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Review

Phase Change Materials in Lime-Based Mortars for the Energy Efficiency of Historic Buildings: State-of-the-Art and Prospects

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Highlights

- PCMs incorporated into lime mortars for applications in historic buildings have been shown to be effective in reducing indoor temperature fluctuations.
- Lime-based mortars showed an increase in durability due to the incorporation of PCMs while their mechanical characteristics depend on the specific binder.
- Current literature has not taken into account important aspects of mortars containing PCMs: the reversibility of the intervention, compatibility with historical substrates, scale-up from laboratory scale to real scale.

Abstract

Historic buildings represent a substantial share of the European building stock. However, their energy retrofit is heavily restricted by conservation principles that often exclude conventional insulation systems. In this context, phase change materials (PCMs) incorporated into lime-based mortars have emerged as a potentially compatible solution, combining latent heat storage capacity with the compatibility traditionally associated with aerial lime, the binder of reference in conservation practice. In some cases, natural hydraulic lime and hydrated lime are also used in heritage conservation applications. The aim of this study, therefore, is to provide a systematic review of peer-reviewed articles published between 2010 and 2026 that illustrate the use of PCM-containing lime mortars applied in historic buildings. The analysis examines PCM types, incorporation methods, thermal and mechanical behavior, durability, and compatibility with conservation requirements. The reviewed studies demonstrate that the incorporation of PCM generally reduces internal thermal fluctuations in buildings along with capillary water absorption. Durability investigations indicate improved resistance to freeze–thaw cycles and salt crystallization of mortars containing such PCMs. However, durability was investigated in less than 20% of the studies reviewed. Lime mortars show a consistent reduction in compressive strength as the PCM content increases; on the other hand, hydrated lime mortars can also offer increases in strength. Although the reviewed studies focused on applications in historic buildings, the reversibility of the intervention and its compatibility with historic substrates was not assessed according to the standards required for the conservation of cultural heritage. This gap represents the main limitation of the research conducted.

Keywords: phase change materials (PCMs); lime mortar; historic buildings; thermal energy storage (TES); building conservation; reversibility; durability; heritage retrofit; conservation compatibility

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1. Introduction

The building sector accounts for approximately 40% of total final energy consumption in the European Union, with heating and cooling representing approximately 80% of energy use within buildings [1]. The financial burden associated with this consumption has been substantially amplified in recent years by the energy price crisis triggered by geopolitical instability, which has accelerated political and public awareness of the need for energy autonomy, cost resilience, and the rapid deployment of sustainable, efficient, and affordable technologies for the built environment.

Among the strategies available for reducing the thermal energy demand of buildings, passive thermal storage through phase change materials (PCMs) has attracted growing research interest over the past two decades. PCMs are substances that are able to absorb and release large amounts of latent heat during a solid-to-liquid phase transition in a well-defined temperature range, effectively dampening indoor thermal fluctuations [2–4]. When incorporated into building envelope components, such as renders, plasters, panels, or concrete elements, they can reduce peak heating and cooling loads and extend thermal comfort periods with direct benefits for energy consumption along with occupant comfort [5–7].

However, most of the research developed on phase change materials for such applications is limited to the context of contemporary construction, targeting new-build or recently constructed residential buildings where the primary objective is energy efficiency, and the material selection is directed by performance and cost criteria alone. Historic buildings have received comparatively only limited attention, despite representing a significant and particularly challenging segment of the European building stock. At the same time, historic buildings are constantly used for a wide range of functions, i.e., as museums, libraries, places of worship, concert halls, conference venues, administrative offices, and residential dwellings. In all these contexts, thermal comfort directly impacts the experience of occupants and visitors. Furthermore, stable temperature conditions are often a prerequisite for the preservation of antique collections, furnishings, and decorated surfaces.

The energy requalification of historic buildings is, however, strongly constrained by the requirements of conservation practices. The principles codified in the ICOMOS Venice Charter [8] and standardized in UNI EN 15898:2010 [9] prohibit interventions that are irreversible, physically, or chemically incompatible with the original masonry or damaging to the historic substrate. Conventional energy retrofit strategies, external insulation composite systems, replacement glazing, and mechanical ventilation are frequently incompatible with these requirements, either because they alter the appearance of the building, introduce mechanical fixings that damage the masonry, or create hygrothermal conditions that accelerate deterioration [10,11]. These constraints have focused research on interventions that are compatible with the materials used to construct historic buildings.

Lime-based mortars occupy a privileged position in this context. In particular, aerial lime has been the primary binder in European construction for millennia, and its use in conservation practice is supported by a robust body of evidence demonstrating its physical and chemical compatibility with historic substrates. This binder offers low compressive strength and high deformability. Its high vapor permeability allows moisture to migrate freely through the wall without accumulating at the mortar–substrate interface. Their carbonation chemistry, the slow reaction of $Ca(OH)_2$ with atmospheric CO_2 to form $CaCO_3$, is mineralogically compatible with calcareous and siliceous substrates alike [12,13]. Although aerial lime is the reference binder for conservation interventions, natural hydraulic lime (NHL) and hydrated lime (HL), classified according to EN 459-1, are increasingly used in the renovation of historic buildings, particularly when greater short-term strength is required.

Thus, the incorporation of PCMs into lime-based mortars can represent a successful strategy able to simultaneously address important challenges, i.e., improving the thermal performance of historic buildings and guaranteeing occupant comfort through an intervention based on a material that respects the reversibility, compatibility, and durability requirements of conservation practices. Research on this specific combination, PCM and lime binder in a heritage-conservation context, has grown measurably since 2010 but, to the best of our knowledge, has never been the subject of a systematic review.

Several review papers have addressed energy retrofitting strategies for existing buildings and the role of innovative materials, including PCMs, in reducing heating and cooling demand. Soares et al. [14] provided a broad overview of ten research topics on building energy performance, positioning PCMs within the wider landscape of thermal storage technologies and identifying the need for further research before their generalized use in retrofit applications. Kamel and Memari [15] and Ghazwani et al. [16] reviewed envelope retrofit techniques for residential buildings across different climate zones, both including PCMs among a range of advanced materials alongside aerogels, vacuum insulation panels, and improved glazing systems. From their studies, it was concluded that the combination of different systems is more effective than interventions based on single solutions. Chung-Camargo et al. [17] extended this analysis to tropical and humid climates, confirming the potential of PCMs as passive strategies in residential and educational buildings. Nair et al. [10] specifically addressed the challenge of energy retrofitting in heritage buildings, reviewing a range of strategies from draught-proofing to photovoltaics. In this work, only a brief section was dedicated to PCMs. In particular, their direct application on historic surfaces is not recommended due to the risk of thermal stress and mechanical damage to the original structure; the use of prefabricated panel systems is recommended as a safer alternative. This cautious position is shared by Ascione et al. [18], who modeled the application of PCM wallboards in a heritage educational building, demonstrating potential energy savings through simulation, but without any in situ validation. This also reflects the tendency of the recently published literature on PCMs to rely on modeling rather than experimental evidence.

While these contributions collectively establish the relevance of PCMs in the broader retrofit context, no study focuses specifically on their incorporation into lime-based mortars, nor does it evaluate the pros and cons with respect to the conservation requirements on which interventions in historic buildings are based. Furthermore, the compatibility of PCM-containing mortars with historical substrates, reversibility of the intervention, and long-term durability are not addressed in any of the existing reviews. All these aspects are, therefore, taken into consideration in this paper, considering them as the main unresolved issues in this context. To the authors' knowledge, this is the first systematic review to exclusively examine PCM-containing lime mortars and assess their effectiveness with respect to the specific requirements of heritage conservation practices as well.

With this aim, this paper presents a review through a systematic search of the peer-reviewed literature covering the period 2010–2026. The review addresses four research questions: (RQ1) what PCM types, lime binders, and integration methods have been investigated; (RQ2) to what extent the existing research addresses the specific requirements of heritage conservation, such as reversibility, substrate compatibility, durability, and scale of application; (RQ3) what are the mechanical and thermal performance characteristics of the resulting PCM-containing lime mortars; (RQ4) what are the principal gaps in the current evidence base, and what priorities should guide future research. The following sections provide a systematic analysis of each aspect separately.

2. Methodology

A systematic search of the peer-reviewed literature was conducted across several academic databases: Web of Science, Scopus, ScienceDirect, Google Scholar and CNKI (China National Knowledge Infrastructure). The search covered publications from January 2010 to April 2026. Seven search strings were identified and applied across all three databases (Table 1).

