

Materials and Structures

ADDITIVES and ADMIXTURES for MODERN LIME-based MORTARS

--Manuscript Draft--

Manuscript Number:	MAAS-D-22-01477
Full Title:	ADDITIVES and ADMIXTURES for MODERN LIME-based MORTARS
Article Type:	RILEM TC Report
Keywords:	additives; admixture; lime mortars; performance; Evaluation
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Funding Information:	
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	enhance the performance of lime mortars. However, recently developed additives and admixtures need to be further evaluated with reference to their compatibility with other mortar constituents, and their effects on the overall mortar and render durability need to be studied. Finally, adopting similar terminology for additives/admixtures in lime and cement based mortars will facilitate better comparison and assessment issues.
Additional Information:	
Question	Response
Provide the total number of words in the manuscript (excluding figure caption and table caption)?	13999
Provide total number of FIGURES?	1
Provide total number of TABLES?	14

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ADDITIVES and ADMIXTURES for MODERN LIME-based MORTARS

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This review was prepared by Pagona-Noni Maravelaki, Kali Kapetanaki, Ioanna Papayianni, Ioannis Ioannou, Paulina Faria, Jose Alvarez, Maria Stefanidou, Cristiana Nunes, Magdalini Theodoridou, Liberato Ferrara, Lucia Toniolo within RILEM TC LHS-277 “Specifications for testing and evaluation of lime-based repair materials for historic Structures” and further reviewed and approved by all members of the RILEM TC LHS-277. Chair: Emer. Prof. Ioanna Papayianni. Deputy Chair: Dr. Jan Válek. TC Members: Jose I. Alvarez, Anna Arizzi, Beril Bicer-Simsir, Violeta Bokan-Bosiljkov, Arnaldo M. Carneiro, Claudia Brito De Carvalho, Paulina Faria, Liberato Ferrara, Caspar Groot, Davide Gulotta, John J. Hughes, Ioannis Ioannou, Kali Kapetanaki, Heejeong Kim, Loucas Kyriakou, Cristiana Lara Nunes, Pagona Noni Maravelaki, Sagrario Martinez-Ramirez, Didem Oktay, Vasiliki Pachta, Andreja Padovnik, Ioanna Papayianni, Chiara Pasian, Sara Pavia, Giovanni Pesce, Ulrike Peter, Meera Ramesh, Divya Rani, Sriram Pradeep Saridhe, Michele Secco, Maria Stefanidou, Petra Stukovnik, Cristina Tedeschi, Magdalini Theodoridou, Lucia Toniolo, Jan Valek, Rob van Hees, Maria Rosario Veiga.

Abstract

The scope of this collective paper produced in the frame of RILEM TC 277-LHS is to provide sound knowledge on the use of additives/admixtures in lime-based mortars, based on the literature and practice. The most widely known additives/admixtures are systematically presented. Their main effects and testing of their performance have been properly tabulated. It is well known that a plethora of additives/admixtures are produced every year by chemical industries. However, when using them in lime-based mortars, compatibility and durability aspects are of primary importance. The introduction of additives/admixtures in lime mortars was imposed by the need to improve important properties of these composites in the fresh and hardened state, namely, workability, durability, early-age and long-term strength and to reduce defects, such as shrinkage and long setting time. In this review paper, the terminology proposed by EN 16572 is followed, designating additive as a constituent added in small quantity to the binder, and admixture as a substance in quantities at least 1% w/w added to the mix. The additives/admixtures are classified according to their action and their validation with specific testing methodologies highlights the dosage

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4 sensitivity and the need of developing further standardization. The combination of different
5 additives proposed in several studies, resulted as the most promising strategy to enhance the
6 performance of lime mortars. However, recently developed additives and admixtures need to be
7 further evaluated with reference to their compatibility with other mortar constituents, and their
8 effects on the overall mortar and render durability need to be studied. Finally, adopting similar
9 terminology for additives/admixtures in lime and cement based mortars will facilitate better
10 comparison and assessment issues.
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15 16 1. Introduction

17 18 1.1 Definitions

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21 The terms **additives** and **admixtures** (henceforth adds and adms) refer to ingredients that are
22 added in mixtures where cement, lime, gypsum and clay are used as binders, with the aim of
23 improving the fresh and hardened state physico-mechanical properties and the durability of
24 mortars. According to definitions given in EN 16572 (2015), “additive (EN) or addition (ASTM)
25 is a constituent usually added in small quantity to the *binder* to modify its manufacture or
26 properties (for example accelerators, plasticizers, water repellents and air-entraining agents),
27 whereas admixture is a substance other than the binder, aggregate or water, added in quantities of
28 at least 1 % w/w to the *mix* to alter its properties” [1]. The same EN further denotes that “pigments,
29 pozzolana (as long as it is added in small quantities and not as a latent binder) and fibrous
30 substances may be classified as admixtures”. Therefore, based on EN 16572 (2015), an additive is
31 added to the binder system (consider the case of factory-made binders), whereas admixtures are
32 added to the mixture. It should be also clarified that, in many cases of lime-based mortars,
33 pozzolans and cement act as latent binders. Additives and admixtures intend to enhance and
34 ameliorate specific properties of the lime mortars, such as workability, durability, or early-age and
35 final strength, and to reduce defects, such as shrinkage and long setting time. Nowadays, the
36 increasing use of waste and by-product adds/adms in mortars may also decrease the embodied
37 energy of the end-product.
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44 In this review, the definitions of EN 16572 (2015) stated above will be adopted, even though there
45 is a contradiction with terms frequently used in the literature and cement technology. In the
46 literature, the specification between additives/admixture derives from the terminology used in
47 concrete technology: “admixtures are ingredients added to the concrete batch immediately before
48 or during mixing” [2]. Similar definition can be found in ACI 116R-90 (ACI, 1990) for Cement
49 and Concrete Terminology. In this case, the term “addition” is defined as a material that is inter-
50 ground or blended in limited amounts into a hydraulic cement during manufacture, either as a
51 “processing addition” to aid in manufacturing and handling the cement, or as a “functional
52 addition” to modify the properties of the finished product [3].
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1.2 State of the art

The literature highlights the use of natural additives in mortar production throughout the centuries and all over the world [4,5]. More specifically, Sickels (1981) [4], reported that analyses of old mortars, plasters, renders and other ancient materials, carried out in recent decades, provided insights into the use and composition of organic admixtures and their contribution to the performance of the end-product. Neuburger (1930) [5] discovered that Arabic gum or tragacanth, animal glue from Rhodes, the blood of hippopotomus and the milky juice of figs mixed with egg yolk, all served as adhesives or binding substances. Egg albumen, keratin, and casein were other common Egyptian natural organic polymeric binders [6]. In Vitruvius time, fig juice, rye dough, hogs lard, curdled milk, blood and egg whites were employed to toughen and regulate mortar setting performance [7]. Blood and egg whites have also been used to retard the setting time of mortars, along with sugar. Different inclusions, either in fibrous form or as aggregates, were used in old mortars of different technology throughout history by researchers, aiming always to improve the properties of the end-product [8].

In the past decades, research on synthetic adds/adms was limited to concrete and cement-based mortars, but recently the use of traditional and modern adds/adms has been successfully extended to applications in lime-based mortars [9,10,11]. Nowadays, biopolymers are continuously used in the architectural sector of several countries, inspired from natural additives, which were identified with the aid of analytical techniques in traditional mortars which proved in the field their excellent durability and long-term performance [12]. It is worth remarking that most natural additives above-mentioned are mostly “edible” products, the use of which is no longer recommended. Therefore, efforts should be concentrated on the use of wastes and by-products to provide the same positive effects, thereby reducing the consumption of raw materials that are needed to feed humans and animals.

With the aim of further enhancing the performance of lime mortars, specifically expressed by low compressive strength, prolonged hardening time, low resistance to moisture, the use of additives becomes essential to take advantage of the benefits of these composite materials both in restoration and contemporary projects. There are several types of adds/adms, which may be classified according to their action, composition and morphology.

Regarding the lime-based mortars entailed for the repair of historic structures, compatibility with original material should be taken into account. In technical terms, compatibility of a repair mortar is governed by a list of characteristics [13]. This means no direct or indirect damage to the original material and ensuring the long-term stability of the intervention. Therefore, any assessment on the effectiveness of adds/adms in lime-based repair mortars for historic structures should also consider physico-chemical compatibility requirements [14,15,16].

In the following sections, sound knowledge concerning practice and research advances on the use of admixtures/additives will be presented and their benefits and drawbacks on the performance of lime mortars will be discussed. In particular, the most important properties for assessing the additive/admixture performance, with the aid of specific testing methodologies, are presented.

2. Classification of additives according to their action

The classification of additives according to their action is considered as the first step in an attempt to clarify the significance of introducing these materials in the design of mortars. Afterwards, the evaluation methods used for the introduction of additives in lime mortars and their contribution to the performance of the composite material are discussed and summarized at the end of almost each section. Furthermore, Figure 1 highlights the action of each additive/ admixture in the fresh and hardened state properties. The scaling bar denoted by (+) and (-), with dark and light shading, respectively, refers to increasing and decreasing performance of each property.

