiles or landfills when there are no viable recovery routes. LKD varies in composition depending on the raw material and processing conditions; studies on quicklime indicate that impurities such as silica, aluminium, iron, magnesium, and manganese can affect the CaO content, significantly reducing it [33]. In construction applications, there are several publications on the use of LKD from lime kilns in concrete and mortar as a substitute for cement: (i) in cement mixtures with ash (LKD in 15% to 50% of the mass of the cement–ash part), it has been shown to increase material hydration, improve mechanical strength by 27% to 54%, and accelerate hardening between 7 and 180 days of curing [34]; (ii) replacing up to 50% with LKD accelerated setting time but reduced final strength [35]; total replacement of cement with lime dust calcined at 950 °C

in a mixture with the addition of natural pozzolan resulted in an increase of more than 51% in strength compared to the reference composition [36].

Concerning LKD from the paper industry, LKD is also generated in the kraft paper industry. The kraft process, which uses sodium hydroxide (NaOH) and sodium sulphide (Na_2S) to pulp wood, is the dominant pulping process in the pulp and paper industry. About 130 million tons/year of kraft pulp are produced globally, accounting for two-thirds of the world's virgin pulp production and for over 90% of chemical pulp [37]. Within this recovery cycle, the rotary kiln calcines the lime sludge (CaCO_3) to regenerate the lime used in causticization, generating LKD as a by-product. During this stage, some of the phosphorus from wood and other inputs accumulates in the sludge and, upon calcining, forms compounds such as rhenanite (NaCaPO_4) [38]. As a result, LKD has lower CaO availability and, due to its fineness (2.5–12 μm vs. 8–35 μm for lime mud) and its enrichment in phosphorus and alkalis, shows reduced reactivity, which affects the efficiency of the causticization process [39]. In the construction sector, this specific application of LKD from the paper industry has not been reported in the peer-reviewed literature. However, lime mud and lime sludge from the paper industry has been investigated as a partial replacement for cement, fine aggregate and filler, yielding technically relevant outcomes.

In mortars, the progressive substitution of fine aggregate with lime mud at levels of 6, 12 and 18% increased compressive strength by approximately 10, 17 and 23%, respectively, reaching a maximum value of 42 Mpa at 17% replacement, attributed to its nucleation effect and finer particle size [40]. In general, for cement replacement, research findings converge in indicating that the optimal range lies between 10 and 30%, whereas higher levels typically require the incorporation of other supplementary cementitious materials to preserve mechanical strength [41].

In high-performance materials, Oinam et al. (2024) evaluated the use of lime mud as a filler in cementless ultra-high-performance concrete (UHPC), observing that 30% replacement of silica powder increased compressive strength by 5.4% compared with the control, while also improving matrix densification and reducing the environmental footprint in life-cycle assessment (160–176 kg $\text{CO}_2\text{-eq/t}$ compared with the reference value) [42].

Even more significant results were obtained when lime mud was previously calcined (550–850 $^\circ\text{C}$) and used as an alkaline activator in GGBFS-based UHPC, achieving compressive strengths of up to 150–180 Mpa and a remarkable reduction in porosity [43].

Another field of investigation has been the production of alternative clinkers. Recent studies reported that the incorporation of up to 50% of lime sludge in raw clinker mixtures maintained saturation indices and silica and alumina moduli within industrial ranges, yielding main phases of C_3S (37–59%) and C_2S (22–24%) at 1450 $^\circ\text{C}$, with acceptable free lime contents [44]. Complementarily, the review by Vashistha et al. (2019) summarised previous experiences where lime sludge was evaluated in mortar, concrete and aggregate blends, identifying an optimum substitution range close to 10–30% [40]. In a subsequent experimental study, the same authors demonstrated that combining lime sludge nanosilica derived from other residues enabled the synthesis of belite clinkers at temperatures as low as 900 $^\circ\text{C}$, significantly reducing the energy demand compared with the conventional route [45].

According to these studies, it can be concluded that the research about these lime-based by-products from the paper industry has focused on its use as a partial replacement in cement mortar and concrete, as a filler or alkaline activator, and as a raw material in clinker and brick production.

This work proposes, for the first time, the development of eco-efficient mortars, contributing to the research on less-calcined-material mortars, using lime kiln dust from the

paper industry and seashell waste. The novelty of this study lies in the use of a vinegar solution (VS), prepared by reacting cleaned and dried oyster shells with commercial white vinegar (~5% acetic acid), as an alternative mixing liquid. This reaction partially dissolves calcium carbonate from the shells, generating a calcium-rich solution that enhances system reactivity.

1.3. Vinegar Solutions with Calcium or Calcium Acetate in Mortars

Several studies have demonstrated that acetic acid reacts with CaCO_3 from marine shells to produce calcium acetate ($\text{Ca}(\text{CH}_3\text{COO})_2$), a more reactive calcium compound than calcium carbonate, acting as a reactive precursor in cementitious and environmental applications [46,47].

In cementitious systems, low dosages of calcium acetate have been shown to accelerate hydration and moderately enhance early strength, whereas excessive amounts may lead to over-hydration and loss of mechanical performance [48]. Abed et al. (2023) reported that concrete incorporating 5.1% calcium acetate exhibited 28–39% higher compressive strength and an 83% reduction in water absorption, with denser microstructures observed by SEM [49]. Similarly, Dinh and Quynh (2025) observed that 0.60% calcium acetate in blended Portland cements increased 28-day strength by 23.8%, while higher dosages caused early-age strength losses [50]. Cao et al. (2021) further emphasised the need to assess durability and shrinkage, since most studies have been restricted to Portland cement systems with commercial calcium acetate [51].

In contrast, the present study employs household white vinegar (~5% CH_3COOH) to react with oyster shells, producing a vinegar-based solution (VS) rich in dissolved calcium species. This approach avoids calcination, minimises energy consumption, and provides a partially dissolved reactive calcium source to enhance the setting and hardening of lime-based mortars. To date, no evidence exists of vinegar-treated oyster shells being applied in mortars formulated with lime kiln dust from the paper industry, which presents a clear research gap.

A bibliometric search in Scopus reinforces this research gap about combined oyster shells or other sources of calcium with vinegar and lime kiln dust or lime-based binders. When the terms “vinegar” or “acetic acid”, “lime” and “calcium acetate” were jointly searched, only two papers were identified, both from the same research group, focused on the synthesis and calcination of calcium acetate for CaO production. This reaction pathway has also been proposed as an eco-friendly alternative to traditional shell calcination, as it significantly reduces the decomposition temperature ($\approx 750^\circ\text{C}$ compared to 900°C) and produces CaO of higher chemical purity ($\approx 91.5\%$ vs. 87.8%) through the calcination of calcium acetate [46,47,52].

Through a more general web search, two articles were found in the field of archaeology. There is an ancient mosaic from the Byzantine period that resembles limestone but with unusual properties, and researchers have doubts about whether the material may be an unusual, rigid chalk or a chemically transformed material. Opening the possibility of a chemical conversion of the chalk (basically formed of calcium carbonate) using a weak acid (such as vinegar), which would only affect the calcite around the accessible pores, leaving the bulk of the chalk and its microfossils in a well-preserved state. The authors state that if a chemical modification of soft chalk into a hard material was indeed used, it would constitute a “lost” technology that could even be useful in the present day [53].

And Davidovits et al. (1981) mentioned the process of dissolving rocks with plant acids and subsequent geopolymerization for the composition of geopolymers based on soda, silica and alumina compounds [54].

In addition, at the University of Minho, the simultaneous mixture of vinegar with oyster shell powder (without calcination) with only 3% of lime (in pastes and without added water) was tested but only obtained viable results (strength and water resistance) using accelerated carbonation curing, and would require a high consumption of vinegar [55].

However, no publications were found on the use of vinegar-reacted shell solutions (VS) in mortars, especially incorporating lime kiln dust from the paper industry, confirming that the present work addresses a statistically unexplored field of research.

1.4. Scope of the Study

The main goal of this research is to develop eco-efficient binders that reduce the dependence on calcined raw materials, such as limestone or clay, through the valorization of calcium carbonate-rich residues. In this context, experimental mortars were formulated using oyster shell powder and lime kiln dust from the paper industry (LKD), both employed without prior calcination.

The proposed strategy involved the use of commercial white vinegar (of household use) to partially dissolve the calcium carbonate from oyster shells, generating a vinegar-based calcium solution (SV) with improved reactivity. This solution was then combined with oyster shell powder and/or LKD to produce eco-efficient mortars with reduced calcined materials, as schematically illustrated in Figure 2. The commercial quicklime was also incorporated, but this was replaced by LKD or oyster shells in different percentages (25, 50, 90 and 100%) in order to use the smallest possible amount. These mixtures could be used in different applications, such as mortars for construction or rehabilitation or blocks for nonstructural walls.

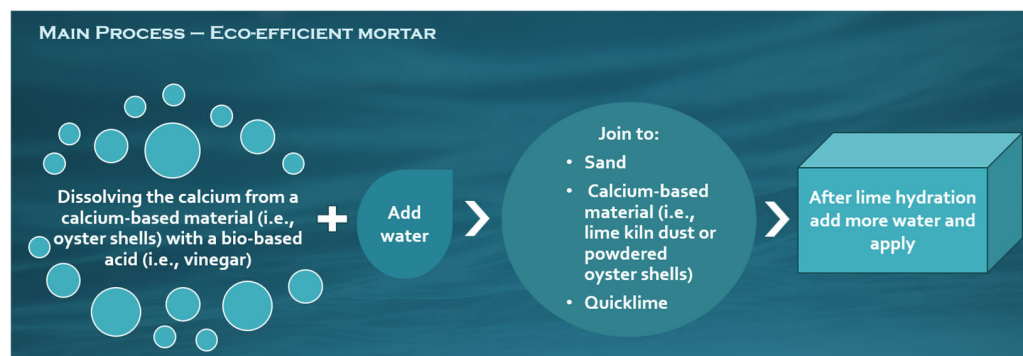


Figure 2. Schematic representation of the process for producing eco-efficient mortars using calcium sources of biological origin (oyster shells) and vinegar-based calcium solutions.

2. Materials and Methods

2.1. Materials

2.1.1. Lime Kiln Dust from the Paper Industry (LKD)

The LKD was collected from the kraft recovery kiln of a Portuguese factory, (DS Smith Paper Viana, Viana do Castelo, Portugal) which produces approximately 400,000 tonnes of kraft liner paper annually. This residue is mainly composed of calcium carbonate (≈ 81.5 wt.% CaCO_3), as confirmed by thermogravimetric (TGA), Figure 3, and X-ray fluorescence (XRF) analyses, Table 4. The TGA curve shows a mass loss at around 800°C , corresponding to the decarbonation of $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$, consistent with high Ca content and low organic fraction, Figure 3.

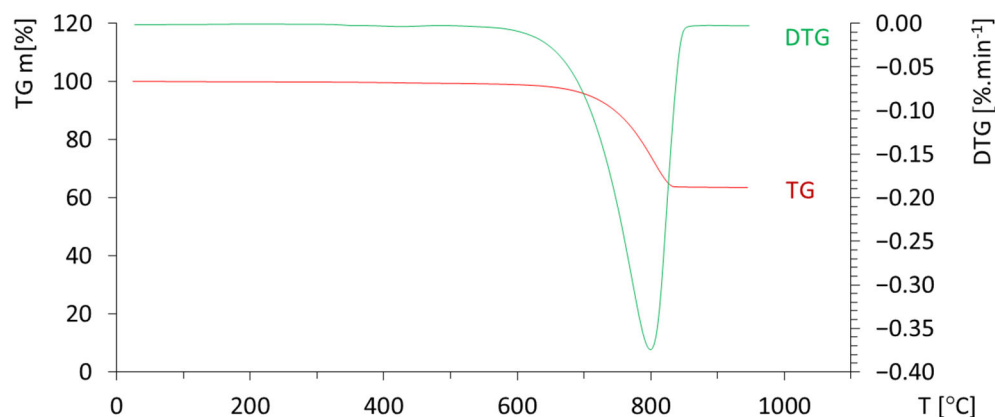


Figure 3. Thermogravimetric (TGA/DTG) analysis of LKD.

