

Review

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A review of mechanical properties and carbonation behavior evolution of lime mortar for architectural heritages restoration

Zhenmeng Chen¹, Hui Liu² , Lingjie Xu¹, Wei Ge³

¹School of Environmental Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, China.

²School of Urban Construction Changzhou University, Changzhou 213164, Jiangsu, China.

³Department of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, Anhui, China.

Correspondence to: Dr. Hui Liu, School of Urban Construction, Changzhou University, No.21, Gehu Middle Road, Wujin District, Changzhou 213164, Jiangsu, China. E-mail: liuhui@cczu.edu.cn

How to cite this article: Chen Z, Liu H, Xu L, Ge W. A review of mechanical properties and carbonation behavior evolution of lime mortar for architectural heritages restoration. *Miner Miner Mater* 2024;3:3. <https://dx.doi.org/10.20517/mmm.2023.26>

Received: 29 Aug 2023 **First Decision:** 18 Dec 2023 **Revised:** 15 Jan 2024 **Accepted:** 26 Jan 2024 **Published:** 31 Jan 2024

Academic Editor: Andrea R Gerson **Copy Editor:** Dong-Li Li **Production Editor:** Dong-Li Li

Abstract

Using lime mortar to connect, protect and decorate buildings was a very common technique in ancient times. Understanding the mechanical properties and carbonation mechanism of lime mortar is the basis for successful restoration and protection of architectural heritage. The compatibility and durability of lime mortar and architectural heritage promote the study of related mechanisms, so that it can adapt to the current reality. In this paper, the factors affecting the mechanical properties of lime mortar are summarized, and the carbonization principle of lime mortar is analyzed. The effects of water-binder ratio, aggregate mineralogy and particle size, inorganic additives and organic additives on the mechanical properties of lime mortar were elaborated in detail, especially the action behavior of organic additives in the carbonation process of lime mortar. Suggestions for enhancing the mechanical properties of lime mortar are put forward, which provides a theoretical basis for improving the compatibility and durability of materials in the restoration of ancient buildings.

Keywords: Lime mortar, mechanical property, inorganic and organic additives, carbonation mechanism, restoration of architectural heritages



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INTRODUCTION

As one of the world's oldest building materials, lime mortar is used more widely in today's construction projects, and it is used in many of the most iconic buildings. The Egyptians had proficiently used lime plaster to build one of the limestone wonders of the world - Cheops pyramid (more than 100 m) in circa 4000 B.C. - circa 3000 B.C.^[1-3]. We can find so many classic Roman structures and monuments that have survived to the present day, such as the Roman Colosseum, Maison Carrée, baths of Diocletian, Roman Theatre of Merida, Roman Pantheon, etc.^[4]. The Chinese used lime mortar to cement the stones together to build the 2,500 km Great Wall which has lasted for hundreds of years and is still well preserved^[5]. They are a crucial part of all old buildings and play different roles: Using for connection, protection, and decorative purposes^[6].

Lime, as a calcium-based inorganic material, had been widely used in ancient times. As early as circa 7500 B.C., a plaster made from lime and unheated crushed limestone had been found in the area that is now Jordan^[7]. The use of lime was spread and applied on a small scale by the ancient Greeks (2800 B.C. - 1000 A.D.). They let people know that lime mortar not only has good durability but also can improve the overall aesthetics of the building^[8]. The Romans were good at using the beneficial properties of lime and were familiar with the construction processes. They developed a new concrete called Roman mortar by mixing lime, sand, and pozzolanic materials used in the buildings^[9,10]. Into the Middle Ages (circa 1300 A.D. - 1800 A.D.), lime also played an important role in the building material for homes.