Table 1. Search strings applied across Web of Science, Scopus and ScienceDirect (2010–2026). All strings were executed with the field qualifier Title/Abstract/Keywords.

Search String	Focus
(“phase change material” OR “PCM”) AND “historic building”	Heritage context
(“phase change material” OR “PCM”) AND “heritage”	Heritage context
(“phase change material” OR “PCM”) AND “lime mortar”	Binder-specific
(“phase change material” OR “PCM”) AND “restoration”	Conservation
(“phase change material” OR “PCM”) AND “retrofitting”	Energy retrofit
(“phase change material” OR “PCM”) AND “retrofit”	Energy retrofit
(“phase change material” OR “PCM”) AND “plaster”	Application type

The overall study selection process is summarized in the PRISMA flow diagram, reported in Figure 1.

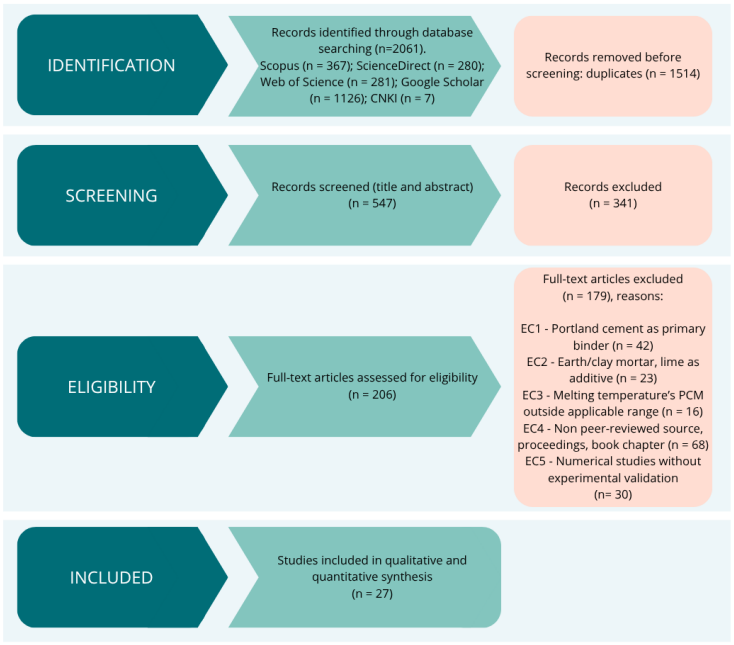

Figure 1. PRISMA flow diagram of the study identification, screening, and eligibility assessment process.

Of the 2061 records identified across the five databases, 1514 duplicates, retrieved by multiple strings, were removed prior to screening. A total of 547 records were screened for titles and abstracts; 341 of these were excluded at this stage, and the remaining 206 were assessed in full-text for all potentially eligible records against a predefined set of inclusion and exclusion criteria (Table 2). Disagreements in borderline cases were resolved through discussion and conservative application of the criteria described below.

Table 2. Inclusion and exclusion criteria applied during title/abstract screening and full-text eligibility assessment.

Inclusion Criteria	Exclusion Criteria
IC1. PCM incorporated as additive or aggregate within the mortar mix	EC1. Portland cement as the primary binder (lime present only as minor additive, i.e., cement–lime blends)
IC2. Lime-based binder as the primary binding component (aerial lime, hydrated lime or natural hydraulic lime)	EC2. Earth/clay-based mortars in which lime functions solely as a stabilizing additive
IC3. Experimental study (laboratory specimens or in situ tests)	EC3. PCM melting temperature over 75 °C (not activatable under normal indoor conditions)
IC4. Peer-reviewed article published in scientific journal	EC4. Conference proceedings, book chapters, and non-peer-reviewed reports
IC5. Explicit reference to historic buildings, architectural heritage, or conservation/restoration contexts	EC5. Purely numerical studies without experimental validation

The boundary between inclusion and exclusion deserves particular attention regarding the definition of lime as the primary binder. Two categories of studies were systematically excluded despite their topical proximity to the review scope. First, cement–lime composite mortars in which Portland cement constitutes the main binding agent and lime is added in a secondary role were excluded; in fact, these materials exhibit fundamentally different mechanical behavior, carbonation kinetics, and chemical compatibility with historic substrates compared to pure lime systems [19]. Second, earth-based (clay) mortars in which hydrated lime functions as a minor stabilizing additive were excluded, as the dominant binder and the associated physic-mechanical behavior are categorically different from those of lime-based systems [20].

The requirement that studies make explicit reference to a historic building or conservation context (IC5) reflects the specific focus of this review.

Following the screening process, full texts of eligible studies were read in their entirety and data were extracted using a structured grid organized into eight thematic groups: (i) PCM characteristics (type, melting temperature, and latent heat capacity); (ii) binder type; (iii) PCM integration method; (iv) climate compatibility (i.e., the alignment between PCM melting temperature and building use conditions); (v) heritage relevance (reversibility and compatibility with historic substrates); (vi) mechanical properties (compressive and flexural strength, open porosity and carbonation development); (vii) thermal performance (thermal conductivity and temperature attenuation); and (viii) durability (freeze–thaw, salt crystallization resistance and thermal-cycling damage).

The systematic search identified 27 publications meeting the inclusion criteria, spanning from the first documented study in 2010 to April 2026. Figure 2 shows the annual distribution and cumulative growth of the corpus. The overall publication pattern reveals two distinct phases: a slow-growth phase between 2010 and 2021, during which an average of fewer than one publication per year entered the corpus, and an acceleration phase from 2022 onwards, with an average of approximately four publications per year. This acceleration coincides with the broader policy impulse provided by the European Green Deal (2019) [21] and the revised Energy Performance of Buildings Directive (2024) [1], which together strengthened the regulatory case for the energy upgrading of existing, including historic, building stock.

The geographic distribution of the corpus reflects the concentration of research activity in southern and western Europe, with Spain, Italy, Portugal, and Cyprus accounting for the majority of contributions. This distribution is consistent with the dual concentration of

lime-based building traditions and Mediterranean climate conditions across these countries and aligns with the policy priority assigned to energy upgrading of historic building stock in the EU's renovation wave strategy.

Despite the growing volume of publications, the corpus remains methodologically heterogeneous: studies substantially differ in the PCM types investigated, the formulation of lime mortars tested, the range of properties characterized, and the extent to which heritage-specific requirements such as reversibility, compatibility with historic substrates, and durability under conservation-relevant stress conditions are addressed. The following sections provide a systematic analysis of these dimensions.

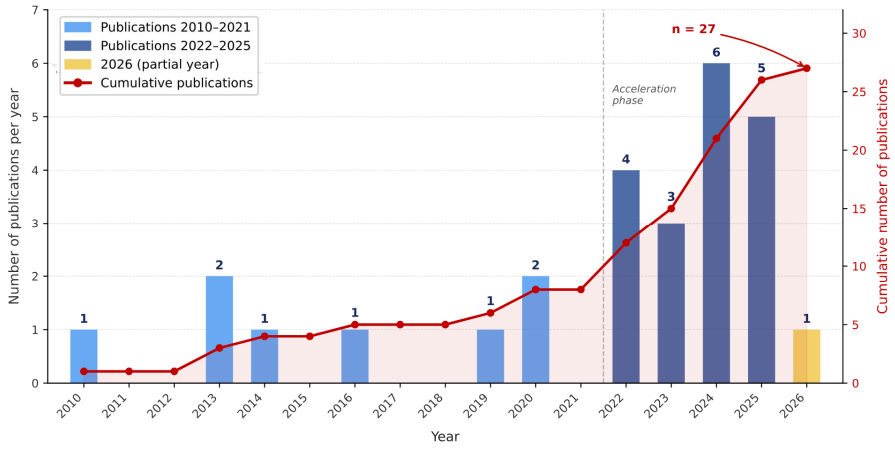

Figure 2. Annual and cumulative number of peer-reviewed publications on PCM incorporated in lime-based mortars for historic building applications, 2010–2026. The dashed vertical line separates the slow-growth phase (2010–2021) from the acceleration phase (2022 onwards). The 2026 bar represents publications retrieved up to April 2026.

3. PCM Types, Binder Systems, and Integration Methods

The eligible corpus includes four distinct PCM categories, three binder types, and three main integration strategies. Figure 3 provides an overview of how these aspects are distributed across all the included studies. The following subsections discuss each feature in detail.