Table 4. Chemical composition of KLD obtained from XRF analysis.

Materials	Chemical Compounds (%)									
	Ca	P	Si	K	Ti	Cl	Mn	Sr	Fe	Others
LKD	77.20	15.85	5.60	0.50	0.25	0.22	0.16	0.10	0.05	0.07

The XRF analysis revealed a predominant Ca fraction (≈ 77.20 wt.%), followed by P (≈ 15.85 wt.%) and minor constituents such as Si (≈ 5.60 wt.%), K, Ti, and traces of Mn, Sr, and Fe. The phosphorus content is characteristic of lime kiln dust from de kraft paper process, where phosphorus compounds (e.g., NaCaPO_4) are carried over from the pulping liquor. These P-bearing phases are known to reduce CaO availability and reactivity, influencing both hydration and carbonation behaviour in lime-based binder (Table 4).

A laser particle size analysis was performed, yielding a D50 equal to $29.7 \mu\text{m}$. Once LKD was used in the calcined (at 800°C by 4 h) and uncalcined states, an analysis of the density shows that LKD is denser after the calcination process, showing a retraction of the material. However, this is less dense than quicklime (3.310 kg/m^3). The densities observed were 2.718 kg/m^3 for LKD and 2.906 kg/m^3 for calcined LKD.

2.1.2. Oyster Shells

The oyster shells used in this study were supplied by an aquaculture company (Aquagoma—Produtos Rio e Mar Lda, Viana do Castelo, Portugal). The oyster species used were *Crassostrea angulata* (Portuguese oyster) and *Crassostrea gigas* (Pacific oyster, a non-native species widely cultivated in Portuguese aquaculture), as shown in Figure 4. After an isolated mortality event, the collected shells were cleaned with running water and dried at 105°C for 24 h. These were used whole for the preparation of vinegar-based solution (VS) and used in powder. For that, these were ground in a Los Angeles ball mill following sequential 15 min cycles until reaching a particle size below $75 \mu\text{m}$ ($40.4 \mu\text{m}$). The resulting powder is fine, white, and odourless, with an apparent density of 2710 kg/m^3 .

This powder was also used uncalcined and (for comparison of results) calcined at 800°C for 4 h. Unlike the LKD, the density obtained after calcination was 2336 kg/m^3 , lighter than quicklime (3.310 kg/m^3). This reduction in density is a clear indication of mass loss due to ignition during the calcination process. This variation suggests that the calcination process promoted an expansion of the material, possibly due to the formation of new structures, thus requiring further analysis of this process.

TGA confirmed a single major mass loss near 800°C , associated with CaCO_3 decomposition to CaO and CO_2 , with an overall CaCO_3 content of ≈ 95.5 wt.% Figure 5.

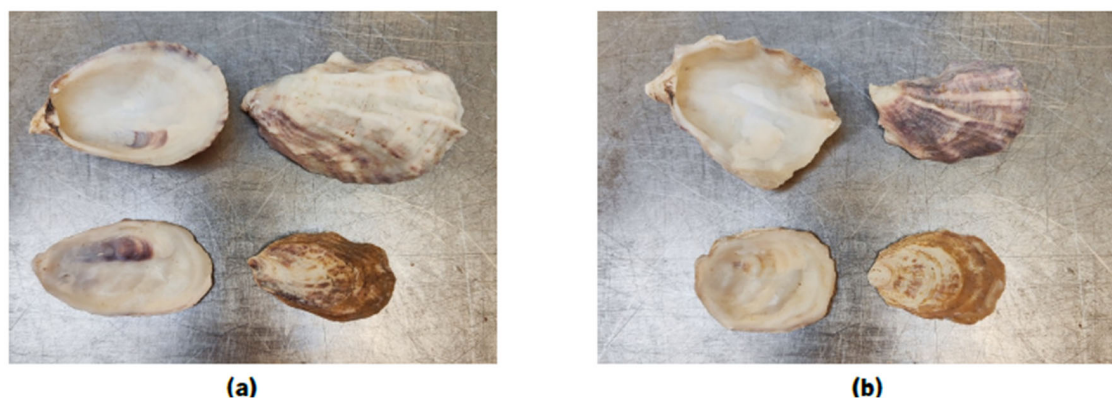


Figure 4. (a) *Crassostrea angulata* (Portuguese oyster); (b) *Crassostrea gigas* (Pacific oyster, cultivated in Portugal).

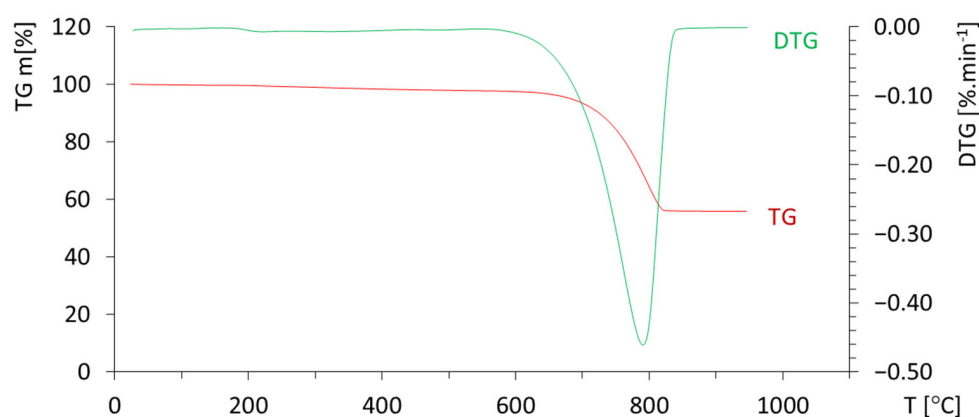


Figure 5. Thermogravimetric (TGA/DTG) analysis of oyster shell.

XRF result showed CaO $\approx$ 84.82 wt.%, P $\approx$ 7.72 wt.%, and Si $\approx$ 6.01 wt.%, with trace elements below 1 wt.%. These data indicate that the oyster shell powder is a high-purity calcium source, comparable to commercial limestone, Table 5.

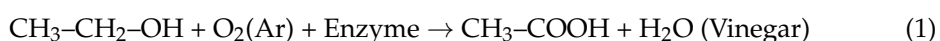
Table 5. Chemical composition of oyster shell powder obtained from XRF analysis.

Materials	Chemical Compounds (%)									
	Ca	P	Si	K	Ti	Cl	Mn	Sr	Fe	Others
Oyster shells	84.82	7.72	6.01	0.46	0.28	0.25	0.01	0.32	0.09	0.04

2.1.3. Solution of Vinegar with Oyster Shells (VS)

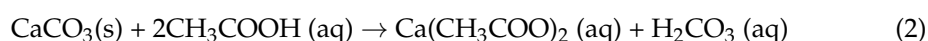
The vinegar-based solution (VS) was prepared to generate a reactive calcium medium through the partial dissolution of oyster shells in acetic acid. The process involved mixing cleaned and dried oyster shells with commercial white wine vinegar (5% of acetic acid CH₃COOH) in a ratio of 1 L of vinegar per 500 g of shells. The mixture was left to rest for 48 h at room temperature, allowing partial dissolution of CaCO₃ and the formation of calcium acetate (Ca(CH₃COO)₂) and other soluble calcium species. The resulting liquid was then filtered and diluted with water at a 1:1 ratio before being used as a reactive agent in mortar preparation.

The vinegar used consisted of an aqueous solution of 5% acetic acid and 94% water, produced exclusively through into acetic acid via the oxidation reaction:

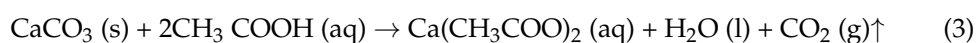


Acetic acid is a weak aliphatic monocarboxylic acid (CH_3COOH) that mixes readily with water and acts as a mild, biodegradable reactant. The physicochemical characteristics of the vinegar employed were density $\approx 1045 \text{ kg/m}^3$ at 25°C , $\text{pH} \approx 2.4$, and viscosity $\approx 1.06 \text{ mPa}\cdot\text{s}$.

This solution provided a low-energy, sustainable alternative to thermal activation, capable of improving the reactivity of the calcium carbonate (add in powder to the mixtures) from both the shells and the LKD by forming soluble calcium acetate that accelerates the setting and carbonation processes in eco-efficient mortars. The formation of calcium acetate results here, as with other bases: carbonate reacts in the presence of the acid from vinegar to form carbon dioxide (CO_2), observed by the effervescent reaction (bubbles). The chemical reaction is expressed below [55]:



or



2.1.4. Quicklime

A Portuguese commercial calcitic quicklime was used with the following provided chemical composition (Table 6), showing that this material is purer in calcium than LKD, which contains phosphorus and a higher amount of silica in its composition.

Table 6. Chemical composition of commercial calcitic quicklime (QL).

Materials	Chemical Compounds (%)							
	CaO	Mg	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	S	CO ₂
Quicklime	≥ 81	15.85	5.60	0.50	0.25	0.22	0.16	0.10

2.1.5. Sand

A natural siliceous Portuguese sand commercially designated as S40/45 (Parapedra, Rio Maior, Portugal) was used as fine aggregate. The material was employed in its dry state according to the manufacturer's technical specifications. The sand presents a neutral pH (≈ 7) and Mohs hardness of 7, with a whiteness index of $L \approx 82.5$. The non-compacted bulk density is 1.58 g/cm^3 , while the particle density reaches 2.62 Mg/m^3 , and the moisture content ranges between 3 and 5%. Chemically, the sand is composed mainly of SiO_2 ($\approx 99.4 \text{ wt.}\%$), and trace levels of Na_2O , K_2O , TiO_2 and P_2O_5 , all below $0.2 \text{ wt.}\%$, Table 7. The maximum particle size is 1 mm, and the refractive index is 1.55, confirming its high purity and suitability for laboratory mortars and eco-efficient binder formulations.

Table 7. Chemical composition of natural siliceous sand.

Materials	Chemical Compounds (%)									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO
Sand	99.4	0.05	<0.025	0.02	0.06	0.20	0.02	0.02	0.01	0.00

2.2. Mixing Process and Compositions

Quicklime or CaO was used as the base material for the reference mixture, against which substitution levels with paper-industry lime kiln dust (LKD) and oyster shell powder (both calcined or uncalcined). Since lime hydration is highly exothermic and expansive, a two-phase hot-mix method (Figure 6) was adopted to ensure complete hydration before casting into moulds.

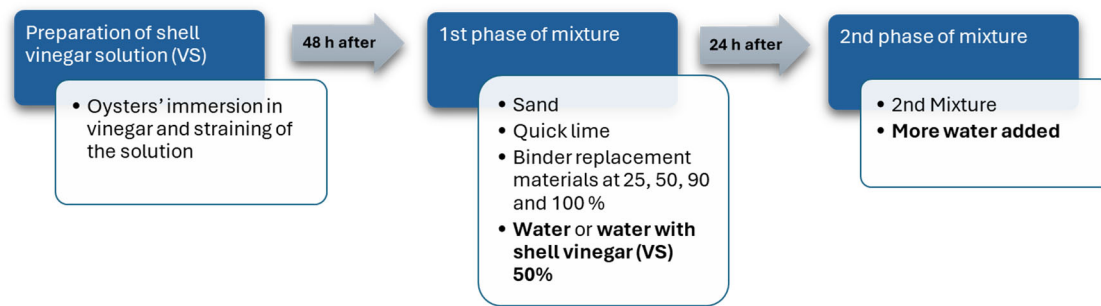


Figure 6. Preparation process of the mixtures.

After obtaining the vinegar solution, the mixtures were prepared in two phases:

- 1st Phase (hot mix), the binder (quicklime $\pm$ substitutes) was dry-mixed with sand and then combined with either water or the vinegar solution (VS). This stage initiates hydration and activates the reactive lime components.
- 2nd phase (after 24 h), the semi-dry mixture was re-mixed with additional water to adjust the appropriate workability.