2.1. Air-entraining agents

Air-entraining additives are organic substances that allow a controlled number of air bubbles to be incorporated in the fresh and hardened state of mortars. In the literature, various research works explicitly investigated the role of air-entraining agents on the setting and hardening of lime mortars. An air-entraining additive improves mortar workability through the formation of air bubbles, which are incorporated into the mortar and become part of the matrix that binds the aggregates together in the hardened state. These small air bubbles, which are produced in a controlled quantity, are uniformly distributed and incorporated in the mortar during mixing and remain there after hardening. The molecule of an air-entraining agent is composed of a hydrophilic and a hydrophobic group. In an aqueous medium, considering that air is trapped inside the fresh mortar, these molecules orient themselves at the air-water interface, so that the hydrophilic end is in contact with the water and the hydrophobic one is outside it, thus forming stable spherical voids [17].

It has been demonstrated that the introduction of air bubbles dispersed uniformly through the mortar paste also increases mortar total porosity (closed and open porosity), thus minimizing damage caused by freezing in the masonry [17]. Given that the total porosity increase is generally associated with a decrease in the mechanical strength, care should be taken in the amount of the air-entraining agent added, so that the resistance of the mortars to external stress and weathering shall not be compromised. In addition, an air-entraining agent may assist to the increase of durability of lime-based mortars subjected to salt crystallization.

The improvement of mortar workability via the formation of air bubbles could influence textural quality and carbonation [18]. Cultrone (2005) stated that the air-entraining agent Sikanol-MR (Sika, S. L) significantly altered the texture of the mortars by creating rounded pores and eliminating or reducing the drying cracks, but it seems that this had no effect on the carbonation process [19].

The surfactants are synthetic or natural molecules than can act as air-entraining compounds. Due to their bi-polar nature, exhibiting a non-polar part usually oriented towards the aerial medium, and a polar fragment anchored in the lime matrix, the surfactants could stabilize the air bubbles inside the mortar [20].

Silva et al., (2020) studied three different surfactants: sodium dodecyl sulfate (SDS), sodium alfa olefin sulfonate (AOS) and cocamidopropyl betaine (CAPB) [21]. The latter was the most effective air-entraining agent due to its amphoteric nature, but, at the same time, increased the porosity and pore diameter (pores from 4 to 500 microns), thus causing a dramatic drop in the mechanical resistance of the end-product. As opposed to that, SDS and AOS, which are anionic surfactants, increased pores in the range 4-40 microns, leading to moderate changes in compressive strength, and positively affecting the hygric properties by reducing the capillary water absorption.

Organic air-entraining agents (OAEA) have been studied in lime and lime-pozzolan mortars. Results showed that those OAEA do not affect carbonation, provide higher pores and permeability, but decrease the mechanical properties, compared to the pure lime mixtures [19,22]. These agents could be used to increase mortar durability towards temperature stress and salt crystallization.

Table 1 classifies the studies of the literature for the use and purpose of air-entraining agents in lime-based mortars taking into account the binder composition, type and quantity of agent added.

Table 1. Summary of studies for the use of air-entraining agents in lime-based mortars

Binder composition	Additive	% wt.	Reference	Purpose of use
CL + BSL or OPC	Air-entraining agent	0.05	Cerulli 2003	Improvement of: -Workability -Freeze-thaw resistance -Salt decay resistance
CL CL + NP	Sikanol-MR (Sika, S.L)	0.10	Cultrone 2005	
CL	Silipon –Aqualon	0.05-0.15	Seabra 2009	
CL	Sodium dodecyl sulfate (SDS)	0.01-0.05*	Silva et al., 2020a	
CL	Sodium alfa olefin sulfonate (AOS)	0.005-0.020*		
CL	Cocamidopropyl betaine (CAPB)	0.01-0.50*		

CL - Calcitic lime, NP - natural pozzolan, % addition - refers to % wt. addition to binder, BSL - Blast furnace slag, OPC - Ordinary Portland Cement

* - % addition to the total dry weight of mortar (binder + aggregate)

2.2 Plasticizers-superplasticizers

Plasticizers or superplasticizers are low-molecular-weight polymers that reduce the water needed to achieve the desired mortar workability, without affecting its consistency. As a result, fluidity and workability, at a constant water/binder ratio, are improved with the use of plasticizers or superplasticizers, giving rise to higher mechanical strength and resistance to shrinkage. The chemical composition of plasticizers and superplasticizers comprises groups of lignosulphonates (anionic surfactants), polyglycol esters and carbohydrates [22].

The mechanism of action of plasticizers and superplasticizers relies on the reduction of the surface tension of water, as well as the electrostatic repulsion between the binder particles, as a result of

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4 the orientation of the additive molecule in the interface liquid-solid, which prevents the adsorption
5 of water molecules on the surface of the binder particles, thus increasing the free water in the
6 system. The influence of poly-parameters on the action of plasticizers is evidenced in several
7 works referring to the water to lime ratio, the quantity and nature of admixture, such as pozzolans,
8 cement, etc. Generally, the use of plasticizers improves the stability, water retention and
9 rheological behavior of the material in the fresh state [22,23,24,25]. Indeed, according to Seabra
10 et al., (2009), the plasticizer or water-reducing agent Peramin SMF – Perstorp, even in small
11 amounts, changed the rheological behavior of the fresh composite, as confirmed by the diminishing
12 torque values due to the increase of free water in the system [22]. Polynaphthalene sulfonate
13 (PNS), lignosulfonate (LS) and condensate of melamine-formaldehyde sulfonate (SMFC)
14 plasticizers were found to be less effective than polycarboxylated ethers (PCE). Another drawback
15 of sulfonates is related to the introduction of sulfate ions into the mortar mixture. PNS showed
16 higher dispersing effect than LS on account of its higher adsorption onto portlandite, C-S-H, C-S-
17 A-H, and C-A-H particles [24]. Plasticizers increase the compressive strength of mortars and may
18 eventually reduce the setting time, depending on the dosage, without affecting the morphology of
19 the composite. Therefore, plasticizers could be used in mortars that should reach high mechanical
20 properties [22,23,25].

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27 On the other hand, superplasticizers, without affecting the consistency, permit simultaneously a
28 high reduction in the water content of a given mortar mix and a considerable increase in their
29 slump/flow. Experience from practice has shown the dosage dependent performance of
30 superplasticizers. In the cases e.g. of inclusions of fine material rich in calcium aluminates or
31 pozzolans rich in carbonate content (e.g. fly ash), the effectiveness of superplasticizers is reduced
32 and their dosage should be determined by trial mixes.

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36 The chemical composition and molecular architecture of the superplasticizers are extremely
37 important, with respect to the efficiency of these admixtures. Among the different families of
38 superplasticizers, polycarboxylated ethers (PCE) have shown the best compatibility and
39 improvement effects in lime mortars, with those compounds with longer side chains being
40 particularly effective [26]. The slump retention ability of lime mortars with PCE was the highest.
41 Steric hindrance was considered to be the main action mechanism. Fernández et al., (2013)
42 reported that the addition of a PCE superplasticizer in air lime mortars containing also nanosilica,
43 affects positively the rheological properties of the mortar, increasing the flow-ability, whilst
44 accelerating the setting process by avoiding the formation of agglomerates from the interaction of
45 hydrated lime particles and nanosilica through a steric hindrance mechanism [23]. Moreover, the
46 mechanical strength was also increased by the nanosilica and superplasticizer, which modified
47 favourably the microstructure, as proved by pore size distribution and SEM observations.

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52 Furthermore, superplasticizers could be mixed with photocatalytic agents to reinforce their action.
53 The agglomeration of photocatalysts in water media was avoided with the use of PCE
54 superplasticizers. Therefore, coatings with superplasticizers showed improved photocatalytic
55 effect of TiO₂, since the superplasticizers enhanced TiO₂ distribution and percolation in the thin
56 coating layers. In air lime mortars, coatings with polycarboxylate-based superplasticizers
57 improved the NO removal rates, compared to superplasticizer free coatings: an average increase
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of NO degradation by 15% under UV and by 76% under solar light was found [24]. Accelerated weathering of these coatings showed that the NO removal was moderately reduced, and the TiO₂ nano-particles were slightly washed out, supporting long-run activity [24].

Table 2 classifies studies from the literature for the use and purpose of plasticizers-superplasticizers in lime-based mortars considering the binder composition, the type and quantity of agent added.

Table 2. Summary of studies on the use of plasticizers-superplasticizers in lime-based mortars

Binder composition	Additive	% wt.	Reference	Purpose of use
CL	Peramin SMF – Perstorp	0.05-0.15	Seabra et al., 2009	-Improvement of workability -Increase of mechanical strength -Avoidance of agglomeration of nanoparticles - Stability -Water retention - Rheological behavior
CL	Melflux 2651 F (BASF)	0.50-1.00	Fernandez et al., 2013	
CL	52IPEG 5.8	1	Perez-Nicolas et al., 2018	
CL	23APEG	1		
CL	45PC6	1		
CL	Melcret 500F, BASF	1		
CL+MK	Polycarboxylate	2.0*	Arrizi 2012	

CL - Calcitic lime, MK - metakaolin, % addition - refers to % wt. addition to binder, * - this % wt refers to the addition to the total mass.