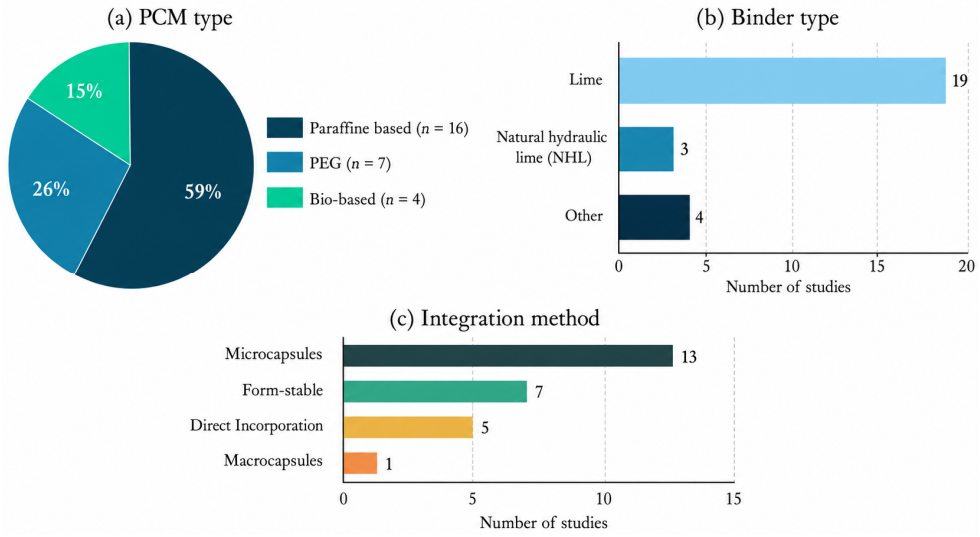

Figure 3. Distribution of all the included studies according to (**a**) PCM category, (**b**) binder type, and (**c**) integration method.

Four studies in the corpus investigate PCM incorporation in a heritage conservation context using material systems other than lime-based mortars and are classified separately

as "Other" in Figure 3b. Bernardi et al. [22] embedded three different microencapsulated paraffins (all supplied by BASF under the trade name Micronal®, one characterized by a Tm = 21 °C and the other two with Tm = 26 °C) in gypsum panels and silicone coatings. They were, then, tested in laboratory conditions and in situ at the Museo di Santa Croce in Florence (Italy) on wooden panels and canvas paintings. This is the only study in the corpus to report experimental evidence from a historic building of cultural importance, and it is also the only one to take into account conservation principles, such as reversibility and non-invasiveness. In particular, the paper highlights a risk associated with the use of PCMs, namely: their contact with historic surfaces can generate thermal gradients during their phase transition, with an associated risk of damage to paint layers or wooden substrates, a hazard that has not received further attention in the literature on lime-based mortars. Choi et al. [23] applied a composite panel of spent coffee grounds with microencapsulated PCM (ENERCEL 28, Tm = 28 °C) to the interior of a centenary Korean timber-framed building registered as cultural heritage. They evaluated energy and acoustic performance of the obtained composite through DesignBuilder and ODEON simulations. Thermal storage performance has been improved through the use of PCM, with reductions in energy consumption for heating and cooling, most notably for heating. Additionally, reverberation time has been reduced from values above 1.2 s to 0.6–0.7 s, and the sound pressure level has improved by approximately 70 dB.

Achaku et al. [24] studied the optimal positioning of PCM layers within the thick, multi-layered external walls typical of Victorian-era historic buildings, particularly in temperate climates. They found that positioning them between 88% and 93% from the outside surface of the wall maximized energy savings (i.e., reduction in cooling requirements by 5.3%–6.2%) without compromising the integrity of the historic property. Yuk et al. [25] developed an interior finishing material combining diatomaceous earth and microencapsulated PCM, demonstrating their crack resistance, moisture stability, and a reduction in energy consumption for heating and cooling of more than 10% when applied to historic buildings. Although none of these four studies considered a lime-based binder, they were nevertheless included in the corpus as borderline cases that broaden the knowledge base on the application of PCMs in conservation-sensitive contexts and raise questions, particularly regarding thermal gradients and reversibility—issues also relevant to lime mortars.

3.1. PCM Types

Three categories of PCM are represented in the corpus: paraffin wax, poly(ethylene glycol) (PEG), and bio-based PCMs derived from agricultural by-products. Table 3 summarizes the main thermal properties of each PCM as characterized in the reviewed studies.

Table 3. Thermal properties of the PCMs investigated in the corpus. Tm: melting temperature; ΔH_m pure: melting enthalpy of pure PCM; T_m mortar: melting temperature of mortar containing the PCM; ΔH_m mortar: melting enthalpy of mortar containing the PCM.

PCM Type/Trade Name	Chemical Class	T_m (°C)	ΔH_m Pure (J g^{-1})	T_m Mortar (°C)	ΔH_m Mortar (J g^{-1})	Ref.
PEG 800	Poly(ethylene glycol)	18	150	15	~12	[26,27]
PEG 1000	Poly(ethylene glycol)	~43	129	~28	~8	[28,29]
Rubitherm RT 35 HC	Paraffin wax	39	~240	~30 (5%wt of PCM) ~35 (10%wt of PCM)	~2 ~4	[30]
Micronal DS 5001	Paraffin (microcapsules)	~26	110	-	-	[31]

Table 3. *Cont.*

PCM Type/Trade Name	Chemical Class	T_m (°C)	ΔH_m Pure (J g^{-1})	T_m Mortar (°C)	ΔH_m Mortar (J g^{-1})	Ref.
Micronal DS 5008	Paraffin (microcapsules)	~23	135	-	-	[32,33]
Micronal DS 5038 X	Paraffin (microcapsules)	~25	~100	-	-	[34,35]
Microtek (LTPCM)	Paraffin (microcapsules)	~18	162	~18	~3	[36,37]
Microtek (HTPCM)	Paraffin (microcapsules)	~25	166	~25	~4	
Bio-based PCM (Vivtek 29)	Vegetable oil by-products	~33	~171	~29 (5%wt of PCM) ~29 (10%wt of PCM) ~30 (20%wt of PCM)	~1 ~2 ~4	[38,39]
Bio-based PCMs [1]	Fatty Acid	75	~193	-	-	[40]
Bio-based PCMs & Paraffine wax	Stearic Acid Palmitic Acid Lauric Acid Paraffine wax	~69 ~63 ~46 ~58	~170 ~199 ~172 ~218	~69 ~63 ~46 ~58	~170 ~199 ~172 ~218	[41]
Beeswax	Natural wax (bio)	~60	~160	-	-	[42]

[1] The bio-based PCMs fall outside the indoor-activation range defined in Table 2 and are retained only as a boundary case to illustrate the thermal discrepancy when PCM selection is not based on climatic conditions.

A common feature of all the PCMs analyzed is their organic nature. In fact, none of the reviewed studies analyzed inorganic PCMs (e.g., salt hydrates) in combination with lime mortars. Organic phase change materials offer a combination of thermal and chemical properties compatible with lime-based systems. They have negligible corrosion vulnerability towards mineral binders and metallic elements, a property of primary importance in the alkaline environment characteristic of lime mortars (pH ≈ 12–13), an environment capable of rapidly degrading inorganic counterparts [43,44]. Their melting temperature ranges can be varied, from around 10 °C to over 80 °C, depending on their molecular structure and chain length, allowing for adaptation to the external conditions of historic buildings. Their thermal stability and the constancy of the enthalpy of phase change following repeated heating–cooling cycles are confirmed in the analyzed studies [30,39]. Organic phase change materials are also chemically inert with respect to the main hydration and carbonation products of lime, reducing the risk of secondary reactions that could compromise it over time [37,45]. Furthermore, their low toxicity and, in the case of bio-based PCMs, their renewable origin, are in line with the sustainability objectives underlying the application of these materials to architectural heritage [28,40–42]. As an example, a life-cycle assessment (LCA) performed by Rubio-Aguinaga et al. [38] reports a reduction in global warming potential of up to 89.1% relative to paraffin-based alternatives, making bio-based PCMs the most promising candidates for sustainability-oriented heritage retrofitting.

3.2. Binder Types

Aerial lime (classified as CL 90-S) is the dominant binder in the reviewed studies, while natural hydraulic lime (NHL, primarily NHL 3.5) and hydrated lime (HL) represent the second binder category, always in a heritage or energy-renovation context (according to EN 459-1, [46]). This predominance reflects the primary role of aerial lime as a reference binder for restoration mortars in European and Mediterranean countries, countries where aerial lime has been consistently used in the historic building heritage.