Table 8 summarises, in kg/m^3 , the component masses and liquid contents added in each phase. The volume ratio of 1: 2 (binder–sand) was maintained across all formulations. The liquid–binder ratio includes both mixing stages and was empirically tuned to achieve similar workability and confirmed with the flow table test. As substitution increased, the total liquid/binder ratio tended to decrease, suggesting that finer and less reactive particles from the residues required less added water to achieve comparable flowability.

Table 8. Compositions studied.

Mixtures	Materials (kg/m^3)						Ratio Liquid/Binder
	Quicklime	Sand	Lime Kiln Dust (LKD)	Calcined LKD	Oyster Powder (OS)	Calcined OS	
QL_w	639	1278					1.79
QL_vs	648	1295					1.60
QL_LKD25%_vs	486	1295	133				1.57
QL_LKD50%_vs	324	1295	266				0.93
QL_LKD90%_vs	65	1295	479				0.80
LKD100%_vs		1242	621				0.62
C_LKD_w		1244		622			0.84
C_LKD_vs		1261		631			0.60
QL_OS25%_vs	486	1295			133		1.36
QL_OS50%_vs	324	1295			265		0.65
QL_OS90%_vs	65	1295			477		0.76
OS100%_vs		1242			621		0.58
C_OS_w		1182				591	0.9
C_OS_vs		1198				599	0.68

Specimen identification codes indicate the binder type, residue, replacement level, and the use of vinegar solution (QL: quicklime; LKD: lime kiln dust; OS: oyster powder; C: calcined residue; vs: vinegar solution). The mixtures were cast into $40 \times 40 \times 160$ mm moulds, and the specimens remained in the moulds for 5 days, and then were demoulded and conditioned ($22^\circ\text{C} \pm 2^\circ\text{C}$; 60–70% RH) until testing.

2.3. Testing Methods

The experimental programme comprised physical, mechanical and durability tests in accordance with European and international standards. Considering the fresh-state properties, the workability of the mortars was assessed through the consistency measurement by the flow table method, following EN 1015-3 [56]. Each mixture was tested immediately

after preparation, and the average flow diameter of two perpendicular measurements was recorded as consistency.

The hardened state of the mortars was evaluated for mechanical behaviour and durability indicators, considering different curing periods. The following tests were performed:

- Compressive strength (EN 1015-11 [57]) at 28 and 60 days using the equipment LR50K Plus model by LLOYD Instruments—AMETEK (Berwyn, PA, USA). This test is conducted after the flexural strength test, using three halves of the fractured specimens (for each mixture). The initial load was approximately 15 N, applied at a constant mechanical speed of 0.005 mm/s;
- Flexural strength (EN 1015-11 [57]) at 28 and 60 days with three specimens of each mixture with $40 \times 40 \times 160 \text{ mm}^3$, also using the equipment LR50K Plus model by LOYD, starting with an initial load of 15 N and proceeding at a constant mechanical speed of 0.005 mm/s until the specimen failed.
- Water absorption by capillarity (BS EN 1015-18 [58]) at 28 days, evaluating the mass increase in specimens when their base is immersed in 1 cm of water. Two intact halves of the specimens from the flexural strength test (each mixture), previously sealed with silicone on the lateral faces, were used. The coefficient of water absorption by capillarity (C) was determined between 10 and 90 min, calculated as the average of the results and expressed in $\text{kg/m}^2 \times (\text{min})^{1/2}$.
- Water absorption by immersion (E394 [59]) at 28 days. The specimens employed were also two intact halves of the flexural strength test.
- Microstructure analysis at 7 days of curing, performed with an ultra-high-resolution field-emission scanning electron microscope, NanoSEM-FEI Nova 200 (FEG/SEM) (Thermo Fisher Scientific, Waltham, MA, USA), with an integrated microanalysis X-ray system (EDS—energy dispersive spectrometer of EDAX- Pegasus X4M, AMETEK, Berwyn, PA, USA). Small fragments were taken from samples (cubes of $20 \times 20 \times 20 \text{ mm}^3$), dried, cold-embedded in synthetic resin (unpolished) and coated with a thin layer of gold–palladium alloy (Au-Pd with 80–20 wt%). In addition, an X-Ray diffraction (XRD) analysis with the Bruker D8 Discover equipment (Bruker Corporation, Billerica, MA, USA) was carried out. For this purpose, powder samples were prepared from the same series of cubes. The results were quantitatively analysed with the Match! software (version 4.2 Build 342) through the Reference Intensity Ratio (RIR) method.

3. Results and Discussion

3.1. Fresh State Characterisation

As shown in Table 9, all mixtures with (LKD) or (OS) presented flows with diameters between 17 cm and 23 cm. In addition, the mixtures presented good consistencies to visual observation. These statements indicate a workable consistency within the expected range for lime-based mortars.

The progressive addition of LKD or OS seems to slightly increase the fluidity of the mixtures. However, the liquid/binder ratio increases slightly in the first phase (during the hydration of quicklime) and considerably reduces the need for liquid in the second phase as the amount of waste added increases, ultimately leading to a reduction in the liquid/binder ratio.

The reduction in the liquid/binder ratio observed can be attributed to the predominance of uncalcined calcium carbonate-based particles, which exhibit a lower water demand than reactive quicklime during the second mixing phase. In addition, the fine particle size of LKD promotes improved particle packing, reducing the amount of free water required to achieve adequate workability.

Table 9. Workability: Slump flow, observations and liquid/binder ratio.

Mixture	Workability		Ratio Liquid/Binder	
	Flow (cm)	(1st Phase)	(2nd Phase)	(1st + 2nd Phases)
QL_w	19.5	0.50	1.29	1.79
QL_vs	21.5	0.50	1.10	1.60
QL_LKD25%_vs	19.5	0.52	1.05	1.57
QL_LKD50%_vs	19.5	0.55	0.38	0.93
QL_LKD90%_vs	23.0	0.60	0.21	0.80
LKD100%_vs	22.0	0.62		0.62
C_LKD_w	20.0	0.84		0.84
C_LKD_vs	18.0	0.60		0.60
QL_OS25%_vs	17.5	0.52	0.84	1.36
QL_OS50%_vs	17.0	0.55	0.10	0.65
QL_OS90%_vs	18.8	0.60	0.16	0.76
OS100%_vs	18.5	0.58		0.58
C_OS_w	18.4	0.90		0.90
C_OS_vs	18.5	0.68		0.68

In general, the mixtures with LKD showed a moderate liquid demand, while those containing (OS) tended to present fewer fluid mixtures and a lower liquid/binder ratio. The lower flowability of OS-based mixtures compared to LKD systems is consistent with the more inert behaviour of oyster shell CaCO_3 in the fresh state.

The improved flowability observed in mixtures containing the vinegar-based solution (VS) suggests that the presence of dissolved calcium and acetate ions reduces the interparticle friction and enhances dispersion during mixing, particularly in systems containing quicklime.

Overall, these results confirm that the hot-mix method ensured adequate workability, even with high substitution rates, while the vinegar–shell solution (SV) improved flowability compared to plain water, particularly in mixtures containing quicklime.

3.2. Hardened State Characterisation

3.2.1. Chemical Composition and Implications for the Hardened State

As mentioned, and in accordance with Tables 4 and 5, the LKD and the oyster shell powder used show the presence of phosphorus (15.85% and 7.72%, respectively).

Phosphorus plays a decisive role in lime reactivity. According to Mousavi & DeMartini (2020), in the kraft process, phosphorus reacts with CaO during slaking to form rhenanite (NaCaPO_4), an insoluble phase that binds calcium and reduces the available CaO by approximately 5 wt% for each 1 wt% of P [38]. This progressive deactivation explains why LKD from the paper industry cannot be effectively recalcined.

A similar effect was observed by Ulmgren and Rådeström (1997), who reported that phosphorus in lime muds precipitates as hydroxyapatite and carbonate–apatite phases ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$; $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)_2(\text{OH})_2$), which immobilise part of the calcium in insoluble compounds and, therefore, decrease the efficiency of recalcination and slaking [60].

Complementarily, Karlemo documented that the accumulation of non-process elements such as P, Si and Na in recycled lime from Finnish Kraft mills results in compositional heterogeneity and reduced CaO availability [61], consistent with the loss of reactivity described by Mousavi & DeMartini [38].

This partial immobilisation of calcium due to a phosphorus-rich phase could limit the reactivity of CaO but may also influence fresh-state behaviour by reducing the amount of free CaO available for early hydration reactions [38,60].

However, these components can be dissolved in acidic media and/or heat treatment at different temperatures, according to research on the synthesis of hydroxyapatite from seashells or eggshells for biomedical applications (bone regeneration), since this material is also naturally present in human bones [62]. Thus, the use of vinegar and heat hydration may contribute to the dissolution of hydroxyapatite from LKD and from the oyster shells used. After drying, new reactions may occur with the available calcium and CaO, as well as with water and CO₂.

3.2.2. Compressive Strength

The compressive strength results for the studied mortars after 28 and 60 days are shown in Figure 7, grouped according to the type of residue used, LKD or OS.

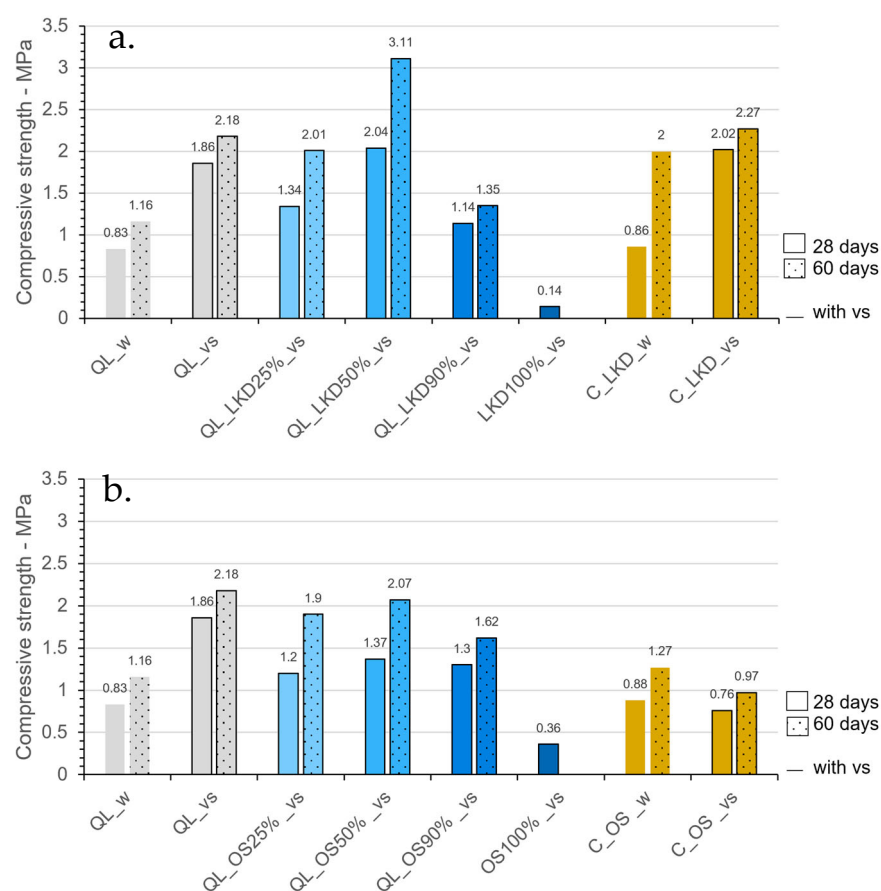


Figure 7. Compressive strength of mortars with partial substitution of quicklime (QL) by LKD (a) and OS (b) after 28 and 60 days of curing.

The standard deviation obtained between the samples tested was between 0.03 and 0.16, with the values obtained for each specimen being shown in Figure 8.