Lime was also used very early in China, dating back to the Zhou Dynasty (7th century B.C.)^[11]. The lime was calcined using clamshells, and attained lime had good humidity resistance and gelling properties. Up to the Northern and Southern Dynasties (420-589 A.D.), a new kind of lime product, Sanhetu, turned up, which was composed of three main materials (lime, sand and clay) and a small number of organic additives^[12-15]. The Sanhetu, called Chinese Roman mortar, had not only high strength but also good water proofing properties after hardening. People in the Qing dynasty used it to build dams^[14]. Different from foreign countries, Chinese lime mortar had another characteristic, which was a small number of organic additives [sticky rice (SR), egg white, plant extracts, or animal blood] in lime mortar^[11]. The organic-lime mortar had higher strength, higher water resistance and long-term durability, which had been widely used as binding material in ancient Chinese structures. The researchers still found that the preservation of the Great Wall is mainly due to the addition of SR to its lime mortar^[14,16]. Thus, it can be seen that lime has proven performance, and the traditionally organic lime mortar has played a significant role in the Chinese construction buildings. Nowadays, traditional lime mortar attracts new attention from architects and scholars due to its great compatibility for restoring ancient buildings. Unfortunately, the excellent Chinese organic Sanhetu (COS), which had been used in China for a long time, due to the emergence of Ordinary Portland Cement (OPC) over 170 years ago, disappeared almost overnight^[17].

After the emergence of cement, due to its faster setting time and higher compressive strength^[18], cement mortar and concrete began to be widely used. However, researchers have found that soluble salts in OPC leach over time, quickly destroying the surrounding material. In the past few decades, the harmful effects of OPC on various restorations and modern buildings have been confirmed^[19]. It is incompatible with many natural stones, and most of the ancient buildings use natural stone; lime mortar is the most suitable for preserving old buildings, whether due to ethical arguments or technical reasons^[20,21]. Lime is obtained by calcination of limestone and chalk, mainly including quicklime CaO, hard burnt lime CaO, slaked/hydrated lime Ca(OH)₂ and dolomite lime^[17]. Currently, lime-based binders can be divided into two categories: air lime and hydraulic lime. Air lime generally refers to hydrated lime, which is mainly composed of Ca(OH)₂ and is an air hardened binder commonly used as lime mortar^[22]. Hydraulic lime, as a hydraulic binder with

both hydraulic and air-hardening properties, can be divided into natural hydraulic lime and artificial hydraulic lime. The carbonation reaction of $\text{Ca}(\text{OH})_2$ in lime mortar [reacting with CO_2 in the air to form calcium carbonate (CaCO_3)] ensures its strength^[23-25].

In recent years, most studies have focused on the mechanical properties of lime mortar. However, there is a lack of rigorous research on the durability of lime-based mortar and its compatibility with architectural heritage. The purpose of this study is to develop repair mortar by determining the parameters of lime mortar that are most suitable for protecting and repairing ancient buildings. For this reason, a large amount of literature was collected on Scopus, Web of Science, and Science Direct with water-binder ratio, additives, mechanical properties, carbonization, durability and lime mortar as the keywords. The effects of water-binder ratio, aggregate properties and particle size, and additives on the mechanical properties of lime mortar were evaluated. The carbonation mechanism of lime mortar is analyzed to provide a theoretical basis for improving the compatibility and durability of materials in the restoration of ancient buildings.

IMPACT FACTORS ON MECHANICAL PROPERTIES

Water-to-binder ratio

For hydraulic lime mortars, a high water-binder ratio increases their porosity and weakens the overall structure, thus reducing their mechanical properties^[26,27]. On the contrary, unlike cementitious or hydraulic lime mortar, the strength of air-lime mortar is not reduced with the increasing of water/air lime ratio^[28]. Generally, the water content in air-lime mortar is always controlled to keep equal consistency (15-17 cm) by flow table test^[10]; namely, water content depends on the aggregate type and grain size. Compared with the water cement ratio, aggregate type and particle size have a greater impact on the performance of air lime mortar^[29].