The distinction between aerial lime and hydraulic lime is substantial for the effects of the introduction of PCM on the mechanical properties of mortars, as will be discussed in Section 6, and for conservation compatibility, as will be discussed in Section 5. Aerial lime binders develop strength exclusively through carbonation (i.e., the slow reaction of $Ca(OH)_2$ with atmospheric CO_2 to form $CaCO_3$), and are characterized by low final compressive strength (typically CS I, 0.4–2.5 MPa, according to EN 998-1, [47]), high vapor permeability, and good deformability [12]. These characteristics make them the preferred choice for application on porous historic substrates such as limestone, sandstone, and ancient brick, where a mechanically weak, breathable mortar is required to protect the substrate from cracking. Natural hydraulic limes set both hydraulically (through hydration of silicates and aluminates) and by carbonation, achieving higher and faster strength development (up to CS III, 3.5–10 MPa, according to EN 998-1, [47]) while retaining reasonable vapor permeability. In conservation practice, NHL mortars are accepted for structural consolidation; however, higher-grade formulations (NHL 3.5–5) are generally considered unsuitable for finishing renders on fragile historic substrates, where their greater stiffness and faster strength development may induce damaging mechanical stresses in the original substrate [48].

3.3. Integration Methods

The three main strategies for incorporating PCMs into lime mortars are: form-stable impregnation of a porous aggregate with fluid PCM; direct addition of microencapsulated PCM to the fresh mortar; direct addition of non-encapsulated PCM.

Poly(ethylene glycol) (PEG) is the only PCM employed in a form-stable configuration. The approach developed by Frigione et al. [28] reported that this polymer was included by vacuum impregnation into the porous network of waste Lecce stone (pietra leccese) granules. The latter were, then, used as aggregates in the mortar mix. Two molecular weights were investigated, PEG 1000 and PEG 800, the latter introduced to shift the phase-transition window towards lower temperatures, extending applicability of the PEG-doped mortar to continental climates [26]. The melting enthalpy of PEG was reduced from the pure polymer to the composite aggregate, to the hardened mortar, as expected for a PCM incorporated into a building element. A notable advantage of the form-stable approach is the negligible PCM leakage, confirmed even at temperatures well above its melting point, due to the effective retention of the polymer within the stone pore network [26]. From a sustainability perspective, this method can valorize a locally sourced waste material (i.e., Lecce stone), which acquires value instead of having to be disposed of, aligning with circular economy principles. However, Guzmán García Lascurain et al. [45] demonstrated that uncoated PEG can migrate into the lime binder matrix during mixing, interfering with calcite crystal interlocking during carbonation. This inconvenience can be limited with the application of a $Ca(OH)_2$ coating on the impregnated granules.

Microencapsulated paraffin waxes constitute the most frequently used PCM category in the reviewed studies. Commercial products, predominantly from the Micronal® range (BASF) and from Microtek Laboratories, consist of a paraffin core encapsulated within a melamine-formaldehyde or polymethylmethacrylate (PMMA) shell. This product (displaying melting temperatures around 18–25 °C) is commercially available as dry powder with particle sizes of 50–300 µm. The main advantage of microencapsulation is the ability to protect the PCM core: The shell in fact prevents direct contact between the organic phase and the alkaline lime matrix, limiting chemical degradation and PCM losses, even during repeated thermal cycles. However, the integrity of the shell, and consequently the effectiveness of the PCM, can be compromised during mixing or following repeated thermal stresses. The presence of a shell also reduces the latent heat per unit mass of PCM

compared to the same bulk material [37,49]. Again, enthalpy is reduced upon incorporation into the mortar matrix (Table 3).

The direct addition of non-encapsulated bulk paraffin represents the simplest integration strategy from a process point of view. In this approach, the PCM is added to the fresh mortar in its molten state and no further steps are required. This operational simplicity has disadvantages since, in the absence of a protective shell, the liquid paraffin can penetrate the pore network of the mortar, with significant consequences to the mechanical properties and durability of the mortar, as will be illustrated in Paragraphs 6 and 8. Even with this approach, a substantial enthalpy reduction is observed. On the other hand, Santhaman et al. [41] reported the same latent heat values for mortars containing PCM and for pure PCM, in contrast to what was observed in all other studies.

4. PCM Melting Temperature and Climate Compatibility

A critical aspect in the selection of PCMs for construction applications is the relationship that must exist between the melting temperature of the material and the climatic conditions of the application site. The PCM phase transition temperature window, in fact, must overlap with the desired internal temperature range in the building, to ensure the comfort of the inhabitants [50,51]. On the other hand, as shown in Figure 4, most of the investigated PCMs present melting temperatures above 32 °C, which is quite a high value if the objective of the PCM is to ensure human thermal comfort.

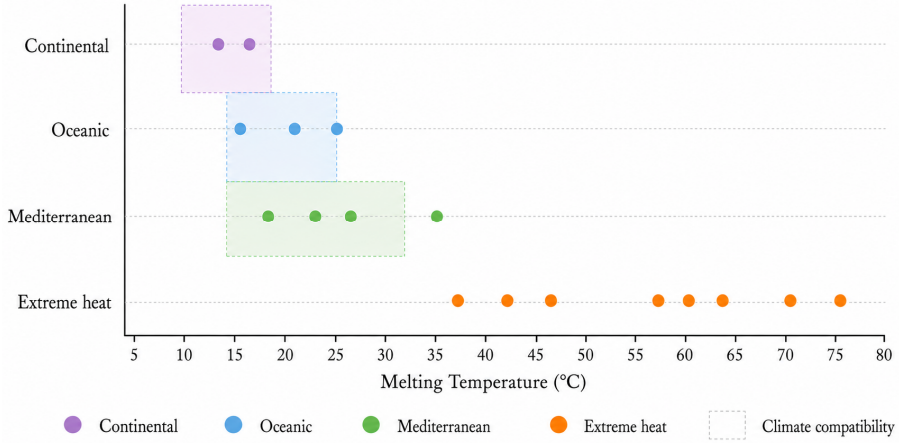

Figure 4. Distribution of investigated PCMs according to their melting temperature (Tm) and climate activation compatibility. Shaded bands indicate the expected indoor activation ranges for each climate type: continental (12–18 °C); oceanic (18–24 °C); Mediterranean (22–30 °C).

Several authors selected PCMs with higher Tm, predicting that their introduction into the mortar matrix will lower the transition temperature of the pure polymer, a phenomenon documented mainly for form-stable systems [26–30]. In microencapsulated systems, in fact, the shell preserves the thermal behavior of the paraffin core, keeping its melting temperature stable [36,37].

It should be emphasized, on the other hand, that in most of the examined studies focused on historic buildings, assessments of climate–PCM compatibility are missing. In many cases, a PCM is chosen based on previous studies reported in the literature, without any relation to the required thermal comfort conditions. A first exception is represented by Rubio-Aguinaga et al.'s [38] investigation. This study proposes three PCMs with different melting temperatures to be employed in different Spanish climate zones: a bio-based PCM (Tm ≈ 29 °C) offers good performance in areas with hot summers, while low-melting-point paraffin (Tm = 18 °C) allows for maximum energy savings in colder areas. In the study reported in [52], the results of thermal tests, which simulated the typical temperature

ranges of southern Italy, demonstrated a reduction in energy requirements for cooling in summer and heating in spring and autumn with the addition of a PEG-based phase change material in hydraulic lime mortars. The best results were recorded for temperatures representative of spring and autumn. In a similar study from the same authors [53], HL mortar containing form-stable PCMs based on PEGs of different grades, i.e., displaying various range of melting/solidification temperatures, showed high thermal performance. In particular, when a PCM composed of a PEG mixture (i.e., 50/50% by weight of PEG800 and PEG1000) was incorporated in this mortar, energy savings of approximately 8% in summer and approximately 12% in spring and autumn were recorded.

5. Evaluation of Conservation Principles

The principles on which conservation practices are based, as codified in the ICOMOS Venice Charter (1964) [8] and standardized in UNI EN 15898:2010 [9], require that any intervention must be reversible, physically and chemically compatible with the original substrate, and scalable in order to be valid in real applications.

Figure 5 summarizes the profile of the studies in relation to the specific characteristics of cultural heritage.