The relatively low standard deviation (0.03–0.16 MPa) indicates good repeatability of the mechanical tests. Therefore, strength differences above 0.5 MPa observed between reference and VS-activated mixtures can be considered significant and representative of real material behaviour rather than experimental dispersion.

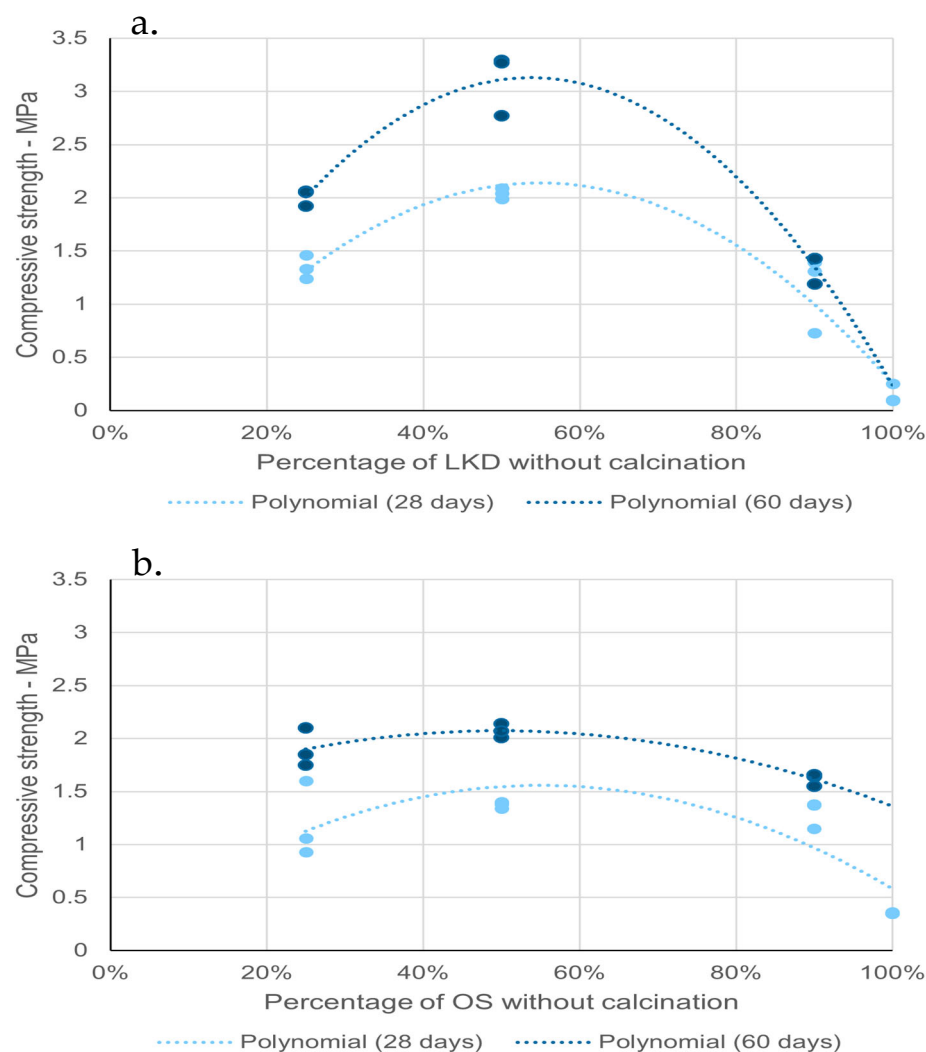


Figure 8. Polynomial trend of compressive strength at 28 and 60 days for increasing substitutions of LKD (a) and OS (b); each point corresponds to a test sample.

All mixtures exhibited higher compressive strength after 60 days, confirming the continuous development of mechanical cohesion typical of aerial lime mortars [53].

Overall, according to the obtained results, all compositions, except the mixture with 100% replacement of quicklime by LKD (LKD_vs), developed strengths above 0.3 MPa at 28 days, which lies within or slightly above the typical range reported for aerial lime mortars (0.3–1.6 MPa) [63].

Moreover, the results obtained with replacement levels of 25%, 50% and 90% achieved compressive strengths ≥ 0.4 MPa at 28 days. In accordance with EN998-1 [64], this is sufficient for rendering and plastering mortars in general classified as CSI (0.4 to 2.5 MPa). The 50% LKD substitution meets the minimum for CSII (1.5 to 5 MPa at 28 days), with 2.04 MPa, showing the most efficient mechanical performance. This optimum suggests a balance between available reactive CaO and the progressive formation of the less reactive Ca-P phase, which increasingly limits strength development at higher substitution levels.

At 28 days, the reference mixtures prepared with water, QL_W, reached 0.83 MPa, while the addition of VS increased the strength to 1.86 MPa, an improvement of $\approx 124\%$. The increase largely exceeds the experimental variability, confirming the effectiveness of the vinegar-based solution as an activating medium in lime-based systems. This agrees with Seesanong et al. [46], who reported that calcium acetate derived from oyster shells accelerates lime carbonation due to the presence of pre-dissolved CO₂, promoting the

formation of dense CaCO_3 crystals. This interpretation is consistent with the accelerated carbonation and matrix densification previously reported for calcium acetate-containing lime systems. A similar trend was observed here; the VS-containing mortars exhibited a faster early-age gain and continued developing strength up to 60 days, except for the mixture with calcined oyster shell powder, C_OS_vs, which reduced resistance compared to the reference compositions.

Beyond that level, the presence of phosphorus ($\approx 15.85\%$, Table 4) in LKD reduces the free CaO available for carbonation, as also described for phosphorus-rich lime muds by Mousavi & DeMartini (2020) and Karlemo (2023) [38,61]. Consequently, the QL_LKD90%_vs and LKD_vs exhibited the lowest strength values, associated with the formation of poorly reactive CA-P compounds such as rhenanite or hydroxyapatite.

Regarding the comparison of mixtures tested without calcination and with calcination, it can be observed that the mixtures with calcined residues (LKD and OS powder) have greater resistances than the corresponding mixtures without calcination (LKD_vs and OS_vs). However, the mixtures with 50% substitution (with 50% uncalcined material) show higher resistances. In addition, mixtures with 90% substitution (with 90% uncalcined material) still present quite acceptable values for rendering mortars in general, so these could be a better option in environmental terms. Overall, the results indicate a trade-off between mechanical performance and environmental efficiency: intermediate substitution levels (50%) maximise strength, whereas higher substitution levels (90%) can still provide acceptable performance while using substantially less lime.

Considering the effect of incorporated residues for lime replacement with the VS as an activator, Figure 8a,b, show a polynomial trend line relating compressive strength and the substitution percentage, considering all samples tested at 28 and 60 days. The consistency of these trends at both curing ages, together with the low experimental scatter observed in the compressive strength results, supports the reliability of the identified behaviour.

Within the LKD series, the trend indicates an optimum near 50%, where the balance between the reactive CaO and the residual Ca-P phase yields the highest mechanical response. The strength increase observed around this optimum clearly exceeds the experimental variability, indicating a meaningful material response rather than random dispersion.

The mixtures containing OS showed a more stable evolution, seen in Figure 8b; the strength values stay close for 25% and 50% substitution, with a slight decline at 90%. This reduced sensitivity to the substitution level is consistent with the predominantly inert nature of crystalline CaCO_3 in oyster shells.

When comparing the best-performing mixtures, both residues can effectively enhance strength. Moreover, the results suggest that LKD and shell particles, combined with the calcium acetate from the VS, may be acting as nucleation sites for CaCO_3 recrystallization, improving particle packing and cohesion, and showing a biogenic reactivity. This interpretation is consistent with the accelerated carbonation and matrix densification previously reported for calcium acetate-containing lime systems.

3.2.3. Flexural Strength

The flexural strength values at 28 and 60 days are shown in Figure 9, grouped according to the binder system: mortars using LKD and OS. The standard deviation obtained between the samples tested was between 0.01 and 0.16, with the values obtained for each specimen being shown in Figure 10a,b, with a polynomial trend line relating flexural strength and the substitution percentage. The low standard confirms the good repeatability of the flexural tests and allows for reliable comparison between mixtures.

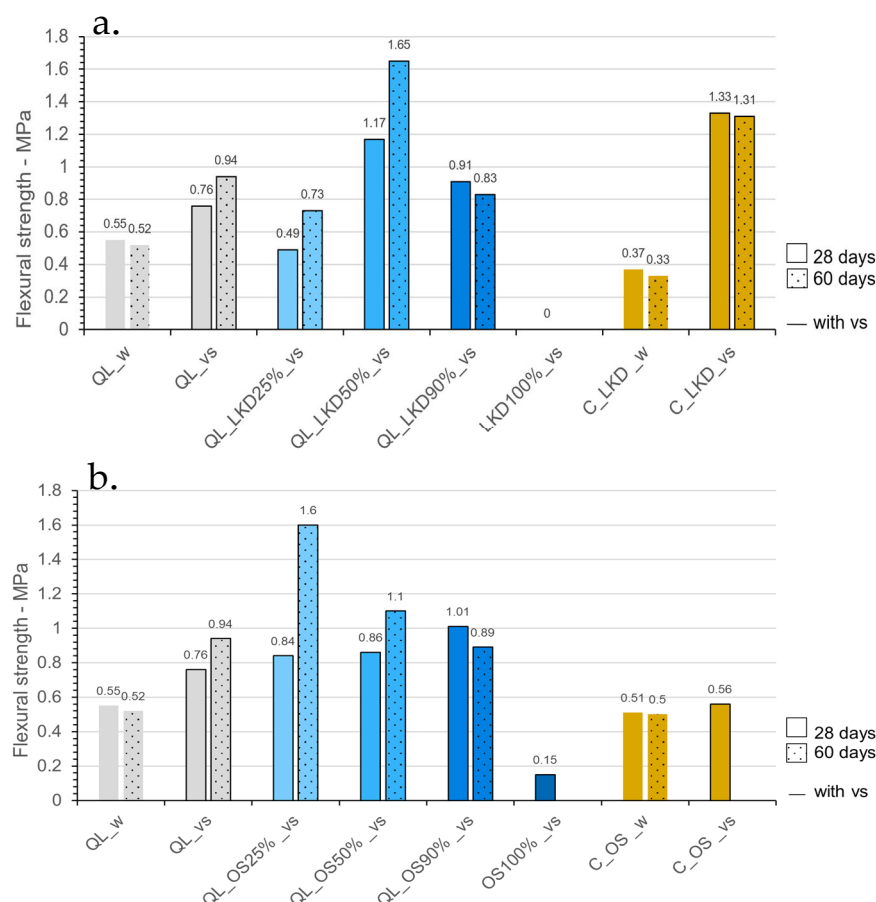


Figure 9. Flexural strength of mortars with partial substitution of quicklime (QL) by lime kiln dust (a) and oyster shells (b) after 28 and 60 days of curing.

The results show the same trend as the results obtained for compression, except for mixture QL_OS25%_vs from the oyster shell powder (OS) group.

Within the LKD series, the polynomial trend, shown in Figure 10a, highlights the optimum (~50%), consistent with the compressive strength results. Furthermore, it can be noted that the use of SV enhanced the bending performance of all LKD mortars except for the mixture with 100% of substitution (LKD_vs); the reference QL_vs mixture (with VS solution) increased by approximately 38% compared with QL_w (with water); The QL_LKD50%_vs mixture attained the highest overall value (1.65 MPa). This improvement exceeds the experimental variability and supports the role of the vinegar-based solution as a mild activator contributing to enhanced early cohesion and bending performance.