2.3 Water repellents

Water repellent agents reduce the water absorption by capillarity, hence improving the durability towards weathering agents involving, in some cases, water transport (e.g., freeze-thaw, salt crystallization, wetting-drying, biological colonization), without affecting the drying kinetics. Izaguirre et al., (2009) proposed the addition of two different anionic surfactants, sodium oleate and calcium stearate, commercialized as water repellents for cement-based mortars, into lime-based mortars and found clear improvement in water absorption by capillarity and durability against freeze-thaw, as a result of the formation of air voids, mainly due to the air-entraining ability of these surfactants [20]. Falchi et al., (2013) proposed powdered silane and calcium stearates as water repellents for pozzolana-lime mortars [27]. Both additives provided good water-repellency, even if they modified some physical properties and the hydration kinetics of the composite materials. In particular, the silane strongly enhanced the mortar resistance to salt crystallization due to the complete water-repellent effect induced. Maravelaki-Kalaitzaki et al., (2007) proposed the impregnation of hydraulic-lime mortars with an oligomeric organo-siloxane; the composites exhibited improved resistance to salt-decay and mechanical stress after treatment [28].

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4 Low water absorption through capillarity, high permeability, enhanced durability of the material
5 towards freezing–thawing cycles and delay in setting time were achieved with the addition of water
6 repellents [20,27,29].
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9 Lime-metakaolin plasters and renders were treated with zinc stearate and the effect of
10 hydrophobization was studied by Vejmelkova et al., (2012) [30]. Increasing the content of zinc
11 stearate in the mortar mix a rapid led to a decrease in the coefficient of water absorption, together
12 with a reasonable decrease in both flexural and compressive strength. Furthermore, a positive
13 effect on vapor diffusion and thermal properties through a 1% wt. of zinc stearate addition was
14 observed.
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17 Čechová et al., (2010) [31] and Papayianni et al., (2013) [32] studied the addition of linseed oil in
18 lime mortars as a traditional water-repellent agent. The addition of 1% wt. linseed oil proved to
19 increase the mechanical strength and reduce the water absorption of mortar, without inducing
20 significant effect on the total open porosity. The resistance to salt crystallization, as well as to
21 freeze-thaw cycles, was also improved. On the contrary, a 3% wt. addition of linseed oil resulted
22 in a hydrophobic mortar with lower mechanical strength.
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25 Lime-based renders with multiple additives, such as an adhesion improver (ethylene–vinyl acetate
26 copolymer, EVA), a water-repellent agent (sodium oleate), a viscosity modifier (a starch
27 derivative) exhibited durability towards freezing-thawing cycles and sulfate attack, rendering them
28 as effective candidates for application in cultural heritage and contemporary buildings [25].
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31 Silva et al., (2020) compared the behavior of sodium oleate, triethoxyoctyl-silane and alkylsilicone
32 resin in dosages up to 0.6% [33]. For the silane derivative, the authors concluded that the low
33 solubility of this product in water explains its uneven distribution in the mortar mix and this
34 accounts for its moderate effectiveness. In the case of the silicone resin, the interaction between
35 functional groups gives rise to insoluble polysiloxane networks and a poor distribution in the lime
36 mortar. The silicone resin exhibited a lower reduction in water absorption, but increased the
37 mechanical strength. The sodium oleate reduced water absorption, induced insignificant changes
38 in the pore size distribution without modifying the water vapour permeability, but decreased the
39 mechanical strength of the composite.
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42 Table 3 reports studies from literature on the use and purpose of water repellents in lime-based
43 mortars exemplifying the type of additive and dosage.
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Table 3. Summary of studies on the use of water repellents in lime-based mortars

Binder composition	Additive	% w.t	Reference	Purpose of use
CL+MK	Cellulose derivative	2.0	Arrizi 2012	-Decrease of water absorption by capillarity -Hydrophobicity -Increase of mechanical strength -Durability
CL+NP, CL+NP+WC	Linseed oil	1.0	Papayianni et al., 2013	
CL+MK	Zinc stearate	1.1-15.0	Vejmelkova et al., 2012	
CL, CL+NP	Calcium Stearate	0.5-1.5	Falchi et al., 2013	
CL, CL+NP	Silres A	0.5-1.5		
CL	Sodium oleate	0.3-2.4	Izaguirre et al., 2009	
CL	Calcium stearate	0.3-2.4		
CL	Sodium oleate	0.05–0.6	Silva et al., 2020b	
CL	Triethoxyoctyl-silane	0.2–0.5		
CL	Alkylsilicone resin	0.1–0.5		

CL - Calcitic lime, MK - metakaolin, NP - natural pozzolan, WC - white cement; % wt. - refers to the addition to the total dry mortar's weight mass.

2.4 Viscosity modifiers

The viscosity modifiers are compounds that influence the fresh state properties of mortars and are intended to improve homogeneity and cohesiveness of the mixture. Therefore, the mortar workability is enhanced, along with some of the mechanical properties, especially in mixtures rich in fines [22]. The commercial and natural organic additives that have been proposed as viscosity modifiers may also function as water retainers, plasticizers and air-entraining agents.

Those additives in grouts and flowable mortars exhibited a positive effect by modifying the air content and consequently the pore size distribution, thus enhancing the durability to freezing-thawing cycles. The dosage of the additive is very critical, since it affects the water demand and, as a result, the mortar's properties [20,34].

Seabra et al., (2009) demonstrated that a water-retaining agent (hydroxypropylmethyl cellulose, HPMC – Walocel), a plasticizer or water-reducing agent (Peramin SMF – Perstorp) and an air-entraining agent (Silipon –Aqualon) changed considerably the rheological behavior of lime mortars [22]. More specifically, the water-retaining agent exerted a thickening effect immediately after its addition, followed, after some agitation time, by a thinning effect due to the influence of the air-entraining agent in the mortar. Conversely, the use of small amounts of plasticizer diminished torque values due to an increase of free water in the system; both the plasticizer and water-retaining agent reduced the water needed to achieve the desirable workability. Finally, the air-entraining agent reduced the flow resistance of mortar by introducing air bubbles.

Izaguirre et al., (2010) tested different dosages of potato starch into air lime-based mortars in order to check its efficiency as a rheology modifier [34]. This starch polymer was found to be strongly dosage-dependent: it acted as a thickener when the incorporated dosage was up to 0.30% of lime weight; conversely, above that dosage, it behaved as a plasticizer. The thickening effect took place

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4 because the polymer molecules that were adsorbed onto lime particles functioned as a flocculant,
5 as confirmed by zeta-potential and particle size distribution results. In addition, for large amounts
6 of polymer, steric hindrance and electrostatic repulsive forces appeared, leading to a dispersion
7 mechanism which explained the plasticizing effect observed in the fresh mortar behavior [34].
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10 Izaguirre et al., (2011) proposed two different commercial viscosity modifiers, namely
11 hydroxypropyl methylcellulose and a guar gum derivative (hydroxypropylguaran), to be added
12 into lime-based mortars in order to test their performance, namely on the water retention, air
13 content and setting time, density, shrinkage, water absorption through capillarity, water vapour
14 permeability, long-term compressive strength, pore structure and durability [35]. Hydroxypropyl
15 methylcellulose, unlike its well-known effect in cement-based materials, showed a very limited
16 viscosity enhancing behaviour in air lime mortars, attributed to an adsorption mechanism of this
17 additive on the $\text{Ca}(\text{OH})_2$ crystals. On the other hand, the guar gum derivative, which has a larger
18 quantity of ionized groups at alkaline pH, exhibited a reduced adsorption onto slaked lime
19 particles, giving rise to an increase in viscosity and a larger water-retention capacity, which in fact
20 resulted in a delay of setting time [35]. Furthermore, the guar gum derivative raised the air content
21 and changed the pore size distribution of the hardened mortars, thus lowering the water absorption
22 through capillarity and improving durability in freezing–thawing cycles.
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28 González-Sánchez et al., (2021) have reported positive effects on air lime rendering mortars using
29 simultaneous combination of a viscosity enhancer (potato starch), an adhesion booster (ethylene–
30 vinyl acetate copolymer, EVA), a water repellent (sodium oleate) and mineral admixtures
31 (metakaolin or nanosilica) [36]. These additives in mortars with metakaolin enhanced the
32 adherence to the substrate and lowered the superficial cracking. The mixtures including nanosilica
33 presented better durability against aggressive atmospheric conditions [36].
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37 Table 4 summarizes several literature studies on the use of viscosity modifiers in lime-based
38 mortars taking into account the type of binder, type and dosage of additive and purpose of use.
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Table 4. Summary of studies on the use of viscosity modifiers in lime-based mortars