Mineralogy and granulometry of aggregates

The results of Kalagri's research showed that lime mortar containing medium or more coarse aggregates has better mechanical properties (compressive strength up to 14.1 MPa and flexural strength up to 3.4 MPa), while the compressive strength and flexural strength of lime mortar containing fine aggregates with minimum bulk density are only 8.1 and 2.5 MPa. The bending strength values at all curing times show this trend. From the comparison of strength development, it could be found that the mechanical properties of air lime mortars are closely related to the mineralogy and granulometry of aggregates^[30]. In order to restore and conserve the ancient buildings, different types of aggregates used in lime mortar were investigated. As is well known, the most commonly used aggregates are siliceous aggregates (SiO_2) and calcareous aggregates (calcite- CaCO_3). Siliceous aggregates mainly include quartz sand (quarry sand or river or sea sand), crushed stones and ceramics, pebbles, and volcanic materials^[31-33]. In contrast, calcareous aggregates are mainly limestones. Different types of aggregates can result in variation of mechanical behaviors of lime mortars. The results show that calcareous aggregates can produce higher compressive strength than siliceous ones because calcite shows better compatibility between aggregate and binder and provides nucleating sites for lime carbonation. Although not as good as calcareous aggregates, the use of volcanic materials can also achieve the reinforcement of lime mortar's mechanical properties to some extent compared to other siliceous aggregates, making the mortar have better freeze-thaw resistance. The presence of reactive silica in volcanic materials can react with lime to form calcium silicate hydrate (CSH) which improves mortar strength^[34]. On the contrary, even though the crushed ceramics also have reactive silica, the content of reactive silica is lower. The crushed ceramics, as aggregates, are not suitable to prepare lime mortar, but they are better to enhance the waterproof aspects of mortars^[35]. In consequence, limestones and volcanic materials as aggregates are more suitable to prepare lime mortar than other siliceous aggregates.

In addition, the grain size distribution of aggregates is a key factor in the preparation process of lime mortar. The influence of aggregate type and grain size on its (lime mortar) mechanical properties would become prominent when maintaining a constant water-binder ratio. Compared with mortar with a particle size of 4 mm, mortar with a particle size of 2 mm has a lower fresh consistency, smaller pore size in the hardened state, and better mechanical properties due to its small grain particle size and higher demand for water^[26]. Lower grain size, especially less than 4 mm, is more beneficial for improving the compressive strength because large grain size can form high porosity leading to lower compressive strength^[36,37]. Hence, in this respect, larger pebbles and crushed stones are similarly not suitable to prepare lime mortar with high compressive strength. However, the presence of coarse aggregates > 8 mm acting as crack arresters is beneficial to long-term strength^[38]. This is the reason why pebbles have been used for the construction of tall masonry structures in the old days. So, a small number of coarse aggregates are permitted to exist.

In some papers, the shape of aggregates also reveals some effect on the mechanical properties of lime mortars^[34]. Due to the rough multi-angle texture on the surface of clay brick waste powder (CBP) and ceramic waste aggregate (CWA), the flow and diffusion of mortar decrease sharply. The compressive strength of mortar decreased slightly in the early stage but increased significantly in the long term^[37]. This is because CBP has replaced OPC, and its contribution to early strength is not as significant as OPC. CBP and CWA improve the later compressive strength of mortar together thanks to the special surface of CWA, which improves the grip between it and the paste, and the volcanic ash activity of CBP, which postpones the carbonation process of lime. The compressive strength can be improved not by rounded aggregates but by angular ones.

Binder-to-aggregate ratio

Not only water-to-binder (W/B) ratios but also binder-to-aggregate (B/A) ratios influence the mechanical properties of lime mortars. Many scholars have studied this factor affecting the mechanical behaviors of lime mortars^[39]. However, there are two different viewpoints: (i) a 1:3 B/A ratio by volume is recommended to prepare lime mortar using commercial lime powder^[40]; (ii) Compressive and flexural strength of lime mortar increases with the increasing B/A ratio within limits. Generally, the performance of lime mortar at a 1:1 ratio of B/A by volume is better than a 1:3 ratio^[41]. This is mainly due to the fact that the carbonation of mortar with a low binder ratio (1:3) appears to develop more rapidly and inhibits the development of volcanic ash reactions in the short term, slowing down their strength development. The higher the binder ratio (1:1) is, the slower the carbonization rate of the mortar is, and some of the lime can still freely react with volcanic ash within a certain period of time, which has a role in improving its strength; thus, the 1:1 B/A specimens tested after one curing year systematically show the highest strength. In addition, Stefanidou *et al.* found that compared to low B/A ratios (1:4, 1:6), high B/A ratios (1:1.5, 1:2.5, and 1:3) resulted in higher strength values for lime mortars, and in this case, highest compressive strength of lime mortar was at 1:2.5 B/A ratio^[38].