Considering the polynomial trend lines (Figure 10a,b), the LKD group presents a similar result as that obtained for compressive strength, with maximum resistances close to 50%. This optimum reflects a balance between the availability of reactive CaO and the increasing presence of the Ca-P phase, which progressively constrains the mechanical resistances at higher substitution levels. However, the OS-based mortars displayed a more uniform mechanical response in general, but with a distinct peak for the QL_OS25%_vs mixture, followed by a moderate decline at higher substitutions, seen in Figure 10b. Unlike the LKD mortars, the OS systems showed less sensitivity to the substitution level, which is consistent with their higher chemical purity and stable CaCO₃ crystalline phase [46,47]. This behaviour leads to a more uniform flexural response and reduced sensitivity to substitution level, as stress transfer under bending is less affected by variations in reactive phases.

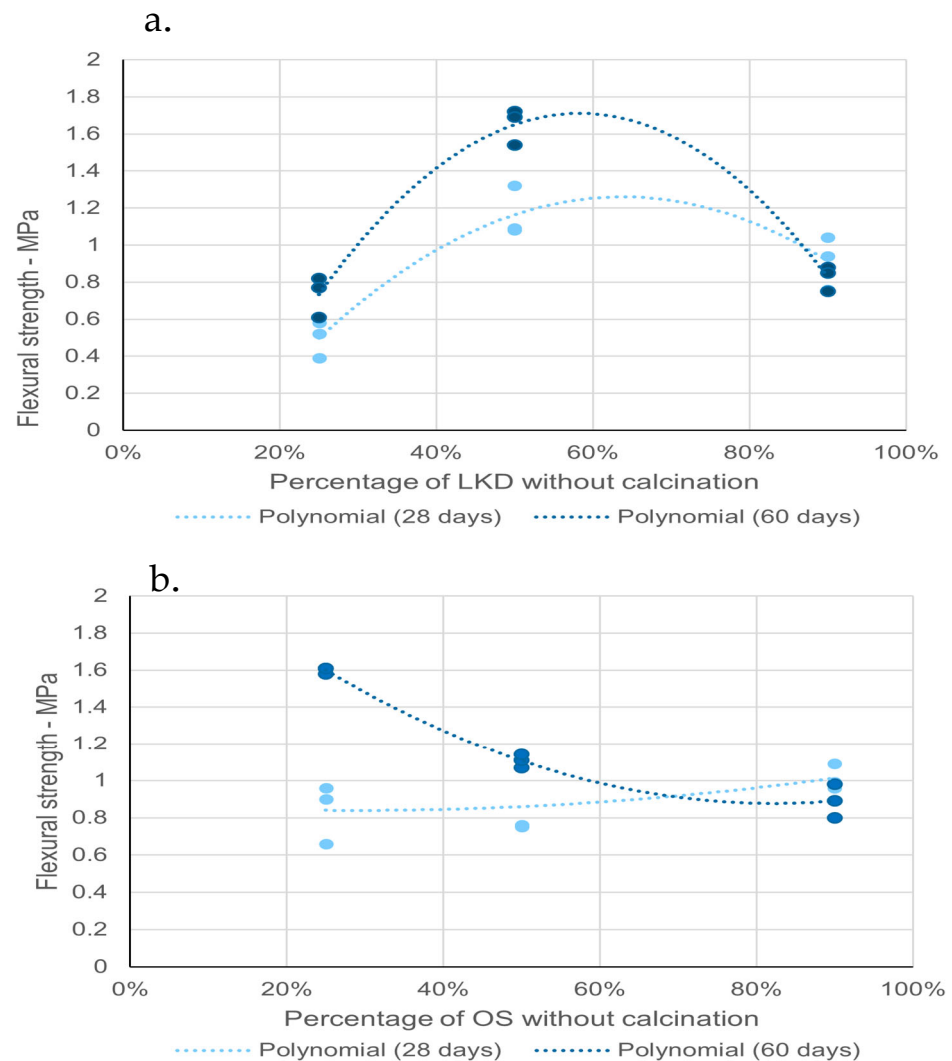


Figure 10. Polynomial trend of flexural strength at 28 and 60 days for increasing substitutions of LKD (a) and OS (b); each point corresponds to a test sample.

3.2.4. Water Absorption by Capillarity and Immersion

Figure 11 presents the results of capillary water absorption for the LKD and OS powder groups. All mixtures exhibited a fast initial water absorption followed by stabilisation, characteristic of lime-based matrices dominated by capillary porosity. The similar shape and evolution of the absorption curves for each formulation suggest a consistent test response, enabling qualitative comparison between mixtures despite the absence of statistical dispersion parameters. However, the mixture with 90% oyster shell powder and activated by the vinegar solution (QL_OS90%_vs) had slower water absorption over time. This could mean that the partial substitution of lime, combined with the acetic solution, favoured a denser and less permeable matrix. The reference lime mortar with quicklime and water (QL_w) reached the highest water absorption, whereas mixtures containing residues and the VS demonstrated a reduction in total absorbed water, with relatively similar absorption curves for both residues. The mixtures with lower absorption levels were the mixtures with 90% of replacement QL_LKD90%_vs in both groups, LKD and OS powder.

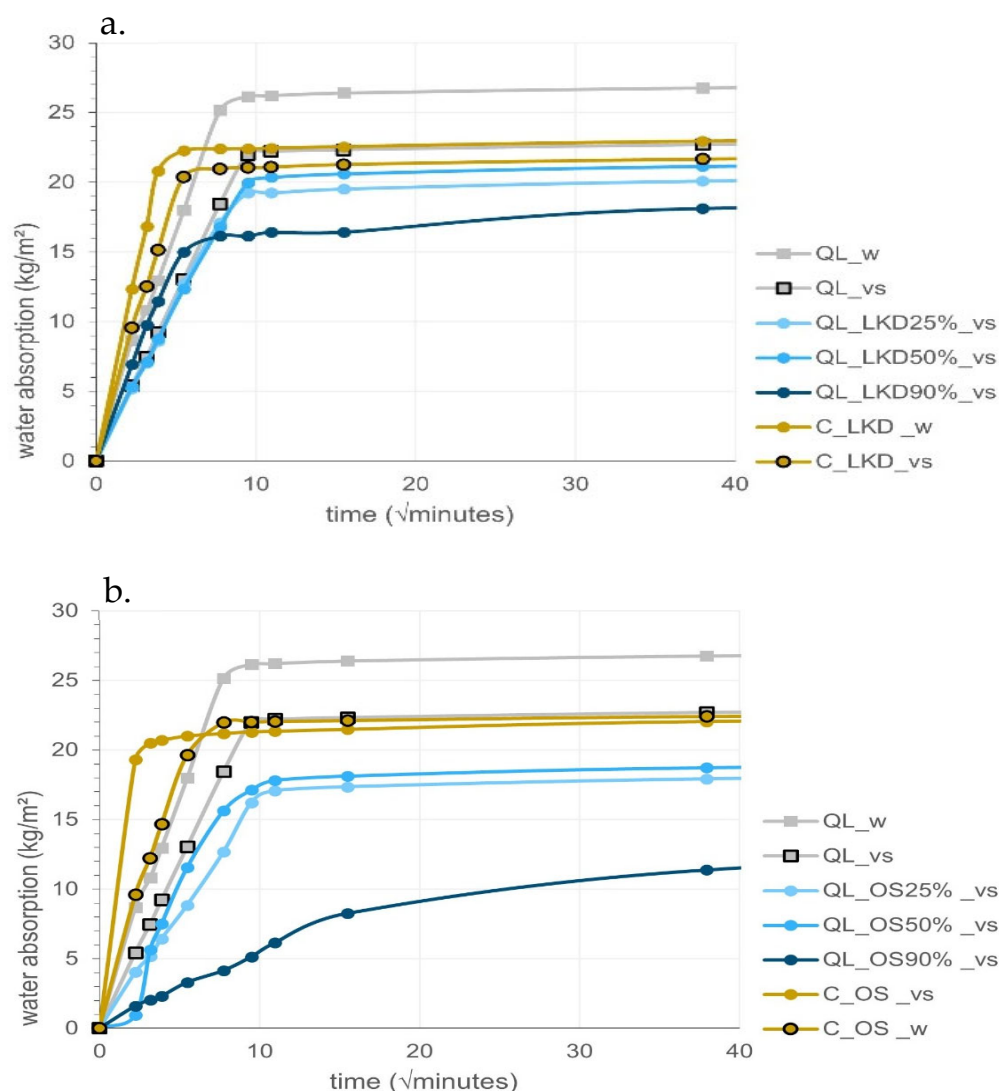


Figure 11. Water absorption by capillarity of mortars incorporating LKD (a) and OS residues (b) after 28 days.

According to the classification of mortars established in EN-998-1 [64], the capillary water absorption coefficient is not specified for these rendering and plastering mortars: general purpose (GP); lightweight (LW); or coloured (CR). However, for one-coat external use (OC) and thermal insulating mortars (T), it should not exceed $0.4 \text{ kg/m}^2 \text{ x min}^{1/2}$. As shown in Figure 11, only the mixture with 90% oyster shell powder and activated by the vinegar solution (QL_OS90%_vs) has a coefficient below this limit, with 0.35. But these high values reflect a porosity typical of lime-based mortars. Nevertheless, all formulations remained above the EN 998-1 [64] limit, indicating that these mortars should be restricted to indoor or low-humidity applications. The use of natural hydrophobic additives (e.g., linseed oil or beeswax emulsion) could further enhance capillary resistance while maintaining vapour permeability [65,66]. Figure 12 shows the water absorption coefficients and the percentage of water absorbed by immersion. Analysing the graph in general, it is possible to observe that there is not always a direct relationship between the absorption coefficient and water absorption by immersion. This indicates that capillary absorption is mainly governed by pore connectivity and surface tension effects, while immersion absorption reflects the total openness of the matrix. Mixtures with the calcined substitution wastes (both LKD and OS powder) have the highest capillarity coefficients. The group of LKD replacements shows a progressive reduction in overall water absorption (capillarity

and immersion) as the replacement percentage increases. At high substitution levels, the reduced content of reactive lime and the increased proportion of inert carbonate phases may contribute to lower water absorption, despite the higher overall porosity typical of lime-based mortars. In the OS powder group, however, there is no linear result or even a trend with substitution in the capillarity coefficients. Nevertheless, there is a trend in the water absorption values by immersion, showing that there is also a reduction in absorption with increased substitution.

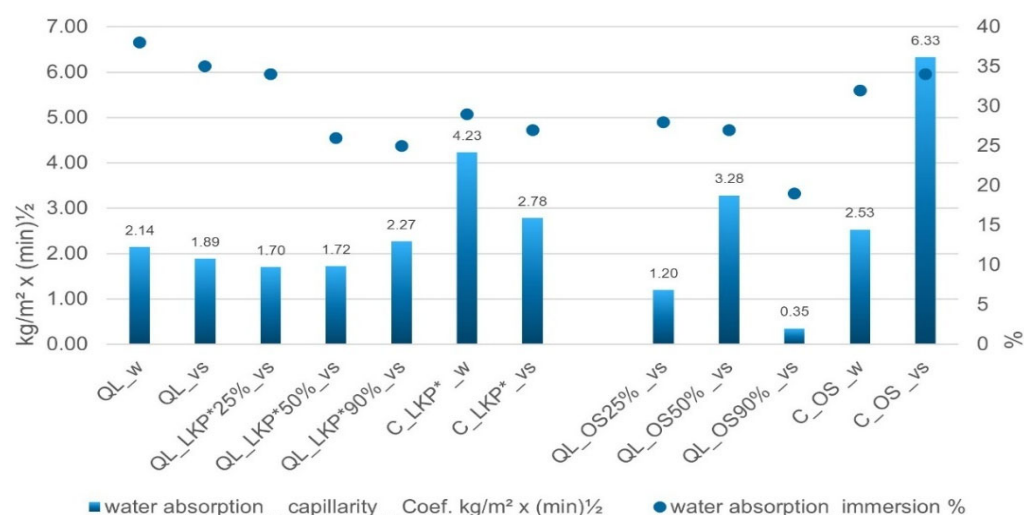


Figure 12. Water absorption coefficients and percentage of water absorbed by immersion.