Binder composition	Additive	% wt.	Reference	Purpose of use
CL	Potato starch	0.03-0.80*	Izaguirre et al., 2010	-Improvement of workability (flowable mortars) -Cohesiveness -No-cracking appearance -Resistance to weathering
CL	Hydroxypropyl methylcellulose (Walocel)	0.05, 0.10, 0.15, 0.20	Seabra et al., 2009	
CL	Hydroxypropyl methylcellulose	0.29	Izaguirre et al., 2011a	
CL	Guar gum derivative	0.29		
CL	Potato starch	0.5	González-Sánchez et al., 2021	
	Ethylene-vinyl acetate copolymer	5-10		
	Sodium oleate	0.5		

CL - Calcitic lime, % addition - refers to % wt addition to binder; * - this % wt refers to the addition to the total dry mortar's weight mass

2.5 Carbonation accelerators

The carbonation reaction in lime mortars is a very significant process for the development of the long-term performance of these composites [37]. The carbonation accelerators affect the carbonation of lime pastes and mortars, providing shorter setting time and higher mechanical strength [38,39]. Shrinkage could be considered as a disadvantage in some cases. Ceramic dust [39], carbonic anhydrase enzyme [40], TiO₂ nano-particles [38,41,42,43,44], synthesized aluminosilicates [45] could be used as carbonation accelerators. The addition of nano-TiO₂ to lime mortars provided a higher concentration of CO₂ in gas form on the surface of the material. The compressive and flexural strength were significantly improved, along with the resistance to weathering parameters.

Maravelaki et al., (2013) [41] and Kapetanaki et al., (2019) [44] studied the ability of hydrated lime and metakaolin, or natural hydraulic lime mortars with nano-TiO₂, to adhere fragments of porous limestone from the Acropolis monuments. The physico-chemical and mechanical properties of the nano-titania mortars were studied and compared to the respective ones without that addition. This study highlighted that the addition of nano-TiO₂ decreases the setting time and increases the modulus of elasticity, carbonation and hydration, comparing to mortars without that addition [42].

Cizer et al., (2018) studied the effect of carbonic anhydrase enzyme on the precipitation kinetics and phase transformations of calcium carbonate, and on the strength development of lime mortars [40]. The carbonic anhydrase catalyzes the reaction between carbon dioxide and aqueous lime and increases: (a) the rate of calcium carbonate crystallization, (b) the yield of the carbonation reaction and (c) the mortar strength at early ages, due to the increasing rate of carbonate ions supplied to

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4 the solution by the enzyme. In addition, this enzyme favors the formation of stable calcite and
5 significantly modifies its morphology by developing new crystal faces.
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8 Ergenc et al., (2018) investigated the effect of the diethyl carbonate on the carbonation of two
9 types of lime mortars, one using lime putty and standard sand and the other one also containing
10 dust and fragments of ceramic [39]. The mortar samples with the diethyl carbonate had steadier
11 carbonation and slight changes in their microstructure.
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14 Rigopoulos et al., (2021) [46] and Kyriakou et al., (2020) [47] used nano-sized dolerite quarry
15 waste and olivine basalt to enhance the carbonation reaction in lime renders. The incorporation of
16 both additions at 15% w/w resulted in mortars with denser microstructure and higher compressive
17 strength. This was attributed to the enhanced diffusion of atmospheric CO₂ through the mortar
18 pore structure and the improved CO₂ uptake of the nano-sized additions. Thermogravimetric
19 (DTA/TG) and powder X-ray diffraction (XRD) analyses, as well as the phenolphthalein indicator
20 test, confirmed that the degree of carbonation of the modified lime renders was indeed notably
21 enhanced. This also had a positive effect on the setting and hardening time of the nano-modified
22 end-products, which could be adopted not only for restoration purposes, but also in contemporary
23 sustainable construction.
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27 Table 5 summarizes the additives used to accelerate the carbonation of lime-based mortars from
28 the literature.
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Table 5. Summary of studies on the use of carbonation accelerators in lime-based mortars

Binder composition	Additive	% wt. or application	Reference	Purpose of use
CL	Nano-TiO ₂	6% CL replacement	Karatasios et al., 2010	-Acceleration of setting time -Accelerated carbonation rate -Increased depth of carbonation - Increase of mechanical strength -Self-cleaning effect
CL+Mt, NHL	Nano-TiO ₂	3-6%	Maravelaki et al., 2013	
CL putty	Diethyl carbonate	Sprayed after 15 days	Ergenc et al., 2018	
CL	Synthesized aluminosilicates	5.0-10.0 ^b	Loganina et al., 2017	
CL putty	Carbonic anhydrase enzyme	0.6 μM ^a	Cirez et al., 2018	
CL	Nano-sized dolerite quarry waste and the olivine basalt	15% CL replacement	Kyriakou et al., 2020	
CL	Nano-sized dolerite quarry waste	5 and 15% CL replacement	Rigopoulos et al., 2021	

CL - Calcitic lime, MK - metakaolin, NHL - natural hydraulic lime, % addition - refers to % wt addition to the binder, a - CA enzyme was dosed at a 0.6 μM concentration to the saturated lime solution and lime putty, b - The synthesized aluminosilicates replaced 5 and 10 % of the binder

2.6 Biological self-healing agents, autogenous self-healing stimulators

Self-healing materials are able, once damage occurs, to repair themselves to restore their original properties or limit further deterioration, without human intervention. Such a function is a vital development in reducing the significant maintenance costs in building structures and the insidious deterioration of valuable heritage structures.

The self-healing agents are proprietary chemical compounds, generally known under the category of “crystalline admixtures” [48], added to the cement/lime mixtures; they are highly hydrophilic and can react with calcium hydroxide to promote the carbonation and formation of non-soluble compounds, which deposit into cracks and seal them, also contributing to recover the pristine level of performance (e.g., compressive strength) of the pre-damaged mortar [49,50]. To the same purpose, the addition into the mortar of hydraulic lime encapsulated into either organic or non-organic shells has also been attempted [49]. As for the encapsulated lime, the cracks break the capsules by intercepting them and the fresh hydraulic lime mortar cargo becomes available to react with the calcium hydroxide and outdoor available agents (water, moisture, air), thus promoting delayed hydration and carbonation reactions, whose products contribute to the sealing of the cracks.

Biological self-healing incorporates naturally occurring microorganisms, such as bacteria, along with chemical precursors which can lead to biomineralization, e.g., of calcite. Although, the alkaline environment in lime mortars is considered harsh for microbial organisms, there are considerable opportunities for successful application on geological materials, due to their

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4 bioreceptivity and suitability for biomineralization. Different ways in which the bacteria, along
5 with the precursor chemicals, can be introduced into porous geological construction materials are
6 currently under study, aiming at defining a protocol for the application and evaluation of the results
7 [51]. In biomineralization, spores trapped within a mineral are exposed by damage and germinate
8 into cells, which heal the damage, re-encapsulating themselves and resetting the cycle. Calcite
9 biomineralization *via* urea hydrolysis can be used as the basic mechanism for assessing self-
10 healing in lime mortars, due to its common mineralogy, porosity and moisture content. The
11 hydrolysis of urea produces ammonia and carbonate; ammonia release acts to raise the pH of the
12 medium which is a favorable condition for the precipitation of calcium carbonate. Carbonate binds
13 calcium ions, which are present in the medium, resulting in the formation of calcium carbonate
14 crystals. The potential of the mechanism to function and modify the microstructure of the materials
15 under study could be detected through simple water absorption tests and the application of other
16 analytical methods and microscopic techniques [51]. Alternatively to the use of bacteria that
17 produce calcite biomineralization, other bioproducts have been studied with the same aim of
18 reducing water absorption of air lime mortars, such as iron supplemented *Escherichia coli* cultures
19 and microbial mixed cultures grown with crude glycerol [52]. The use of these bioproducts
20 decreased the mortar compressive strength, but improved its water-mediated weathering
21 behaviour.
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28 Table 6 lists several studies from the literature on the effects of self-healing agents on lime-based
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Table 6 - Summary of studies on self-healing lime-based mortars

Binder composition	Additive	% wt. or application	Reference	Purpose of use
CL + NHL5 + Cem	Coated granules with sodium fluoride	3.0-6.0	De Nardi et al., 2017a	-Healing capacity -Healing capacity and recovery of compressive strength -Reduce water absorption
CL + NHL5 + Cem	Coated granules with maleic anhydride	3.0-6.0		
CL + NHL5 + Cem	Coated granules with phthalic anhydride	3.0-6.0		
CL + NHL5	Crystalline admixture	3.0	De Nardi et al, 2017b	
CL	E.coli+Fe	Lyophilized, suspended in water and used as mixing liquid	Oliveira et al., 2021a	
CL	MMC			

CL - Calcitic lime, NHL5 - natural hydraulic lime5, Cem - cement, E.coli+Fe - Escherichia coli-based bioproduct; MMC - Crude-glycerol-based microbial mixed cultures bioproduct, % addition by weight of mortar

2.7 Crystallization modifiers

The addition of crystallization modifiers to lime mortars is a novel approach aiming at eliminating salt crystallization damage in historic masonry. Crystallization modifiers are ions or molecules which alter the crystallization process by delaying nucleation (inhibitors), promoting nucleation (promoters), and/or modifying the shape of the crystals (habit modifiers) [53]. Lubelli et al (2010) studied whether the incorporation of sodium ferrocyanide in different percentages in cement-lime mortars influence the durability of these mortars to salt crystallization [53]. It was proved that the addition of sodium ferrocyanide contributed to the reduction of the salt crystallization decay. Granneman et al., (2018) reported sodium ferrocyanide and borax, as modifiers for sodium chloride and sodium sulfate, respectively [54]. The results showed that the selected modifiers may mitigate salt crystallization even after going through the carbonation process of the mortar. Besides, no major effects of the modifiers on the fresh and hardened mortar properties were observed, rendering them as potential crystallization modifiers in restoration mortars. The addition of these agents can reduce crystallization damage of lime mortars.