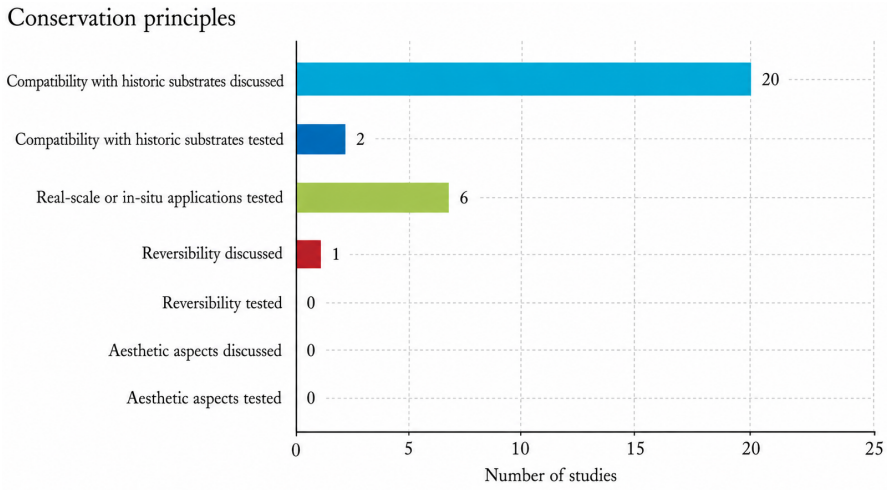

Figure 5. Specific characteristics related to heritage interventions, where each bar represents the number of studies focused on each feature.

Figure 5 shows that the reviewed articles are lacking with respect to specific requirements related to cultural heritage: these gaps should not be considered as an absence of data but rather provide a specific indication for future studies. Reversibility and esthetic aspects represent the most serious unresolved gaps in the corpus. Since both reversibility and preservation of surface appearance are important requirements in heritage conservation practice, their absence from the literature on PCM-containing lime mortars constitutes one of the main limitations identified by this review, as discussed below.

Although most studies report historic buildings as the reference context, the compatibility of PCMs with historic substrates remains largely unexplored. Chemical compatibility at the PCM–lime interface was investigated by Rubio-Aguinaga et al. [36]. The authors demonstrated that melamine-shelled microcapsules stably disperse in fresh lime mortar (pH 12–13) without significant shell degradation. Guzmán García Lascurain et al. [45,54] characterized the mechanism by which uncoated PEG interferes with calcite crystallization during carbonation and showed that a mineral $Ca(OH)_2$ coating mitigates this interaction.

Only six studies conducted tests on a scale larger than laboratory [22–25]. Rubio-Aguinaga et al. [38] carried out a life-cycle assessment of PCM–lime render strategies applied to a 13th-century church (Ermita de Santa Brígida, Spain), although the analysis is

based on energy modeling rather than on in situ material testing. On the other hand, the gap between laboratory performance and real-world applicability is particularly important in the case of applications in historic buildings, where substrate heterogeneity, pre-existing damage, variable porosity, complex multi-layered wall structures and the constraints imposed for their preservation introduce variables that cannot be reproduced in a small-scale sample (i.e., $40 \times 40 \times 160$ mm^3).

The reversibility of the intervention is analyzed in only one study [22] and even in this case reversibility is not directly verified, only discussed as a design principle. In restoration practice, reversibility is generally understood as "removability," achieved primarily through mechanical actions [55]. This premise, however, is directly challenged by the inclusion of PCMs. On the other hand, the inclusion of a PCM in the mortar could alter the microstructure at the mortar–substrate interface; this aspect has never been analyzed in terms of adhesion strength. Therefore, it is unclear whether such composite mortars are still removable using the same low-impact protocols established for traditional lime mortars. It is likely that lime mortars containing PCM may require specific removal strategies.

A further aspect, largely unconsidered, concerns the organic nature of the PCM. In this case, controlled heating to soften the paraffin phase before producing mechanical detachment or solvent-assisted techniques used to remove organic binders could be employed. However, none of these solutions have been tested so far for lime-based systems containing organic PCMs. None of the studies reviewed analyzed removal protocols of PCM-modified mortars from a real historical substrate nor the bond strength at the mortar–substrate interface with aging. Given the importance of reversibility in conservation practices, this represents an unfilled gap in the current literature. Therefore, the development of validated, low-impact removal protocols specific to lime mortar and PCM systems should be considered a priority for future research.

Non-esthetic alteration is completely absent from the reviewed studies. In heritage conservation, it represents another fundamental requirement: any intervention must preserve the appearance of the historic surface, including color, texture, and surface finish. On the other hand, it cannot be excluded that the introduction of PCM into lime-based plasters may alter these characteristics. In this regard, two mechanisms deserve particular attention. First of all, the incorporation of PCM, whether microencapsulated, form-stable or in bulk form, modifies the pore structure of the mortar. This could alter pore connectivity, a key factor for salt migration and the onset of efflorescence. As a result, soluble salts are transported to the surface and crystallize upon evaporation, producing white deposits and, in severe cases, surface detachment [48,56]. Secondly, water vapor permeability, which depends on the same pore network, controls the plaster's ability to allow moisture exchange between the historical substrate and the external environment. Any reduction in permeability caused by the incorporation of PCM into the mortar could promote moisture entrapment within the wall, with consequences for both the substrate and the plaster itself (e.g., increased susceptibility to frost damage and biological colonization) [12,57]. However, in none of the studies examined were the risk of efflorescence nor the change in water vapor permeability of the mortar assessed as a result of the presence of PCM. This represents a further significant gap in the current experimental literature to be filled in durability testing protocols for PCM-modified lime mortars intended for restoration applications.

6. Mechanical Properties

6.1. Compressive and Flexural Strength

All mechanical data presented in this section were measured at 28 days of curing, unless otherwise indicated.

The addition of PCM to lime-based mortars produces a reduction in both compressive (CS) and flexural (FS) strengths, as reported in approximately 80% of studies reporting quantitative results. The extent of this reduction varies considerably depending on the type and content of PCM, the type of binder and the method of integration. A decrease in CS is observed in the mortar with the integration of form-stable PEG composites and microencapsulated paraffins.

Figure 6 reports the compressive strength values of the mortars as a function of PCM content (% by weight), collected from the reviewed papers. The different methods of incorporating PCMs into the mortar are highlighted with different symbols. EN 998-1 class boundaries (CS I: 0.4–2.5 MPa; CS II: 1.5–5.0 MPa) are shown as reference bands.

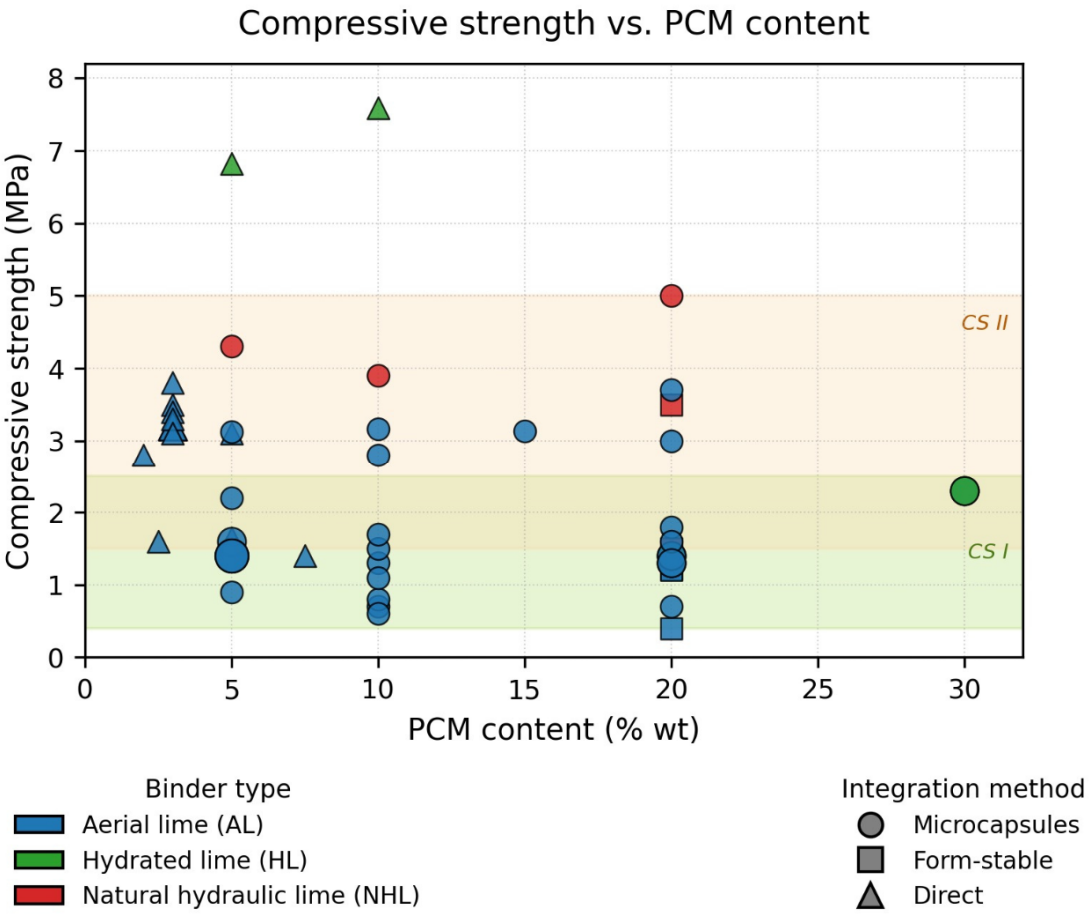

Figure 6. Compressive strength (MPa) of PCM-containing lime-based mortars as a function of PCM content (%wt). A larger symbol size indicates a greater number of matching results.