Comparing the mixtures with and without the VS (QL_w/QL_vs; C_LKD_w/C_LKD_vs; and C_OS_w/C_OS_vs), it can be observed that in the reference mixtures and in the LKD-based mixtures, there is a reduction in absorption (capillarity and immersion), showing the beneficial effect of the joint addition of the VS. This behaviour suggests that the presence of the vinegar-based solution contributes to partial pore refinement when sufficient reactive CaO is available, leading to reduced water uptake. But, in the mixtures with OS powder, the result is unclear, since the values obtained are contradictory and no trend can be verified.

Moreover, there does not appear to be any relationship between the different finenesses of the two materials (LKD has a particle size distribution of 29.7 µm and OS powder has one of 40.4 µm), since no better results are observed in general in mixtures with LKD. This suggests that chemical composition and phase reactivity play a more relevant role than particle size alone in controlling water absorption behaviour in these lime-based systems.

3.2.5. Microstructure Analysis—SEM, EDS and XRD

The microstructure evaluation was performed on the reference mixtures, QL_w and QL_vs, and on the mixtures with the best mechanical performance with 50% of binder replacement, QL_LKD50%_vs and QL_OS50%_vs.

Figure 13 shows the obtained images at two magnifications, 1000× and 15,000×. In general, all mixes exhibit features associated with the hot-hydration process, i.e., “Hot lime mixtures”. The lime matrices of hot mixtures commonly have small crystals (mostly <3 µm) and an open structure, whereas hydrated-lime mortars had a more ordered and dense structure with larger crystals (>10 µm) [67]. Another feature related to steam generation during hot hydration is the presence of a smoother, yet cavernous surface [68]. This feature is particularly visible in the reference mixes, either without or with the VS (Figure 13a,b). It is also somewhat visible in the 1000× image of the mix with 50% LKD (Figure 13g), but it is not observed in the mix with 50% OS, which may be related to the smoother and more

glassy surface of shells compared with lime dust, which may make steam adsorption more difficult, in addition to the lower density and, consequently, lower specific surface area.

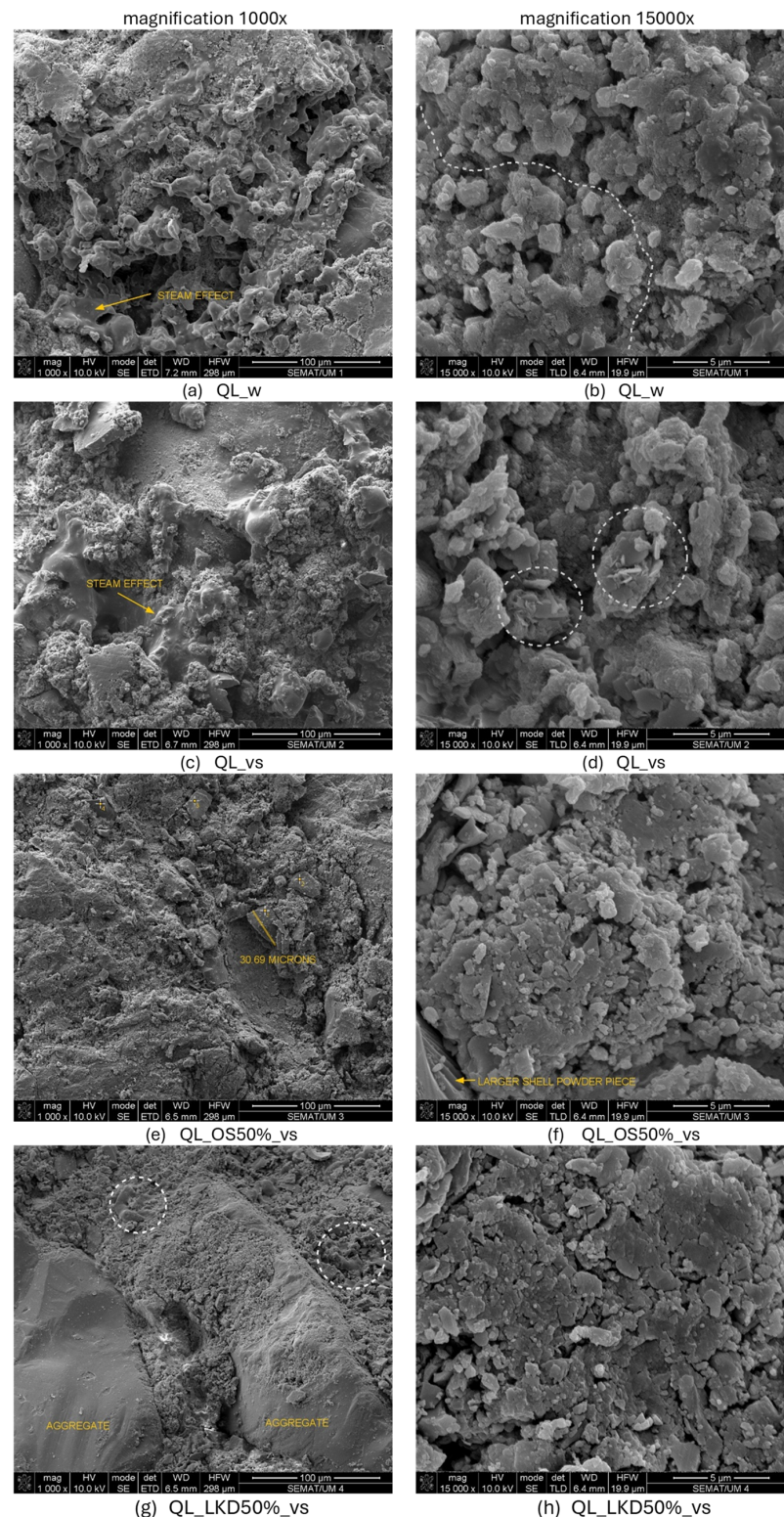


Figure 13. Microscopic images of the mortar samples after 7 days of curing at 1000 $\times$ and 15,000 $\times$ magnification: (a,b) reference mixture with quicklime and water; (c,d) mixture with quicklime and VS; (e,f) mixture of quicklime and 50% replacement by oyster shells with VS; (g,h) mixture of quicklime and 50% replacement by LKD with VS.

Regarding porosity and the structure of particles in the binder matrix, higher porosity is observed in the reference mixes, especially in the water mix, as evidenced by the open porosity that could allow water to pass through, as shown in the $15,000\times$ image of QL_w (Figure 13a,b). Moreover, this mix shows a clearly cavernous structure. By contrast, the vinegar mixes appear more flocculated, particularly QL_vs (Figure 13d). The mixes with 50% binder replacement appear less porous, which may be related to the combination of particles with different densities (OS 2710 kg/m^3 , LKD 2.718 kg/m^3 and quicklime 3.310 kg/m^3).

It is also observed that the mix QL_vs still presents two pozzolanic-reaction agglomerates, visible in the $15,000\times$ image (Figure 13d).

Regarding the EDS results (Figure 14), the mixes incorporating the vinegar solution and containing calcium acetate generally exhibit, as expected, a higher calcium (Ca) peak. However, although the oyster shell powder mix (QL_OS50%) also contains calcium acetate derived from the VS, it shows a comparatively lower Ca peak than does the mix with lime dust QL_LKD50%. This difference may be explained by the higher LKD fineness relative to the shell powder (shell powder $40.4\text{ }\mu\text{m}$; LKD $29.7\text{ }\mu\text{m}$), which likely leads to a more homogeneous distribution of Ca and facilitates its detection during EDS.

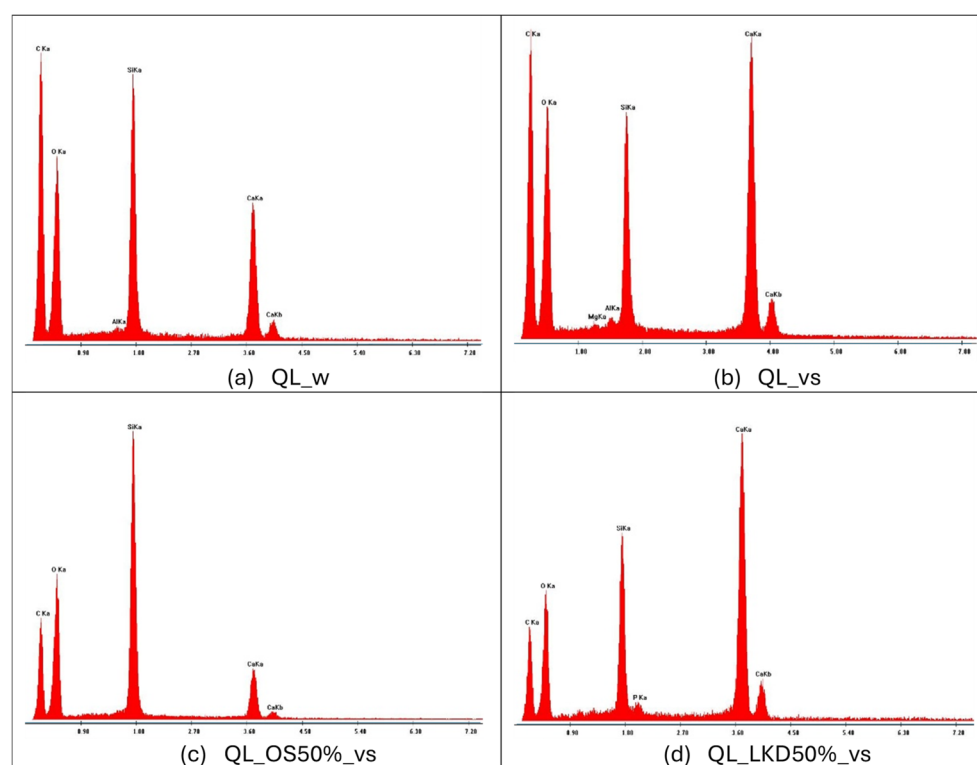


Figure 14. EDS—Peaks of elements present in the studied mortars: (a) reference mixture with quicklime and water; (b) mixture with quicklime and VS; (c) mixture of quicklime and 50% replacement by oyster shells with VS; and (d) mixture of quicklime and 50% replacement by LKD with VS.

In QL_LKD50%, a phosphorus (P) peak is observed, as expected, since phosphorus is more abundant in the lime dust composition than in the shell powder.

In addition, the presence of alumina and magnesium in mix QL_vs supports the occurrence of a pozzolanic reaction (flakes visible in microscopy Figure 14d). Nevertheless, this reaction appears to be localised and is likely associated with residues present in the quicklime (as indicated by the chemical analysis in Table 6).

The atomic and weight contents of EDS (Figure 15) show mutually consistent trends, although they should be interpreted as semi-quantitative and dependent on the analysed

areas. Overall, C and O dominate in all mixes; however, QL_LKD50%_vs stands out for exhibiting a substantially higher calcium content and for being the only mix in which phosphorus is detected. This is justified since LKD shows a higher percentage of phosphorus in its chemical analysis. In parallel, it shows a lower carbon fraction and a higher oxygen fraction when compared with the remaining mixes. In contrast, QL_OS50%_vs presents a higher contribution of silicon and a lower calcium content, suggesting a stronger influence of Si-rich domains in the measured areas.