Table 7 summarizes the above-mentioned studies on the use of crystallization modifiers in lime-based mortars.

Table 7. Summary of studies on the use of crystallization modifiers in lime-based mortars

Binder composition	Additive	% wt.	Reference	Purpose of use
CL	Sodium ferrocyanide	0.94	Lubelli et al., 2010	Resistance to salt crystallization
CL	Borax	1.6-3.2		
Cem + CL	Sodium ferrocyanide	0.001-0.02%*	Granneman et al., 2018	

CL - Calcitic lime, Cem: cement, % addition - refers to % wt addition to binder

* this addition refers to %wt of the dry weight of the mortar

2.8 Nano-particles

Inorganic or mineral particles of 10^{-9} m (nano-dimensions) are mixed with lime binders, providing mortars with self-cleaning properties, as well as improved mechanical properties. Nano-TiO₂ and SiO₂ are common nanoparticles used as additives in lime mortars [23,42,43,55,56,57,58,59].

Nanosilica is one of the most studied types of nanoparticles used as an additive in cementitious composites to improve their characteristics in the plastic and hardened state [60,61,62], investigating the effect of nanosilica on the properties of lime-based systems, reported that the main drawback was that the water/binder ratio increased with increasing amount of nanosilica, whereas the workability and setting time decreased. Superplasticizers have, therefore, been added to tackle this problem [23,62]. Researchers also reported that the mechanical strength increases with increasing amount of nanosilica, whereas the capillary porosity decreases, hence improving the durability of lime mortars [56,57,60,63,57]. A study referring to the addition of graphene oxide (GO) into natural hydraulic lime mortars and the influence of GO percentage and of the type of mixing investigated changes in the composite microstructure, mechanical and physical properties [59]. The best results were obtained with dispersed GO at concentrations of 0.05% and 0.1% wt. of binder. A slight improvement of mechanical and physical characteristics was achieved. This could lead to new mortars with improved properties that can be used for building rehabilitation.

The development of photocatalysts as self-cleaning coatings is an innovative field to mitigate the decay of surfaces induced by atmospheric pollution. TiO₂ nanocomposites have been investigated for their photocatalytic properties. These nanocomposites produce photoactive coatings when applied, without compromising the mortar hardened state properties [42-43, 55,61,38]. Some efforts have been made to enhance the sensitivity of the photocatalysts towards visible light spectrum. Doped-TiO₂ (Fe-TiO₂ and V-TiO₂) nanoparticles have been tested as effective agents to be applied as active coatings [64,65]. The photocatalytic assessment of the Fe-doped TiO₂ nanoparticles indicated that doping titania with a low iron content (0.05 and 0.10 w/w % to binder) makes it possible to degrade organic pollutants under visible radiation [65]. In this study, another interesting finding was the enhancement of carbonation in lime mixtures at early stages.

Table 8 reports several studies from the literature on the addition of nano-particles in lime-based mortars and the effects induced on the mortars' performance.

Table 8. Summary of studies on the use of nanoparticles in lime-based mortars

Binder composition	Additive	% wt.	Reference	Purpose of use
CL CL+CB CL+P CL	SiO ₂	0.5-6.0 3 1.5 6-20	Fernandez et al., 2013 Theodoridou et al., 2016a Nunes et al., 2016b Duran et al., 2014	-Increase of mechanical strength -Photocatalytic activity -Self-cleaning effect -Acceleration of setting time -Slight increase of mechanical strength -Decrease of water absorption
CL, CL+Cem, CL+ Gyp, CL+MK, NHL CL+CB CL	TiO ₂	0.5-6.0 6 3 3-11	Lucas et al., 2013, Maravelaki et al., 13, Kapetanaki et al., 2019 Theodoridou et al., 2016a, Karatasios et al., 2010	
CL	Fe-TiO ₂	0.05-1	Kapridaki et al., 2019	
NHL	GO	0.05-1.0	Faria et al., 2017	

CL - Calcitic lime, P- natural pozzolan, MK - metakaolin, NHL - natural hydraulic lime, Cem - cement, Gyp - gypsum, % addition - refers to % wt addition to binder

2.9 Natural compounds and polymers

Polymers consist of large molecules or macromolecules and are composed of many repeated sub-units. Depending on their composition, polymers are used in lime mortars to provide mixtures with improved properties, such as adhesion, resistance to moisture and weathering. In past centuries, people used to add different organic components in building materials, such as plants' mucilages, animal fats, etc. A vernacular example of the use of natural polymers is the extinction of calcium oxide together with animal fat with abundant water, resulting a water-repellent lime putty. Nowadays, natural organic compounds are still used in India with lime-based mortars [66]. Recently, the influence of natural additions on the physical and mechanical properties of lime mortar was investigated in order to better understand the mechanism of ancient mortars [10,67,68].

Various organic additives have been used as additions, according to their properties and historical use: polysaccharides (e.g. opuntia used either as a powder or as mucilage), proteins (e.g. animal glue and casein) and fatty acids (e.g. olive oil, linseed oil). They were all considered compatible with traditional building materials [10]. The presence of proteins and carbohydrates influences the carbonation and hydraulic reaction in lime mortars and can enhance mechanical properties. Some type of organic additives can also reduce the porosity and the water affinity of the mortar [68]. Fatty acids are mainly used to impart water repellent properties to mortars and improve their durability in severe weathering conditions involving water transport [69]. A common example of a natural organic additive is the mucilaginous juice extracted from nopal cladodes. Its incorporation in the slaking water for the formulation of lime mortars and plasters was studied [70]. Adsorption of polysaccharides on Ca(OH)₂ crystals prevents the development of large

particles, resulting in a very reactive, nanosized portlandite slurry. It also promotes steric stabilization, which limits aggregation, thus enhancing the colloidal nature of the lime putty. Overall, these effects are very favorable for the preparation of highly plastic lime mortars with enhanced properties. None of these potential effects is expected to occur if the nopal juice is added to an already slaked lime, as it is the case of commercial dry hydrated lime [70].

Kang et al., (2020) studied the effect of addition of fully refined sugar (sucrose 99,9%) to the hydration of quicklime and the development of carbonation process and compressive strength of derived lime-based mortars [71]. Water solution containing 3.5 and 7% of sugar were tested; two advantages of the addition of sugar were observed: the delay of quicklime hydration and the formation of significantly smaller hydrated lime particles due to the molecular structure of sucrose that effectively retained absorbed water for a long time, alleviating dry shrinkage and the resulting cracks in lime-based materials. The compressive strength developed at 28 and 56 days in the mortars prepared with the sugar added in lime, are definitely higher. The presence of sugar in the hydrated lime can help the CO₂ to diffuse inside the mortar because the slower carbonation considerably delays the clogging of pores around the surface of mortar [71].

Table 9 summarizes the studies from the literature on the use and effects of natural compounds and polymers in the lime-based mortars.

Table 9. Summarizing studies for natural compounds and polymers in lime-based mortars

Binder composition	Additive	% wt.	Reference	Purpose of use
NHL	Cissus Glauca Roxb (CGR)	15-20 ^a	Ravi et al., 2018	-Increase of mechanical strength -Water repellency -Resistance to salt crystallization -Resistance to frost
CL	Animal glue	5.0	Ventola et al., 2011	
CL	Casein	5.0		
CL	Nopal as powder	5.0		
CL	Nopal as mucilage	5.0		
CL	Olive oil	5.0		
CL	Sugar (sucrose)	3.5 and 7	Kang et. al 2020	
SL	Nopal juice	The quicklime slaked in aqueous nopal juice extract;	Rodrigues-Navarro et al., 2017	
CL, CL+ MK	Linseed oil	1.5	Nunes et al., 2016b	

NHL - natural hydraulic lime, CL - Calcitic lime, SL - slaked lime putty, MK - metakaolin, % addition - refers to % wt addition to binder, a - Content of CGR % by wt. of water

3. Classification of admixtures according to their action

In the following sections, the most commonly used admixtures, which represent substances added in the mortar mixture, are classified in categories according to their multi-function characteristics that influence various mortar properties. More specifically, phase change materials (PCMs), natural and synthetic fibers, pozzolans and white cement are hereby presented and discussed.