It can be observed that NHL or HL-based mortars achieve substantially higher compressive strength values than lime-based mortars at the same PCM dosage, regardless of the integration method. This difference reflects the higher hydraulic reactivity of these binders. No clear relationships are observed between compressive strength and PCM content nor with the inclusion methodology, indicating that the binder type and its composition have a greater influence on mechanical performance.

When a PCM is incorporated into mortar systems, a decrease in its mechanical properties is generally observed [58–60]. However, four independent research groups working on lime-based mortars have recorded an increase in CS, at least up to the contents of PCM analyzed.

The first research was published by Ventolà et al. [31] who added microencapsulated paraffin, at dosages of 5, 10 and 15% by weight, to an aerial lime mortar. Contrary to

expectations, compressive strength increased with PCM content, from 1.72 MPa (reference mortar) to a maximum of 3.16 MPa at 10%wt (+84%), remaining substantially stable (equal to 3.13 MPa) at the highest dosage, i.e., 15%. Mercury intrusion porosimetry (MIP) analysis revealed that the presence of microcapsules increased the total open porosity, which in turn facilitated greater penetration of atmospheric CO_2 into the mortar matrix and accelerated the carbonation of portlandite to calcite. The resulting increase in the degree of carbonation resulted in increased compressive strength. This mechanism is specific to aerial lime-based binders and is not applicable to hydraulic systems.

The second mechanism concerns mortars based on hydraulic lime. Lucas et al. [33] documented an increase in CS in HL mortars containing 30% of microencapsulated paraffin by weight. On the other hand, the same PCM produced no benefit in NHL or gypsum formulations. Theodoridou et al. [35] reported even more pronounced increases in hydrated lime-based mortars containing microencapsulated paraffin at 5, 10 and 20%wt, with compressive strength rising from 1.4 MPa (reference mortar) to 3.7 MPa at the highest dosage (i.e., 20%wt). NHL mortars showed reductions in compressive strength in the same studies. The specificity of this behavior, reported by the mentioned studies, suggests that the microstructure of HL crystals interacts differently with the surfaces of the microcapsules compared to the coarser crystalline pattern of portlandite, typical of aerial lime. However, the precise mechanisms responsible for the observed behavior have not been systematically studied and its elucidation represents a major open question in the field.

The third mechanism is documented by Feijoo et al. [30] for bulk, i.e., non-encapsulated paraffin directly added in aerial lime. In this case, liquid paraffin at low and medium dosages (5 and 10% by weight) penetrates and physically fills the fine pore network of the mortar during solidification, reducing the capillary porosity and densifying the microstructure. This densification produces an increase in CS (7% and 19% at 5% and 10% PCM contents, respectively) and a marked reduction in water absorption and capillary coefficient. However, at higher PCM dosages, the volumetric expansion and contraction of the paraffin during repeated thermal cycling generates stresses within the mortar sufficient to trigger micro-cracks, negating the initial mechanical benefit. This aspect will be further discussed in Section 8.3.

As already mentioned, physical and chemical compatibility in conservation practice imposes other requirements. The repair mortar must be mechanically weaker and more deformable than the original substrate, according to the so-called sacrificial layer principle. It must have a vapor permeability comparable to or greater than the substrate. Finally, it must not introduce chemical species capable of triggering chemical reactions with the minerals of the substrate or with pre-existing salts. Regarding mechanical compatibility, a reduction in compressive strength with increasing PCM content is, in principle, favorable: a weaker mortar is less likely to cause damaging stress concentrations on fragile historic masonry. Therefore, unexpected strength increases observed in some systems require a case-by-case evaluation, as a stiffer mortar may exceed the mechanical strength of the underlying substrate.

It should be noted that complete physical compatibility was not assessed in any of the studies reviewed. None of the reviewed studies evaluated the bond strength of lime-based mortar containing PCM to a representative ancient substrate. Similarly, the vapor permeability of the composite was not measured, nor was the resistance to detachment on weathered wall surfaces. The samples used in all laboratory studies were mortar prisms prepared according to EN 1015-11 [61], whose surface porosity, roughness and mineralogical characteristics are substantially different from those of aged limestone, sandstone or ancient fired bricks.

6.2. Porosity and Microstructural Modifications

The pore structure of the mortar is substantially modified by the incorporation of a PCM—changes that influence the mechanical behavior as already illustrated. The MIP analyses of the works reported in this review reveal essentially two distinct microstructural scenarios.

In systems with microencapsulated PCM included in the aerial lime, the capsules act as soft inclusions within the matrix. Lucas et al. [32] reported an increase in total open porosity with the addition of this type of PCM. Furthermore, a variation in pore size distribution was observed, from 10 to 15 μm in the control mortars to a finer size, i.e., 1–5 μm, in the samples containing 10%, 20% and 30% by weight of PCM. This redistribution of porosity, towards lower values, affects both the capillary transport of water and the kinetics of carbonation, both processes depending on the connection and tortuosity of the pores. As documented by Theodoridou [35], the presence of PCM leads to an increase in total open porosity and reduces the capillary water absorption coefficient by approximately 60%.

In the bio-based PCM system investigated by Rubio-Aguinaga et al. [39], total open porosity increases significantly by 11% at a high PCM dosage (i.e., 20%wt). This phenomenon suggests that, beyond a certain threshold concentration, the space occupied by the microcapsules is not compensated for by the densification of the matrix, resulting in a net increase in the void fraction. Although the compressive strength increases progressively for low PCM contents (up to 10% by weight), a clear decrease is observed if a PCM at 20% by weight is added.

In the case of non-encapsulated systems [30], at low levels, paraffin acts as a pore-filling agent, reducing the volume of fine capillary pores and producing a denser, less permeable microstructure. This work, however, is the only one in which it was shown that the incorporation of free PCM determines a simultaneous decrease in porosity and an increase in CS, related to the absence of an encapsulating shell.

6.3. Carbonation and Long-Term Performance

The relationship between the presence of a PCM and the carbonation process of lime mortars, with implications for the long-term durability of this material in historic buildings, has been addressed by several authors but with results that are not always consistent.

In particular, two opposing effects on carbonation of lime mortars have been documented upon the inclusion of PCMs. Ventolà et al. [31] reported that microencapsulated PCM increases open porosity and, thus, enhances both CO_2 ingress and the rate of calcite formation. On the other hand, Feijoo et al. [30] concluded that the pore-filling action of a free paraffin PCM obstructs CO_2 diffusion pathways and slows carbonation. These results, although consistent with the individual integration methods (encapsulation or direct inclusion), do not allow conclusions to be drawn on the effect of PCM on mortar curing times.

The implications for the conservation of ancient buildings are significant. Unlike Portland cement, which reaches almost complete hydration within 28 days, lime mortars continue to carbonate and gain strength over months or years, depending on the thickness of the plaster, the CO_2 concentration and the porosity of the substrate. Their mechanical characteristic values measured after 28 days of curing, therefore, are representative of an intermediate state and not of their final stable condition.