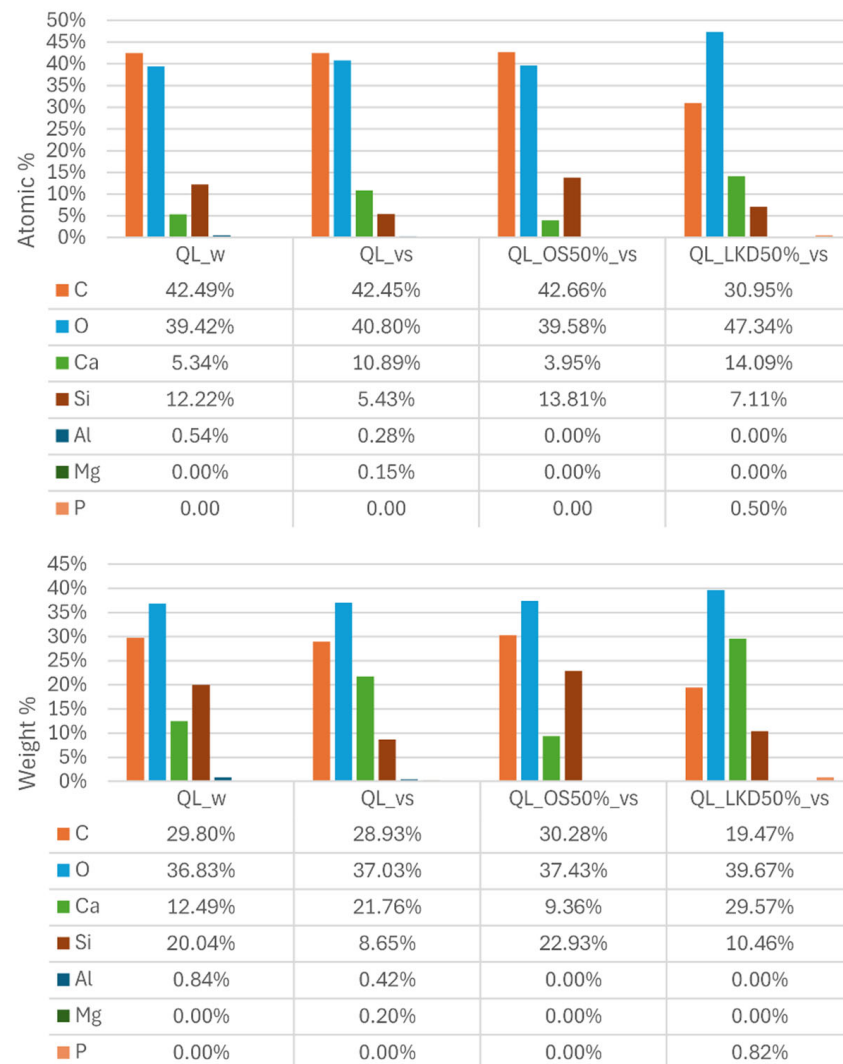


Figure 15. Atomic and weight percentages recorded in the EDS analysis.

Comparing the reference mixes, the vinegar-containing mix (QL_vs) has approximately twice as much calcium as the water-containing mix (QL_w) ($\approx +104\%$ in at. % and $\approx +74\%$ in wt.%). With vinegar as the base condition, the 50% replacement with LKD (QL_LKD50%_vs) results in more calcium than in QL_vs ($\approx +29\%$ in at.% and $\approx +36\%$ in wt.%), whereas the 50% replacement with shells (QL_OS50%_vs) shows the opposite pattern: less calcium than QL_vs ($\approx -64\%$ in at.% and $\approx -57\%$ in wt.%). A explanation for these differences is that the type of replacement material alters the distribution and nature of the phases detected locally by EDS. Lime dust (LKD), being an essentially calcium-based material and generally finer and more reactive, tends to contribute to a matrix with a higher fraction of Ca- and O-rich phases, increasing the likelihood that the EDS beam samples calcium-rich “binder” domains. By contrast, replacement with oyster shells (OS), although also

predominantly CaCO_3 , may introduce greater microstructural heterogeneity and favour the interception of regions where the relative contribution of Si-rich particles (from the siliceous aggregate) is more pronounced, resulting in an EDS signal with higher Si and lower Ca in the analysed areas.

The XRD results obtained in this study (see Table 10) show a higher presence of aragonite in mixtures with the VS, which is justified since this solution contains dissolved compounds from oyster shells, mainly calcium in the form of calcite and aragonite [19]. Similarly, the presence of hydroxyapatite is also justified since it is also present in the mother-of-pearl part of oyster shells [19], whose phosphorus element was verified in the chemical analysis of the shells used (7.72%). The presence of rhenanite (NaCaPO_4) can also be justified in the mixture with shells (QL_OS 50%_vs) since it is a compound with sodium, calcium and phosphorus and, being a marine shell, sodium may be present. Its presence in the mixture with LKD (QL_LKD 50%_vs) is also justified since it is a common compound in this type of industrial by-product, as mentioned above. Additionally, the existence of a greater amount of phosphate compounds in this mixture, including calcium phosphate hydroxide, is justified by the greater presence of phosphorus in the chemical composition of the LKD used (15.85%).

Table 10. Quantitative analysis of phases found in the studied mortars; ratios of carbonates/hydrates and aragonite/calcite; and higher compressive strength obtained at 60 days.

Mixtures	Phase Composition (Weight %) (By RIR Method)								Ratios		Cp
	Quartz	Portlandite	Calcite; Aragonite	Brucite	Gypsum	Carbonated Hydroxyapatite	Rhenanite	Calcium Phosphate Hydroxide	C/H	Ara/Cal	
QL_w	43.3	32.2	20.7; 2.5	0.5	0.8	0	0	0	0.72	0.24	1.16
QL_vs	43.3	38.0	9.5; 5.9	0.7	1.2	1.5	0	0	0.45	0.62	2.18
QL_OS 50%_vs	56.2	16.0	15.2; 6.5	0.3	0.4	2.5	2.7	0	1.36	0.43	2.07
QL_LKD 50%_vs	42.3	7.7	15.9; 14.7	2.3	1.4	2.9	6.0	6.7	2.89	0.92	3.11

Quantitative analysis shows that compressive strength (CS) increases proportionally with the aragonite-to-calcite ratio (Ara/Cal) and tends to increase with the carbonate-to-hydrate ratio (C/H), indicating that both the extent of carbonation and the relative proportion of carbonate polymorphs influence the mechanical performance of the mixes. The positive correlation between higher aragonite contents and higher compressive strength suggests that the relative abundance of aragonite may be associated with denser microstructures. This interpretation is consistent with the work of Malladi et al. [69] on lime mortars containing organic additives in acidified aqueous solutions, which promote the formation of alternative polymorphs (e.g., aragonite) in addition to the conventional calcite. This finding highlights that chemical modification of the medium, particularly acidity, can significantly alter the mineralogical evolution of lime mortars. Although the pH of the vinegar solution modified with calcium from the shells was 5.5, less acidic than the pH of aqueous solution used by these authors [69], which ranged from 3.01 to 3.39. In line with the results obtained here, Malladi et al. also reported higher compressive strength, particularly for specimens subjected to accelerated carbonation [69].

An exception is the vinegar reference mix (QL_vs), which exhibits a slightly lower C/H ratio; however, it contains carbonated hydroxyapatite, as well as higher amounts of gypsum and magnesium hydroxide than the water reference mix (QL_w), indicating that these phases may contribute to increased strength.

In the present study, mix QL_LKD50 shows the highest C/H (+113% relative to the equivalent oyster shell mix), the highest Ara/Cal (+114%), and the highest compressive

strength (+50%), suggesting that the use of lime dust, associated with higher aragonite, phosphorus, and gypsum contents, affects the evolution of carbonate phases and the resulting strength gain. Furthermore, the literature indicates that phosphate-based treatments/additions in lime- or even cement-based mortars can induce the formation of new calcium phosphate phases within the porous matrix, producing a consolidating effect (bond strengthening and local microstructural densification) and improving mechanical properties relative to untreated mortars [70].

The diffractograms of the mortar samples are shown in Figure 16, where the results are in agreement with the quantitative analysis of the phases (Table 10), revealing peaks associated with silicon oxide, calcium hydroxide, calcium carbonates, calcium phosphate and other identified phases. The quantitative XRD result further shows that the mixture with 50% LKD replacement exhibits the highest aragonite-to-calcite and carbonate-to-hydrate ratios, which directly correlate with the maximum compressive strength measured at 60 days, supporting the identification of this substitution level as a mineralogically driven optimum.

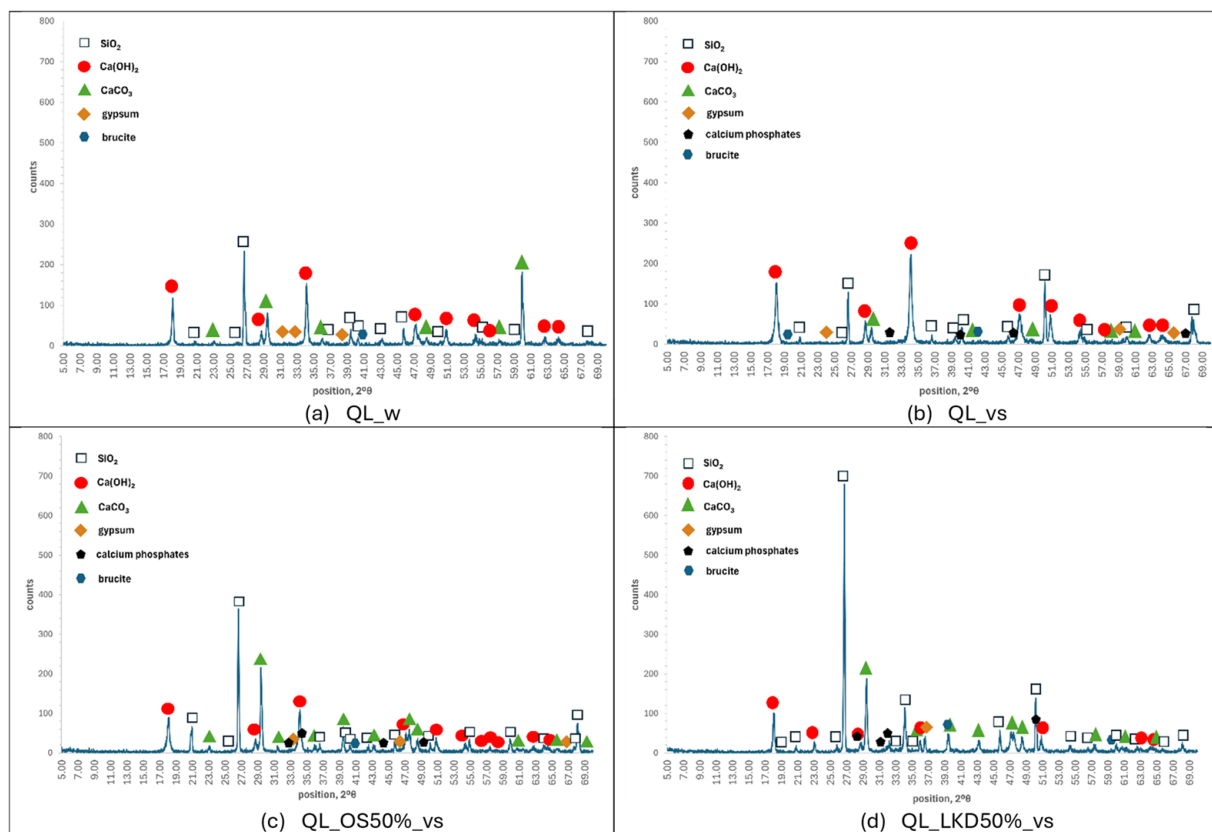


Figure 16. Diffractograms of mortar samples at 7 days of curing: (a) reference mixture with quicklime and water; (b) mixture with quicklime and VS; (c) mixture of quicklime and 50% replacement by oyster shells with VS; and (d) mixture of quicklime and 50% replacement by LKD with VS.

4. Synopsis of Results and Comparison with Other Studies

Table 11 presents a summary of results and a comparison with the results obtained by other authors in studies with aerial lime mortars, some on the use of hot hydration and others on conventional cold hydrated lime.

Table 11. Synopsis of results.