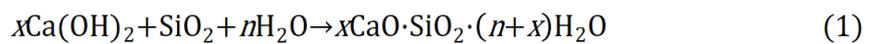
Although there are some disputes about the B/A ratio in lime mortar, the ratio is generally chosen from 1:1 to 1:3 by volume, in particular 1:3. To sum up, due to different B/A ratios, the reaction degree of different ages is different, and the influence is not very obvious at same curing time. In contrast, the addition of additives affects the mechanical properties of lime mortars strongly.

Additives

In addition to the aforementioned impact factors, there are inorganic additives and organic additives as key factors that influence the mechanical properties of lime mortars, which are described in detail.

Inorganic additives

In ancient times, pozzolanic materials, as important inorganic additives, had been added to lime and sand to prepare the concrete^[42]. The initial pozzolanic materials are volcanic dusts that have a high content of active alumina (Al₂O₃) and silica (SiO₂). Active alumina and silica can react with lime to form CSH gel (Equation 1) and calcium aluminate hydrate (CAH) (Equation 2) or calcium aluminosilicate hydrates (CASH) which are primary sources for compressive strength and durability of mortars. In the area without volcanic dusts, calcined clay [metakaolin (MK)], brick dust, ceramic powder or ceramic fragment^[43,44] replaces the volcanic dusts as additives due to the fact that they have the same components. Nowadays, fly ash or silica fume (SF), also as pozzolanic materials, is added to lime mortar, which can not only reduce costs but also dispose of waste^[45].



MK produced by heating kaolinite or kaolin at temperatures of from 600 to 800 °C has been an excellent pozzolan^[46,47]. Utilizing metakaolin or other pozzolanic materials to replace lime partially is a better way to optimize the mechanical properties and durability of lime mortar. Pozzolanic materials exhibit high lime reactivity of pozzolans due to their large proportions of silica and alumina, small grain size and relatively high specific surface, especially the metakaolin^[48]. The superior properties are shown in lime mortar prepared with metakaolin, including higher compressive strength, higher flexural strength, lower permeability, higher durability, higher adhesion of matrix to aggregates, and so on^[49,50]. The compressive strength of lime-metakaolin (LM) mortars can increase by at least 400% than lime mortar without active metakaolin, and the flexural strength also increases by 50%^[34]. With the increase of the MK/lime ratio, the pore size distributions move to narrower pores (< 0.1 μm)^[46], which reduces the porosity of the material and leads to an increase in the compressive strength of LM mortar. The porosity of LM mortar is 10% lower than the reference lime mortar without MK^[51]. These improved properties are attributed to the pozzolanic reaction. Cabrera and Frias have reported the mechanism of hydration of the metakaolin-lime-water system^[48,52]. At the initial stage of reaction (which lasts about 50 h), the consumption rate of lime was very rapid. After hydration of MK/lime (weight ratio 1:1) for two days, CSH gel first appeared, followed by stratlingite (C₂ASH₈) and C₄AH₁₃. It is known that the CSH, C₂ASH₈ and C₄AH₁₃ are the main phases formed during the reaction between MK and lime at ambient temperature^[53-55]. Apart from this, higher strength in LM mortar also depends on the greater C₂ASH₈ and C₄AH₁₃ phase content^[56]. However, the C₄AH₁₃ phase has very low crystallinity with respect to the C₂ASH₈ phase^[53]. As a result, the sequence of the source of LM mortar strength is CSH, followed by C₂ASH₈ and then C₄AH₁₃.