A small portion of the reviewed studies report mechanical characterization results for times longer than the standard ones. These results provide very interesting information, despite the heterogeneity of the types of binder and PCM analyzed and of the level of inclusion in the mortar. Rubio-Aguinaga et al. [39] measured the compressive strength of lime mortars at 28, 91, 182 and 365 days of cure. These authors found that aerial lime mortars containing 5 and 10wt% PCM maintained, or even improved, mechanical performance

compared to the control system, regardless of curing time. On the other hand, the introduction of 20wt% PCM showed a constant decrease in mechanical properties, attributed to the increase in porosity and the reduction in binder cohesion. Theodoridou et al. [35] measured compressive strength at 28, 56, and 90 days of cure of two binders, i.e., natural hydraulic lime and aerial lime. Their results revealed that NHL-based mortars showed a progressive decrease in CS with increasing PCM content at all times of cure. Hydrated aerial lime mortars, on the other hand, exhibited an opposite trend, i.e., CS increased with increasing PCM content throughout the aging period. Palraj and Shanmugavel [40] measured the compressive strength of PCM-doped natural hydraulic lime at 7, 14, 28, and 90 days. They reported a consistent increase in CS with increasing PCM content, regardless of curing time. It should be noted, however, that the PCM levels investigated in this study were rather low (i.e., 2, 3, 5% by weight) when compared to other studies. Similarly, Santhaman et al. [41] measured CS on aerial lime including PCMs at 7, 28, and 90 days of cure: the strength values recorded at 7 days remained fairly stable, with only a modest increase at longer aging times. Again, the amount of PCM included in the mortar was limited (i.e., no more than 5% by weight).

Summarizing the main findings of the reviewed studies, although limited in number and heterogeneous in mortar composition, typology and PCM content, it can be concluded that the mechanical properties measured at 28 days may not be fully representative of the in-service behavior of mortars, in particular for aerial limes where the increase in strength due to carbonation may continue for years. Previously reported results suggested that low PCM contents tend to preserve or slightly improve the compressive strength of mortars over time, whereas high levels (i.e., above 15–20%wt) compromise mechanical properties over time, regardless of binder type. It remains unclear whether PCM can accelerate or slow carbonation depending on the different types of mortar integration. This aspect, on the other hand, is fundamental in applications in the cultural heritage sector, where materials are expected to remain unchanged for hundreds of years.

7. Thermal Performance

7.1. Thermal Conductivity and Specific Heat Capacity

Thermal conductivity (λ) is an important parameter in mortars containing PCMs. A reduction in λ increases the thermal resistance of the mortar and limits the steady heat flow within it. On the other hand, excessively low values worsen latent heat storage efficiency, slowing down the heat transfer to and from the PCM core, delaying its phase transition. The introduction of organic PCMs into lime mortars systematically decreases λ compared to the reference mortar, as reported in the studies analyzed. This is, in fact, a consequence of the low thermal conductivity of organic materials, both in the solid and liquid state [62,63].

The extent of this reduction is variable and depends on the PCM content, the type and composition of the binder, and the curing time. The most marked decrease is reported in the study by Theodoridou et al. [35]. These authors also reported that λ continues to decrease with curing time, consistent with the progress of the carbonation process of the lime matrix. On the other hand, Rubio-Aguinaga et al. [36] did not observe any significant modification of λ of the mortar as a consequence of the addition of PCM. They attributed this result to the development of an optimized mixture (including metakaolin, MK, in the mortar formulation), so as to minimize structural changes in the pores. In the same work, the temperature dependence of λ in lime mortars containing PCM is reported, in particular at temperatures (i.e., 5°, 15°, 25° and 35 °C) covering the phase transition range of the PCM. It was found that the addition of PCM does not significantly alter λ compared to the reference mortar at any of the temperatures tested. However, λ steadily decreases with

increasing temperature regardless of the formulation, reflecting the lower conductivity of organic PCMs in the liquid state compared to the solid state.

A further contribution to the reduction in λ comes from the modification of the pore size distribution, as already reported in Section 6.2: increasing the PCM content makes the pores of the mortar finer, in turn reducing the heat transfer through the pore network, regardless of the intrinsic thermal properties of the PCM.

7.2. Temperature Regulation: Attenuation and Phase-Shift

The main functional advantages of incorporating a PCM into a mortar are the attenuation of internal thermal fluctuations and the temporal shift (phase shift) of peak temperatures. These parameters are measured using experimental setups that vary depending on the scale, boundary conditions, and type of measurement.

On a small scale, Sarcinella et al. [52,53] reported a reduction in thermal fluctuations in samples of mortars containing a PCM tested in a climatic chamber and subjected to cyclic thermal variations. The same research group carried out an evaluation of the energy cost savings associated with plastering systems containing PCM: this study is the only one to also consider the economic aspects of using this technology. At the mock-up scale, Rubio-Aguinaga et al. [36,39] reported a reduction of 6.1 °C in the peak indoor temperature during a heating event, and 3.9 °C during cooling, measured via hotbox simulation. Lucas et al. [31] reported that, for hydrated lime mortars containing 20% microencapsulated paraffin by weight, the PCM system exhibits higher cooling efficiency than heating efficiency. This asymmetry can be exploited in climates where the critical temperatures are summer ones.

Baccega et al. [64], employing COMSOL Multiphysics V5.5 simulation applied on NHL-based systems, reported a thermal time-delay consistent with the incorporation of PCM into the render layer. On the other hand, the lack of experimental validation limits the value of their results to some extent.

In conclusion, it is impossible to derive quantitative values of temperature attenuation values from the reviewed studies due to the diversity of the experimental setups (sample size, PCM content, wall thickness, temperature program, boundary conditions), confirming the need to develop standardized test protocols.

8. Durability

The durability evidence available for PCM-modified lime mortars is encouraging although limited in number and variety of studies. The three main mechanisms related to mortar durability, namely: freeze–thaw cycles, salt crystallization and thermal expansion damage, have been analyzed in at least one study each. Regarding the first two mechanisms, the results obtained by independent research groups were favorable for PCM-modified formulations, regardless of the type of PCM introduced.

Capillary water absorption, while not a direct measure of resistance to degradation, is a standard test (according to EN 1015-18, [65]) used to obtain useful information on the durability of mortars. In this regard, five different studies have highlighted a reduction in the capillary absorption coefficient following the introduction of a PCM. The observed reductions range from approximately 15% to over 90% depending on the type of PCM, its content, and the binder formulation [30,35,39–41].

8.1. Freeze–Thaw Resistance

Resistance to freeze–thaw cycles was evaluated in two independent studies, using similar but not identical protocols. Feijoo et al. [30], following the UNE-EN 12371:2011 standard, subjected conical mortar samples to 10 cycles, each consisting of vacuum saturation with ultrapure water, freezing at −25 °C for 8 h, and thawing at room temperature for 6 h.

Weight loss was recorded every two cycles. Rubio-Aguinaga et al. [39] used a different protocol, namely: immersion followed by freezing at −10 °C, repeating the procedure for 28 cycles or until the sample broke.

Despite methodological differences, the results of both studies are consistent in trend. In the first work, the reference mortar (PCM0) lost approximately 40% of its mass after 10 cycles; furthermore, it progressively lost its geometric integrity, with the appearance of cracks starting from cycle 5. Mortars containing 5% and 10% by weight of PCM (not encapsulated), on the other hand, showed weight losses lower than 0.6%, regardless of the PCM content, without the appearance of visible fractures. In the second paper, the reference mortar failed after only five cycles (damage scale: 10/10), while all PCM-modified formulations withstood the entire 28-cycle program. Mortars containing 10% and 20% bio-based PCM showed only slight surface deterioration (damage scale: 1/10).

The explanation proposed in both studies agrees on the influence of the pore structure: the addition of PCM reduces the population of fine pores (<1 μm), i.e., those most vulnerable to the expansion of ice crystals, the crystallization pressure being inversely proportional to the pore radius. Furthermore, reducing accessible porosity limits the entry of more water that could freeze inside the mortar.

This observation is very important from a conservation point of view since degradation due to freeze–thaw cycles is the main degradation mechanism for external plaster in continental and Northern European climates. The increased durability observed as a consequence of the inclusion of PCM, regardless of the chemical nature, presence of encapsulation and melting temperature, suggests a real advantage of these mortars applied in these climatic contexts.

8.2. Salt Crystallization Resistance

Historic walls typically contain soluble salts, chlorides, sulfates, and nitrates, introduced by rising damp, rainwater penetration, air pollution, or previous interventions. The cycles of crystallization and precipitation of salts in the pores generate stresses within the walls, constituting one of the main deterioration mechanisms in historic buildings. Four of the studies reviewed include salt crystallization tests using salt solutions adsorbed onto previously unsalted samples. This protocol, although capable of assessing the resistance of the mortar surface to salt attack, does not reproduce the real conditions of historic buildings, where the main mechanism is the migration of salts from the substrate towards the evaporation front on the plaster surface.