Type of Hydration	Mixtures	Compressive Strength—MPa		Flexural Strength—Mpa		Water Absorption		EDS	EDS/DRX
		28 Days	60 Days	28 Days	60 Days	Capillarity Coefficient	Immersion %		
Hot lime reference mixtures	QL_w	0.83	1.16	0.55	0.52	2.14	38	Extremely porous and cavernous structure; Partial steam effect	Heterogeneity in carbonation due to few days of curing
	QL_vs	1.86	2.18	0.76	0.94	1.89	35	Porous but flocculated structure; Partial steam effect	Heterogeneity in carbonation due to few days of curing
Hot lime mixtures with LKD + VS	QL_LKD25%_vs	1.34	2.01	0.49	0.73	1.70	34	Less porous structure; Partial steam effect	Presence of phosphorus
	QL_LKD50%_vs	2.04	3.11	1.17	1.65	1.72	26		
	QL_LKD90%_vs	1.14	1.35	0.91	0.83	2.27	25		
Cold LKD + VS	LKD100%_vs	0.14	x	0	x	x	x	Less porous structure; No vapour effect	Less calcium identified
Cold-hydrated calcined LKD 800 °C	C_LKD_w	0.86	2	0.37	0.33	4.23	29		
	C_LKD_vs	2.02	2.27	1.33	1.31	2.78	27		
Hot lime mixtures with OS + VS	QL_OS25%_vs	1.2	1.9	0.84	1.6	1.20	28	Less porous structure; No vapour effect	Less calcium identified
	QL_OS50%_vs	1.37	2.07	0.86	1.1	3.28	27		
	QL_OS90%_vs	1.3	1.62	1.01	0.89	0.35	19		
Cold OS + VS	OS100%_vs	0.36	x	0.15	x	x	x	The steam effect makes the porous and cavernous structure more connected and smoother	Presence of portlandite and calcite; steam-slaked lime has smaller crystallite size
Cold-hydrated Calcined OS 800 °C	C_OS_w	0.88	1.27	0.51	0.5	2.53	32		
	C_OS_vs	0.76	0.97	0.56	x	6.33	34		
Other Authors									
Hot lime mortars ref Pesce et al. 2021 [68]	Water 20 °C Water 75 °C Steam slaked trace 1:3	values close to 0.8		0.25 to 0.45				Presence of fractures in the mixture of hot lime pieces	Presence of organic compounds; Greater presence of aragonite
Hot lime mortars matured for 7 days Margalha et al. 2011 [71]	Hot lime: in pieces trace 1:3;	0.6		0.43		1.33			
	Micronized trace 1:2	0.81		0.42		1.4			
Malladi et al. 2025 [69]	Hydrated lime mixture, Bio-additives trace 1:3 (56 days)		1.29 and 2.4 with CO ₂						Calcite peaks higher in mortars with lower binder content as L2
Cold lime mortars Gameiro et al. 2014 [4]	Hydrated lime Mixture L2 trace 1:2	0.42		0.18					
Cold lime mortars Veiga et al. 2010 [72]	Hydrated lime, different sand types; mixture AL3 trace 1:3	0.97		0.59		0.56			

Table 11. Cont.

Type of Hydration	Mixtures	Compressive Strength—MPa		Flexural Strength—Mpa		Water Absorption		EDS	EDS/DRX
		28 Days	60 Days	28 Days	60 Days	Capillarity Coefficient	Immersion %		
Cold lime mortars Lanas et al. 2003 [73]	Two hydrated limes, A and B race 1:2	Lime A 1 to 1.5; lime B 0.5 to 0.8		Lime A 0.2 to 0.5; lime B 0.2 to 0.4					
Cold lime mortars Scannell et al. 2014 [74]	Hydrated lime Different sand types; trace1:2	0.6 to 1.4						Fewer calcite crystals on silicate aggregate surface; Larger space on aggregate/binder interface than limestone aggregate.	
Mortar with Shell lime calcined at 1000 °C Zhang et al. 2019 [75]	Hydrated shell lime; Addition of rice pulp trace1:2	0.5 0.87 with rice pulp							

Note: The highest values obtained for each type of mixture tested are highlighted in bold.

Overall, the mixes with the addition of the vinegar solution exhibit higher mechanical strengths and lower water absorption compared with the same mixes containing only water. However, the mixes with calcined shell powder, C_OS_w and C_OS_vs, show the opposite results with respect to the addition of VS/strength/absorption. This indication of a lower reaction with the SV solution may be related to the lower density of this material compared with lime dust (2336 kg/m³ in calcined OS and 2906 kg/m³ in calcined LKD), since there is a smaller surface area for interaction with the compounds in the SV solution.

When comparing the results obtained with those reported by other authors, the following can be noted:

- Studies on hot-lime mortars report results very close to those of the quicklime-and-water mix, QL_w, in terms of strength and a porous, cavernous microscopic structure with a smoothing effect due to the presence of steam. No cracking was observed in any mix, since micronized quicklime was used. Considering the studies presented, the vinegar mixes show higher mechanical strength values, particularly QL_vs, QL_LKD50%_vs, and QL_OS50%_vs.
- Studies on cold-hydrated lime mortars show greater variability. Nevertheless, it is possible to observe that, in general, their strengths are lower than those of the quicklime mixes reported by other authors or in the present work. The most comparable mortars in this study would, as expected, be the cold-hydrated mixes using calcined materials: C_OS_w, C_OS_vs, C_LKD_w, and C_LKD_vs. It is observed that the mixes with calcined shell powder show strengths within the ranges reported by other authors. In contrast, the mixes with calcined lime dust show higher values, particularly with the addition of the vinegar solution.

Considering the highest 28-day compressive strengths reported in the cited studies, 1 to 1.5 MPa, for cold-hydrated lime mortar [73], it is observed that even the mixes with the highest replacement levels fall within the same range, with QL_LKD90%_vs at 1.14 MPa and QL_OS90%_vs at 1.3 MPa.

The study by Malladi et al. obtained similar results in terms of the presence of more argonite in XRD, with organic additives fermented in aqueous solution with acidity and

closer resistance at 56 days (close to 60 days). However, for greater resistance, these authors used a carbonation chamber [69].

- Considering the mortars produced with calcined material, a paper was identified that also used a 1:2 mix ratio and shell lime obtained from seashells calcined at 1000 °C, likewise reporting low strengths. However, those authors reported a significant improvement with the addition of rice pulp (starch-based), increasing compressive strength from 0.5 to 0.87 MPa, whereas the VS led to a slight decrease (from 0.88 to 0.76 MPa). For the calcined paper industry LKD, no studies on lime mortars were found to enable a direct comparison. Nevertheless, relative to the use of shell lime, the tested calcined LKD at 800 °C yielded similar strength under conventional hydration with water (0.86 MPa), while the addition of VS increased the strength to 2.02 MPa (an increase of 134.9%). Overall, the results suggest that the VS is more reactive with calcium from LKD than with calcium from oyster shells.

5. Conclusions

This exploratory research focused on the valorisation of lime kiln dust from the paper industry (LKD) and oyster shell residues as sustainable calcium sources to produce eco-efficient mortars, introducing for the first time a vinegar-based calcium solution (VS) derived from shell–acid reactions as an alternative to water to avoid the calcination process. The main findings can be summarised as follows:

- Material characterisation confirmed that both residues are highly calcium-rich and present phosphorus in the composition:
 - LKD presented ≈ 81.5 wt.% of CaCO_3 and 15.85 wt.% of P.
 - Oyster shell powder exhibited ≈ 95.5 wt.% of CaCO_3 , with 7.72 wt.% of P.
- In the fresh state, all mixtures exhibited adequate workability.
- In the hardened state, the vinegar-based solution (VS) proved effective in enhancing the reactivity of lime-based systems, acting as a mild activator once greater resistance was achieved without calcination for raw materials, mainly with LKD. The comparison of the reference mortars shows that VS markedly increases strength as an additive; the reference mixture with quicklime and water (QL_w) reached 0.83 MPa at 28 days, while the use of VS increased strength to 1.86 MPa, an improvement of $\approx 124\%$ (QL_vs), and at 60 days, the increase was more 88%. For calcined LKD material, VS is even more effective at 28 days: C_LKD_vs had +135% relative to C_LKD_w (0.86→2.02 MPa). In the calcined shell oyster (C_OS_vs vs. C_OS_w), the effect is negative. Adding VS reduces strength by -14% (28 d) and -24% (60 d) (0.88→0.76 MPa; 1.27→0.97 MPa).
- Regarding the effect of binder replacement, the mechanical performance improved significantly with the inclusion of both residues:
 - An optimum effect is observed around 50% LKD replacement. Compared with QL_vs, QL_LKD50%_vs increases compressive strength by +10% (28 d) and +43% (60 d) (1.86→2.04 MPa; 2.18→3.11 MPa).
 - The replacement by shells (OS) does not outperform the reference QL_vs and shows only a modest maximum at 50%, showing a decrease in resistance compared to the reference mixture with VS (QL_OS50%_vs: -26% (28 d) and -5% (60 d) (1.86→1.37; 2.18→2.07 MPa). However, the values obtained are still above those normally obtained with lime-based mortars and above those obtained with mortars based on lime produced from shells.
 - Using a 100% substitution (for both LKD and OS residues) did not result in mortars with sufficient strength for application.

- Durability results indicated that mortars meet the requirements for the class W_0 (capillary water absorption without specification) of the EN-998-1 [64] for these rendering and plastering mortars: general purpose, lightweight, or coloured. One mixture, with 90% oyster shell powder and activated by the vinegar solution (QL_OS90%_vs), has a coefficient that meets the minimum value for one-coat external use and thermal insulating mortars ($0.4 \text{ kg/m}^2 \times \text{min}^{1/2}$), obtaining 0.35. Which indicates that most mixtures should be restricted to indoor or low-humidity applications.
- Analyses of the structure of the mortars at a microscopic level reveal that the use of a “hot process” with quicklime, together with the vinegar solution and sand, may explain the higher resistance obtained. This is because the effect of the steam and temperature generated during the hydration phase of the lime prior to moulding was verified. Similarly, a greater presence of aragonite and phosphorus compounds was observed in mixtures with VS, which may also be reinforcing the binding matrix.

In general, it can be concluded that these waste materials and the use of vinegar enable the formulation of eco-friendly mortars with a high reduction in the calcined materials, since even mixtures with 90% substitution achieve strengths compatible with compressive strength class CS I (0.4 to 2.5 MPa at 28 days) and CS II (1.5 to 5 MPa at 28 days), categories for rendering mortars (EN998-1 [64]). Its low energy demand offers a viable alternative to the use of these biogenic and industrial residues in the production of lime mortars.

Future research recommendations.

As this is an exploratory study with promising and innovative findings, further research is required to deepen the understanding of specific aspects:

- Microstructural and mineralogical analysis: Future studies should further investigate the biogenic phases that can be present in vinegar and the interaction of this calcium carbonate using FTIR and thermogravimetric analysis (TGA), to better understand the reaction mechanisms responsible for strength and durability improvements.
- Carbonation assessment: It would be interesting to study the carbonation process over time to verify the effect of vinegar addition on carbonate formation.
- Long-term durability: Further testing under wet–dry, freeze–thaw, and salt-spray cycles should be performed to assess dimensional stability and surface degradation resistance.
- Hygrothermal behaviour: The study of water vapour permeability and evaluation of thermal conductivity.
- Compatibility with other materials: Studies of adhesion to the substrate and studies of the incorporation of natural fibres.

Author Contributions: Conceptualization, R.E.; Methodology, R.M.; Investigation, T.P.; Writing—original draft, R.E. and A.Z.; Writing—review & editing, R.M.; Supervision, R.E. All authors have read and agreed to the published version of the manuscript.

Funding: Research funded by Fundação para a Ciência e a Tecnologia (FCT), Grant “Centro de Território, Ambiente e Construção” (UID/04047/2025), DOI <https://doi.org/10.54499/UID/04047/2025> (accessed on 25 January 2026).

Data Availability Statement: Part of the data is provided in the Thianne Peixoto’s Thesis, “Utilização de conchas de ostras e pó de forno de cal na composição de argamassas ecoeficientes” (In Portuguese) at RepositóriUM (University of Minho repository) <https://hdl.handle.net/1822/95858> (accessed on 25 January 2026). Other original data presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: The authors would like to acknowledge the companies, DS Smith Paper Viana and Aquagoma, which provided the by-products for this study.

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

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