3.1 Phase Change Materials (PCMs)

PCMs can function as latent heat storage systems, absorbing or releasing heat upon changing their phase from solid to liquid or vice-versa [11]. This ability of PCMs makes them suitable to be used as admixtures in the production of thermally efficient composite building materials and products, such as lime-based plasters [72]. To avoid unintended movements in the binding matrix during the liquid phase of PCMs, and also to prevent microstructural changes that could compromise the performance of the mortars, the use of micro-encapsulated materials has been developed [73].

The fresh state characterization of lime mortars with PCM additions was studied by Lucas et al., (2010), who found that there was an increase in workability when PCM capsules were incorporated in air lime mortars [Error! Bookmark not defined.]. In the same study, a decrease in paste thickening was recorded due to the evolution of viscosity and yield stress. It was thus noticed that the rheological characterization of air lime mortar becomes more difficult upon the addition of PCMs to the mixture. Ventola et al., (2013) further investigated the use of PCMs as an admixture in traditional lime mortar [11]. This led to improved thermal insulation properties, compressive strength and carbonation rate. According to Cunha et al., (2016), the use of microencapsulated PCMs in lime-based mortars leads to an increase in water demand during the mixing processes; this is attributed to the fineness of the PCM microcapsules [74]. Furthermore, PCMs induce an increase in the microporosity, as well as a decrease in the flexural and compressive strengths of the hardened end-product. Theodoridou et al., (2016) also studied the effect of microencapsulated PCM addition on the performance of traditional lime-based plasters [72]. Their results suggest that the use of PCMs enhances the thermal properties of air and hydraulic lime composites, but reduces their compressive and flexural strength. In addition to the most commonly tested paraffin waxes (such as the commercial Micronal of BASF [75]), Frigione et al., (2020) [76] and Sarcinella et al., (2020) [77] tested in air lime and hydraulic lime mortars PCMs based on poly-ethylene glycol supported onto fragments of a calcareous stone. According to these studies the proposed PCMs leave unchanged the thermal conductivity when added to aerial lime mortars, whilst reduced the heating and cooling needs of the hydraulic lime mortars.

Table 10 reports several studies from the literature on the type of PCM admixture used and the effects in lime-based mortars.

Table 10. Summary of studies on the use of PMC in lime-based mortars

Binder composition	Admixture	% wt.	Reference	Purpose of use
CL CL+Cem CL+Gyp	Micronal DS 5008, (BASF)	5, 10, 15, 20*	Lucas et al., 2010	-Thermal properties -Thermal insolation
CL	PCM DS 5001 Micronal® (BASF) (wax with a specific alkane chain)	5, 10, 15*	Ventola et al., 2013	
CL	PCM DS 5001 Micronal (BASF)	9.1*	Pavlik et al., 2014	
CL NHL5	Paraffin core with wall in melamine-formaldehyde	21.26 45.38	Cunha et al., 2016	
CL NHL	Micronal DS 5038 X (BASF)	5*	Theodoridou et al., 2016b	
CL	Poly(ethylene glycol)	6.375 69	Frigione et al., 2020	
NHL	Poly (ethylene glycol)	23.02	Sarcinella et al., 2020	

CL - Calcitic lime, NHL - natural hydraulic lime, Cem - cement, Gyp - gypsum, % addition - refers to % wt addition to binder, * - this addition refers to % wt addition to binder and aggregates

3.2 Fibers: natural / synthetic

Fibers are mostly used in mortars in order to improve their engineering properties, such as fracture toughness, flexural strength, control of plastic shrinkage cracking, and, in general, cracking [78]. The use of natural fibers (straw, wooden fibers, animal hair) has been widespread in the past, as it has been found by the analysis of old mortars, in particular when clay was used as the binder, in the case of lime plasters serving as substrate of frescos or other decoration to mitigate cracking [66] or in the case of gypsum plaster substrates.

Fiber-reinforced hydraulic lime mortars can be used for repairing historic structures. The use of glass, basalt and even polymer fibers from recycled bottles has been reported, with known effects on improvement of the mortar mechanical behavior (flexural strength, toughness) in the post-cracking condition [78,79].

The effect of polypropylene fibers on the behavior of air lime-based mortars was studied by Izaguirre et al., (2011) [80]. It was found that, when the fibers were added in low dosage in air lime-based mortars, there was an improvement in various properties, such as strength, permeability, macroscopic cracks reduction or freeze-thawing durability. However, the aforementioned authors also noticed that the addition of fibers in lime-based mortars hindered workability, which required larger amount of water that gave rise to the formation of larger pores.

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4 It was, thus, concluded that only crack reduction and material durability were improved with the
5 addition of fibres in larger amounts.
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8 Electrospun cellulose acetate (CA) polymer fibers have been used by Chousidis et al., (2021) to
9 reinforce lime pastes [81]. Their addition resulted to a tremendous improvement of the mechanical
10 properties of the latter, thus pointing towards the use of electrospun fibrous additives in the
11 development of advanced composite lime-based building materials for traditional and
12 contemporary structures.
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15 Another type of fibrous material, such as the particles of needle-like palygorskite, has been
16 incorporated in air lime binder with metakaolin [82]. It was observed that needle-like palygorskite
17 particles are functional as reinforcing fibers. Another study investigated the influence of nano-
18 structured cellulose fibers (bio-fibrils) on the properties of natural hydraulic lime pastes [83]. A
19 slight decrease of flexural and compressive strength was registered as the percentage of bio-fibrils
20 increased. The only beneficial effect was the decrease in the total capillary absorbed water, as a
21 function of the admixture increase.
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25 Finally, reduced workability and inhomogeneity have been mentioned by authors as a drawback
26 of fiber addition in lime and cement-based mortars [84,85,86] In addition, research has shown that
27 in lime mortars hemp fibers could achieve the same strength in compression and flexure with
28 polypropylene fiber reinforced mortars [87]. Gil et al., (2016) investigated the addition of fibers
29 from End-of-Life tires. It was found that 1% addition of fibers in lime mortars slightly decreased
30 the consistency, without changing the mechanical properties [90].
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34 Table 11 reports several studies from the literature on the type of fibers used and the effects in
35 lime-based mortars.
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Table 11. Summary of studies on the use of fibers in lime-based mortars

Binder composition	Admixture	% wt.	Reference	Purpose of use
CL	Glass fibre	1.0-2.0	Iucolano et al., 2013	-Increase of flexural strength -Improvement of toughness -Effect on the consistency -Increase of fracture energy -Reduction of cracks
CL	Basalt fibre	1.0-2.0		
CL+ Cem	PET fibre	0.5-1.5 ^a	Pereira de Oliveira et al., 2011	
			Izaguirre et al., 2011 (b)	
NHL	Nano-fibrils	0.17-0.80	Rosato 2017	
CL+MK	Palygorskite	4.16-5.26	Andrejkovičová et al., 2013	
CL	End-of-Life tires	0.25-1.0	Gil et al., 2016	
CL+ Cem	Natural fibers of jute, coconut and kelp	1.5 ^a	Kesikidou and Stefanidou 2019	
NHL	Nano-structured cellulose fibers	0.17, 0.4, 0.8	Rosato et al., 2017	
CL	Electrospun CA fibers	0.59 and 1	Chousidis et al., 2021	

CL - Calcitic lime, NHL - natural hydraulic lime, Cem - cement, MK - metakaolin, % addition - refers to % wt addition to binder, a - % addition per volume in dry mortar

3.3 Pozzolans: natural / artificial

Even from the Late Bronze age period, natural or artificial pozzolans were added to traditional lime mortars to improve their mechanical performance and durability, especially the ability to harden in the presence of water. Their effectiveness is well-documented and proven by several applications [Error! Bookmark not defined.,88,89,90,91,92,93,94]. The addition of artificial and natural pozzolanic materials to lime mortars resulted in the production of composites featuring slight hydraulic activity, consisting of calcium aluminosilicate compounds, which transformed the microstructure by reducing the pore radii and increasing the apparent density. As a result, the hardening time of the new materials decreased, as part of the Ca(OH)₂ was consumed by the pozzolanic reaction, whereas the mechanical strength increased.