Feijoo et al. [30] tested the resistance to three saline solutions, namely NaCl, Na_2SO_4, and natural seawater, on cubic samples subjected to repeated immersion–drying cycles in an oven, with desalting every five cycles. PCM-modified mortars showed substantially higher strength than the reference one, regardless of the salt solution analyzed. Furthermore, the mortar not containing PCM lost its geometric integrity and showed the greatest mass loss, while the mortars containing PCM maintained their shape throughout the test.

The improved performance of PCM-containing mortars was attributed to the same mechanism identified in the freeze–thaw cycle results: the reduction in fine pores decreases the crystallization pressure of salts, while at the same time limiting the penetration of further salt solutions.

Theodoridou and Kyriakou [35] performed an artificial aging process with a 10% Na_2SO_4 solution for 15 wetting–drying cycles, starting 90 days after casting. In all formulations containing PCM, a higher resistance to salt damage was observed compared to the reference mortars. The results were also analyzed by binder type: hydraulic lime mortars with PCM completed the entire 15-cycle program without any measurable weight loss, while hydrated lime mortars showed significant, yet small, mass loss compared to

their respective control samples. The authors of the study attributed this behavior to a combination of lower capillary absorption and a shift in pore size distribution toward larger pores in the PCM-modified mortars.

Rubio-Aguinaga et al. [39] used a $MgSO_4$-based salt crystallization test for 28 cycles, with rinsing every 10 cycles. The reference mortar failed after 14 cycles (damage scale: 10/10), while all PCM-modified mortars (at 5, 10, 20wt% PCM) completed the entire program, albeit with some surface deterioration (damage scale: 6/10). The authors noted that, despite the increased porosity of the mortar containing 20wt% PCM, its salt resistance was comparable to that of the lower-dosage mortars, suggesting that a modification of capillary connectivity, rather than a simple reduction in total porosity, might be the resulting protection mechanism.

Santhanam et al. [41] tested the crystallization resistance of NaCl and Na_2SO_4 salts in lime mortars containing fatty acid- and paraffin-based PCMs. They observed that the best-performing formulation (i.e., that containing 3% PCM with Alccofine addition) withstood more than 25 wetting–drying cycles. On the other hand, an increase in PCM content to 5wt% slightly reduced the resistance to this factor, attributed to the microporosity induced by an excess of PCM.

The results of the reviewed studies allow us to conclude that PCM-modified lime mortars generally offer greater resistance to salt crystallization than control samples, regardless of salt type, PCM and mortar composition.

8.3. Thermal Cycling Damage

The thermal stability of PCM after repeated heating–cooling cycles, which assesses the consistency of latent heat accumulation over time, was evaluated in the reviewed manuscripts by cyclic experiments performed at the Differential Scanning Calorimeter (DSC). In particular, Rubio-Aguinaga et al. [39] subjected a bio-based PCM to 40 colorimetric cycles and found no appreciable enthalpy loss. Similarly, Feijoo et al. [30] performed 80 DSC cycles on the paraffin PCM confirming the stability of its thermal storage capacity. These results, conducted on different types of PCMs, indicate that the latent heat storage capacity of organic PCMs is not modified by repeated phase transitions (melting–solidification–melting) simulated in the laboratory.

Although the PCM included in the mortar has good thermal stability, although assessed in the laboratory by DSC tests performed under controlled conditions, the structural integrity of the mortar can be compromised following thermal cycling during service. In fact, Feijoo et al. [30] reported mechanical damage in mortar samples containing PCM after repeated thermal cycling. Such consequences were not found in control samples without PCM.

The mechanical damage observed in mortars containing PCM is related to internal stresses generated by the difference in thermal expansion coefficients between the PCM and the mortar matrix. This problem was studied in detail by the same authors through thermal cycling (performed according to UNE-EN 16140:2019) carried out on cylindrical specimens subjected to 20 cycles of oven drying at 75 °C for 18 h, followed by immersion in water at 20 °C for 6 h, with weight loss recorded every three cycles. While the reference mortar (PCM0) did not show any weight loss or fracture during the entire 20-cycle program, the PCM10 formulation (containing 10% by weight of un-encapsulated paraffin) showed a progressive weight loss, reaching 14% at cycle 20, with evident fractures starting from cycle 12, which progressively enlarged in subsequent cycles. The PCM5 formulation (i.e., containing 5wt% of un-encapsulated paraffin) showed an intermediate behavior, with a weight loss of approximately 8% at cycle 20 and the development of small fractures at the corners of the samples. During repeated solid–liquid transitions of PCM within the

mortar pores, the pore walls are subjected to cyclic internal stresses due to the difference in volumetric thermal expansion coefficients between the organic paraffin and the lime mortar matrix. The damage is amplified when the amount of PCM is high enough to allow the molten material to almost completely fill the pore volume.

Two aspects need to be underlined. First, the risk is dependent on the amount of PCM: it is significant at 10wt% PCM, but only moderate at 5wt%, so there is a threshold, related to the coefficient of thermal expansion, below which the mortar matrix can accommodate the expansion without suffering damage. Second, the PCM used in this study was an un-encapsulated paraffin, with a high thermal expansion coefficient and no shell able to limit its expansion. In microencapsulated systems, on the contrary, the polymer shell is able to limit the volume variation associated with the phase transition, mitigating this phenomenon. Similarly, in form-stable systems, the confinement of the PCM within the rigid pore network of the matrix physically limits volumetric expansion, providing further protection against thermally induced internal stresses. However, it should be emphasized that this hypothesis remains theoretical, since at present no thermal cycling data are available for microencapsulated or form-stable PCM systems contained in lime mortars. Extending the risk of mechanical degradation identified for un-encapsulated paraffin to other PCM integration methods would therefore be premature, and this represents a gap to be filled in future durability testing.

9. Conclusions

This review systematically examined the experimental literature on the incorporation of phase change materials (PCMs) into lime-based mortars for applications in historic buildings, considering peer-reviewed studies published between 2010 and 2026. Although the literature on this specific topic is limited, the results allow us to outline some general conclusions, also highlighting the gaps and unresolved issues in this field.

It is confirmed that the incorporation of PCM in lime-based mortars is able to reduce indoor thermal fluctuations, as demonstrated by in situ characterizations and hotbox simulations.

Several studies have demonstrated a reduction in capillary water absorption associated with the addition of PCM to the mortar, attributed to the modification of the pore size distribution towards finer fractions, with consequent benefits for its resistance to atmospheric agents. Studies testing freeze–thaw resistance and salt crystallization resistance have, in fact, both revealed improvements in durability with the incorporation of PCMs into the mortar.

The mechanical response to the addition of PCM to the mortar is more variable and depends on the binder. In air lime systems, a general reduction in compressive and flexural strength is observed, the extent of which depends on the PCM content, the integration method and the composition of the mortar. In most cases, however, absolute values remain within the CS I range (as defined by EN 998-1), which is considered adequate and mechanically compatible with the historic wall substrates. Mortars containing microencapsulated and form-stable systems offer better mechanical performance than those that include encapsulated paraffin. This latter type introduces additional risks of damage caused by thermal cycling, especially at higher levels.

It is necessary, however, to pay attention to the issues that the current literature has failed to address. Research on PCMs incorporated into building materials originates in the context of energy efficiency in new buildings, where the criteria governing the choice of a PCM are thermal storage capacity, mechanical adequacy, and cost. When research focused on historic buildings, the experimental protocols remained unchanged, neglecting the specific requirements of this application. The reversibility of the intervention, a funda-

mental aspect in this context, has not been tested in any study. Similarly, compatibility with historical substrates, ancient stone, ancient bricks, and multi-salt masonry was assessed only at a qualitative level, but was not measured according to specific standards for the protection of cultural heritage. Durability under conservation-related stress conditions has been assessed in less than 20% of studies, and never on a substrate representative of a real historical artifact. This gap could also arise from a limited adherence to the criteria of interdisciplinarity between materials science for building engineering and the conservation of cultural heritage.

Lime-based mortars containing PCM may represent a promising strategy for improving the energy performance of historic buildings, while respecting traditional construction methods. Scaling up from the laboratory to full-scale, however, requires new protocols to test the reversibility of mortars on real substrates, evaluate their durability under storage-relevant conditions, and validate their thermal performance at building scale.

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Abbreviations

The following abbreviations are used in this manuscript:

PCM	Phase Change Material
AL	Aerial Lime
HL	Hydrated Lime
NHL	Natural Hydraulic Lime
PEG	Poly-Ethylene-Glycol
LCA	Life Cycle Assessment
CS	Compressive Strength
FS	Flexural Strength
PMMA	Polymethylmethacrylate
MIP	Mercury Intrusion Porosimetry
MK	Metakaolin

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