The effect of pozzolanic admixtures on the mechanical, thermal and hygric properties of lime mortars were investigated by Papayianni (1999) and Cerny et al., (2006). In both studies, significant properties of lime mortars, such as compression and flexural strength, heat conductivity capacity, diffusivity of moisture, water sorptivity, coefficient of water vapor diffusion, sorption isotherms, and coefficients of heat and hygric linear expansion were determined. They concluded

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4 that lime-pozzolan mortars showed improved mechanical properties and exhibited better thermal
5 and hygric properties. Therefore, they suggested the use of lime pozzolan mortars as plasters and
6 renders, instead of the traditionally used pure lime mortars [95,96].
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9 The specific surface area of the pozzolan was demonstrated to be the parameter mostly affecting
10 the water demand of the paste, amorphousness being the most relevant property that determines
11 the pozzolan reactivity to a much greater extent than any other pozzolan property [97]. Conversely,
12 the chemical composition of the pozzolan seems to influence insignificantly either its reactivity or
13 the strength of the paste. However, according to Mehta (1987), the mineralogical composition
14 plays a significant role on the reactivity of the pozzolan [98]. Therefore, more than the silica and
15 alumina content, the amorphous fractions are important when comparing pozzolans with similar
16 high surface area.
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20 Vejmelkova et al., (2012) studied the mechanical, fracture-mechanical, hygric, heat and durability
21 properties of lime-metakaolin plasters for renovating historical buildings [99]. They concluded
22 that, when compared with the reference lime plaster, there was an improvement in the mechanical
23 parameters, along with a decrease of 25% in the diffusion coefficient of water vapor. The reduced
24 liquid water transport was attributed to the presence of the metakaolin. They suggested this
25 formulation as adequate for renovating a wide range of historical buildings. Xu et al., (2016)
26 studied natural hydraulic lime-based mortars using diatomite/fly ash as mineral admixtures, with
27 aggregates of masonry waste [100]. The properties of the designed mortars were improved because
28 of the pozzolanic reaction between diatomite, fly ash and $\text{Ca}(\text{OH})_2$. Diatomite was found to have
29 a stronger and better pozzolanic effect; it also improved the compressive strength of mortar,
30 compared to fly ash.
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35 While several studies on air lime natural pozzolan, fly ash, metakaolin and fired red clay
36 investigated the mechanical properties of pozzolanic mortars, they have not included triaxial
37 testing results [99,101,102,103]. The determination of the triaxial behavior of hydraulic mortars is
38 important when considering their brittle nature elastic behavior, in contrast to lime mortars which
39 exhibit a plastic behavior [104]. The evaluation of hydraulic mortars under triaxial conditions
40 becomes more important when considering their application with respect to infill joint fragments
41 of historic structures, where shear stresses develop along the mortar-stone interface, which may
42 result into lateral confinement of the mortar layers. Kaklis et al., (2018) investigated the triaxial
43 behaviour of a pozzolanic mortar consisting of hydrated lime and metakaolin, which was used as
44 a filler between metallic connectors and marble blocks during restoration activities of ancient
45 monuments in Greece [105]. They highlighted the plastic behavior of the mortars under study,
46 enabling them to perform well in the intended conditions.
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53 3.4 Cement: white, Portland

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56 Mosquera et al., (2006) studied the effect of cement addition to hydraulic lime mortars, in partial
57 replacement to the lime binder [106]. Mercury Intrusion porosimetry results in the aforementioned
58 study showed that the diffusivity values were comparatively higher for the lime/cement mixes,
59 compared to the mixes which contained only hydraulic lime as binder.
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4 The research of Arandigoyen et al., (2007) showed that 0-40% addition of cement in lime mortars
5 resulted in a slight increase of mechanical strength, whereas the addition of a small amount of lime
6 in cement mortars led to a high decrease of the mechanical strength [107]. Papayianni (2003)
7 presented that the addition of cement influences essentially the early strength and porosity of the
8 end-products [108]. However, lime-rich mortars exhibit a more plastic behavior, being able to
9 undergo higher deformation. Similar results were also obtained by Cizer et. Al. (2008), who
10 studied mortars composed of 30%, 50% and 70% hydrated lime and lime putty as cement
11 replacement [109]. As the percentage of lime increases, the total porosity also does so, whereas
12 the compressive strength decreases. However, the addition of lime resulted in more plastic
13 behavior.
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18 Silva et al., (2015) investigated the addition of cement in lime mortars used in restoration projects,
19 as substitution to lime-natural hydraulic lime binder [110]. The water transport properties, porosity
20 and mechanical strength of the mortars were studied as these properties influence compatibility.
21 Cement-lime mortars proved to be less porous and therefore less permeable, compared to lime-
22 hydraulic lime mortars. Additionally, it was also mentioned that the presence of soluble salts in
23 cement should be taken into account.
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28 4 Evaluation tests/ Analyses 29

30 The most important properties and the analysis that should be performed to study the effect of
31 additions and admixtures in the fresh and hardened state of mortars are reported in Tables 11-14.
32 The evaluation of adds/adms in lime mortars requires the use of specific tests and techniques that
33 are differentiated concerning the fresh/hardened state of mortars. The tests and the relevant
34 standards that are proposed for the majority of the properties evidence the need for further
35 standardization that could elucidate both the optimum amount of additive/addition and the method
36 of assessment. This review has as objective to summarize the state of the art and portray future
37 developments in the use and assessment of adds/adms in lime mortars.
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41 The influence of adds/adms on the basic properties of fresh and hardened state mortars is illustrated
42 in Figure 1. Apart from the individual contribution of each agent to the improvement of each
43 property, it becomes evident that combining additives and/or admixtures, the beneficial effect is
44 enhanced in both the fresh and hardened state. Supporting evidence is the combined effect of
45 plasticizers, nano-particles, polymers and carbonation accelerators in the increase of compressive
46 strength and decrease of porosity, as illustrated in Figure 1. Furthermore, the all the properties
47 shown in Figure 1 exemplify the influence of additives/admixture in diverse gradient to the fresh
48 and hardened state properties of mortars. Nanoparticles, carbonation accelerators and cement, for
49 example, remarkably reduce the setting time. On the other hand, nanoparticles have a retarding
50 effect on the viscosity and workability.
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Table 12. Fresh state properties and relative analysis of lime mortars with additives

Property studied	Workability	Rheological behavior	Water retention capacity	Air content of fresh mixture	Reactivity	Saturation moisture content	Setting time	Carbonation-Hydration reaction
Analysis/ test	Flow table test	Rheometer Viscotester	Water retention measurement	Pressure method	-pH metering - Conductivity	Gravimetric method	Vicat test	-DTA/DSC - FTIR - XRD - BET - Particle size distribution - Zeta Potential Analyzer
Standard	EN 1015-3 (1999)		UNE 83-816-93 (1993)		RILEM CPC-18 (1980)		EN 196-3 (2016)	
Additives	Air entraining	☑	☑		☑			☑
	Plasticizers-Superplasticizers	☑	☑		☑		☑	☑
	Water-repellents	☑	☑	☑	☑	☑	☑	☑
	Viscosity modifiers	☑	☑	☑			☑	☑
	Carbonation accelerators					☑		☑
	*Self-healing							☑
	Crystallization modifiers	☑						
	Nanoparticles	☑	☑					☑
Polymers	☑				☑		☑	

Table 13. Hardened state properties and relative analysis of lime mortars with additives

Property studied	Morphology-structure				Hygric-physical properties					Mechanical properties	
	Morphology Homogeneity Microstructure	Shrinkage	Density	Porosity	Water absorption	Hydrophobicity	Water vapour permeability	Aesthetic measurements	Thermal properties	Mechanical strength	Pencil hardness
Analysis/ test	OM, SEM, BET	Shrinkage test	Density measurement	MIP RILEM CPC 11.3	Capillarity test	Contact angle measurement	Water vapour permeability test	UV-VIS, chromatometer	-Thermal conductivity, -Specific heat capacity	-Compression test - Flexural test	Hardness measurement
Standard		ASTM C596 (2001)	EN 1015-10 (1999)	EN 1936 (2006), EN 623-2 (1993)	EN 1015-18 (2002), EN 15801 (2010)	EN 15802 (2010)	DIN 52615 1987, EN 1015-19 (1998)			EN 12390-3 (2019), EN 1015-11 (2019)	ASTM D 3363 (2020)
Air entraining	☑			☑	☑		☑			☑	
Plasticizers-Superplasticizers	☑	☑		☑	☑		☑			☑	
Water-repellents		☑		☑	☑		☑	☑	☑	☑	☑
Viscosity modifiers	☑										
Carbonation accelerators	☑			☑	☑					☑	☑
*Self-healing	☑									☑	
Crystallization modifiers	☑		☑	☑	☑					☑	
Nanoparticles	☑	☑		☑		☑		☑		☑	
Polymers	☑				☑			☑		☑	

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Table 14. Fresh state properties and relative analysis of lime mortars with admixtures

Property studied		Workability	Rheological behavior	Water retention capacity	Saturation moisture content	Setting time	Carbonation-Hydration reaction
Analysis/ test		Flow table test	Rheometer	Water retention measurements	Gravimetric method	Vicat test	DTA/DSC, FTIR, XRD, BET, Particle size distribution, Zeta Potential Analyzer
Standard		EN 1015-3 (1999)		UNE 83-816-93 (1993)		EN 196-3 (2016)	
Admixtures	PCM	☑	☑				
	Fibers	☑					
	Pozzolans	☑		☑	☑	☑	☑
	Cement	☑					

Table 15. Hardened state properties and relative analysis of lime mortars with admixtures

Property studied		Morphology-structure			Hygric-physical properties			Mechanical properties		
		Morphology Homogeneity Micro-structure	Density	Porosity	Water absorption	Water vapour permeability	Thermal conductivity	Specific heat capacity	Mechanical strength	Pencil hardness
Analysis/ test		OM SEM BET	Density measurement	MIP RILEM CPC 11.3	Capillarity test	Water vapour permeability test	Thermal conductivity measurement	Specific heat capacity measurement	Compression test Flexural test	Hardness measurement
Standard				EN 1936 (2006), EN 623-2 (1993)	EN 1015-18 (2002), EN 15801 (2010)	DIN 52615 (1987), EN 1015-19 (1998)			EN 12390-3 (2019), EN 1015-11 (2019)	ASTM D 3363 2020
Admixtures	PCM	☑							☑	
	Fibers	☑	☑	☑	☑				☑	☑
	Pozzolans	☑		☑	☑	☑	☑	☑	☑	
	Cement	☑	☑	☑		☑			☑	☑

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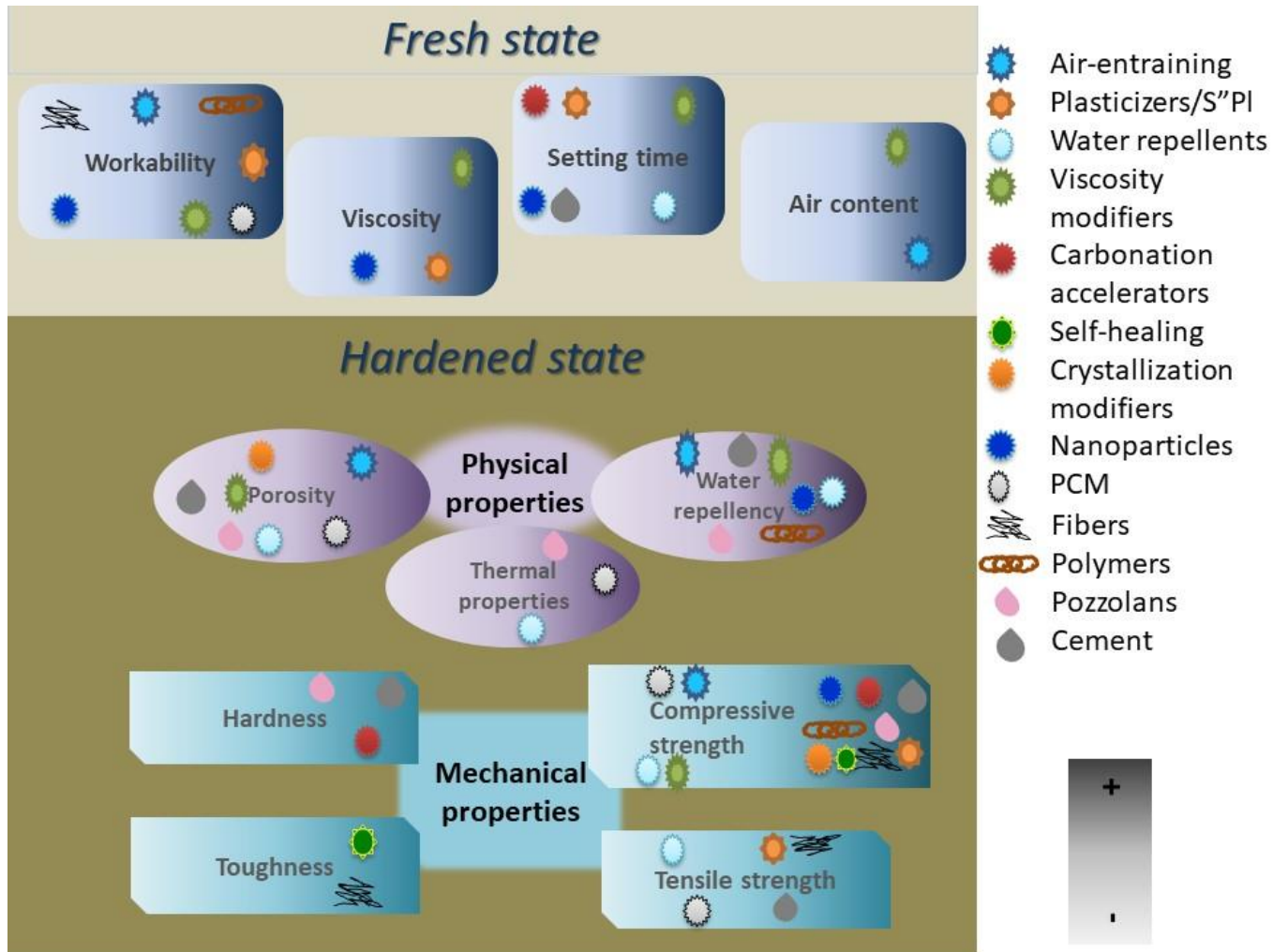


Figure 1. Effect of additives/admixtures on various properties of lime-based mortars

5 Conclusions

The preservation and restoration of historical structures is mostly based on the use of lime-based mortars. Additives and admixtures have been found in lime mortars of different historical periods, originating mostly from locally available materials. They occur in all types of lime-based mortars, while their proportions by weight and volume are differentiated according to the type of mortar and the building technology of each historical period. They were deliberately added in lime mortars in order to improve either the fresh or the hardened state properties of the mixtures. This knowledge was considered as the “secret” of ancient builders, which allowed them to construct different types of structures and buildings, using water-proofed mortars for aqueducts and baths, and occasionally lime-based “concrete”.

Nowadays, additives and admixtures are available in a great variety, due to the evolvement of the chemical industry, and can thus be used very effectively in contemporary lime mortars. They are being developed into much more user-friendly forms, based on modern technology, namely waste recycling, and are no longer making use of products that can be exploited for feeding humans and animals. These materials can promote freeze-thaw resistance, repel water absorption, and allow mortars to be cured more efficiently, make mortars much more plastic and workable, with increased mechanical properties. They can also reduce the overall water content in a mortar, thus significantly reducing problems of drying shrinkage. Therefore, additives and admixtures can be important for both the application (fresh state properties) and for the long-term performance of mortars. Based on their action mechanism, they offer significant benefits to lime-based mortars, giving technicians the ability to apply them in broader application fields.

To examine the efficiency of additives/admixtures in a lime mixture, a protocol should contain tests of the fresh and harden state properties, as well as long-term tests when durability is to be examined. The tests are necessary in order to decide upon the correct dosages or even to assist in the selection between different products. The lack of standards for some important properties that are determined by the additive/admixture dosage and efficiency opens new research possibilities in this field.

The addition of various agents in lime mortars is essential to gain improved properties, as well durability, compared to pure lime mortars. During discussions for this paper, a topic has arisen concerning the terminology used in the literature and the definitions of EN 16572. The terms additives and admixtures refer to the additions to the lime and in the lime mortar mixtures, respectively, with the aim of improving workability, physico-mechanical properties and durability. According to definitions given in EN 16572, additive (EN) or addition (ASTM) is a constituent usually added in small quantity to the binder to modify its manufacture or properties (for example accelerators, plasticizers and air-entraining agents), whereas admixture is a substance other than the binder, aggregate or water, added in quantities of at least 1 % w/w to the mix to alter its properties. Various agents, classified according to their action or shape or nature, were presented in this paper, along with the most important properties to be analyzed. Some additives, such as superplasticizers, air-entraining agents, have been used successfully in repair mortars for more than 20 years. Most of the additives presented in this work have been under investigation mainly

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in the last 20 years, whereas other additives such as vernacular natural polymers, and admixtures such as fibers, pozzolans and cement, are well established in lime-mortar technology. Regarding the assessment of air-entraining agents, plasticizers, superplasticizers, water repellents, viscosity modifiers, crystallization modifiers, nanoparticles of SiO₂ and TiO₂, research advances in the literature, based on evaluation criteria and durability studies, suggest their use in lime mortars, as they enhance the physico-mechanical properties of the end-product. Besides, more innovative admixtures, such as PCMs, along with self-sensing and self-healing stimulators, need to be further investigated regarding certain aspects of their performance evaluation and durability.

This review opens new thoughts and insights concerning further elaboration in the CEN adopted terminology regarding additives/admixtures. Even though the definitions widely used in the cement industry consider the air-entraining agents, the superplasticizers and the viscosity modifiers as admixtures, nevertheless, the EN standardization introduced the term additives for those agents. Therefore, the adoption of this term is imperative in the cultural heritage field. Given that lime-based mortars can include hydraulic mortars, namely air lime-pozzolan mortars, when limes with hydraulic properties are used and when cement is added to lime mortars, a similar terminology to the cement/concrete mortars would better indicate the improvement achieved after the use of additive/admixture and allow comparisons between different types of mortars.

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Ethics declarations

Conflict of interest

The authors declare no competing interest.