However, the environmental conditions can affect the hydrated phases. The curing temperature showed a principal influence on the formation of crystalline products of C₂ASH₈, C₄AH₁₃, and hydrogarnet (C₃AH₆) in the pozzolanic reaction^[57]. According to^[58], the sequence of appearance of the hydrated phases was CSH, C₂ASH₈ and C₄AH₁₃ at 20 °C, while at 60 °C, the sequence was CSH, C₂ASH₈, C₄AH₁₃ and C₃ASH₆. High temperature (60 °C) can cause the transformation of metastable phases (C₂ASH₈ and C₄AH₁₃) into C₃ASH₆, which becomes the predominant phase^[59]. Besides, the MK/lime ratio also influences the crystalline products formed during the reaction process between MK and lime^[47]. At 20 °C, a high MK/lime ratio favors the formation of the C₂ASH₈^[53]. Namely, a high MK/lime ratio is beneficial to the compressive strength, but a lower MK/lime ratio can raise the average flexural strength by about 5%^[60]. Hence, it is better that the LM mortars are prepared by the MK/lime ratio of 1:1 by weight at 20 °C.

In addition to the pozzolanic reaction, there is another competing reaction existing in the LM mortar, which is $\text{Ca}(\text{OH})_2$ absorbing atmospheric CO_2 to give rise to carbonation reaction^[60]. The dominant reaction in LM mortars decides the composition and properties of mortars, such as compressive strength, flexural strength, porosity, *etc.* Pavlík and Užáková reported that the LM mortars curing at RH 65% with air led to lower strength than that at RH 100% without CO_2 because the pozzolanic reaction was limited due to lack of water^[49]. Because carbonation reaction is a slow and long-term process and the formation of CSH gel is in two days, the early strength of LM mortar is mainly attributed to the pozzolanic reaction and the later strength is from both pozzolanic reaction and carbonation reaction. To sum up, metakaolin, as an inorganic additive, can optimize lime mortars' properties, primarily due to metakaolin and lime's pozzolanic reaction.

It has been proved that the performance of lime mortar can be improved by pozzolanic reaction between pozzolanic material (such as fly ash and SF) and lime. When increased from 20% to 25%, the compressive strength of lime fly ash mortar of 0.738 MPa increased by 2.320 MPa. At the same time, the setting time is shortened due to more fly ash instead of lime. The initial setting time of 25% lime was shortened by 70 min, and the final setting time was shortened by 180 min^[61]. The results show that the repair mortar with better strength can be obtained by using 25% fly ash instead of lime mortar. The study of Xu *et al.* found that compared with the control mortar, the apparent density, water absorption and shrinkage of the modified mortar were reduced, and the mechanical properties and durability were improved. In general, SF is more effective than isobutyltriethoxysilane (SO) in improving the main physical and mechanical properties of mortar. The reason is that SF reacts with $\text{Ca}(\text{OH})_2$ to generate more hydrate products to make the pore structure finer. The modified mortar's compressive strength is the highest. In terms of flexural strength and bond strength of mortar, the combined use of SF and SO has the greatest effect because SO plays a bridge coupling role between the components of mortar. The presence of SO greatly improves the durability of mortar, which is related to its water repellency. The durability of mortar prepared with SF and SO is the highest^[62]. Compared with mechanical properties, the restoration of architectural heritage pays more attention to durability, so it is particularly critical to select appropriate inorganic additives.

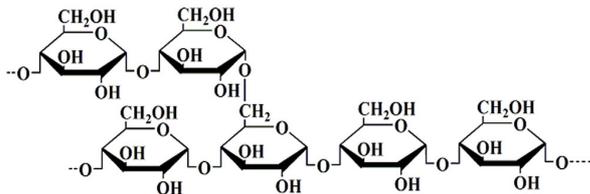
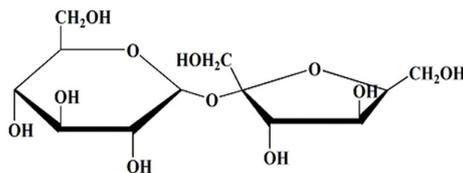
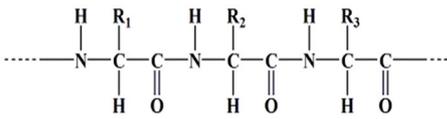
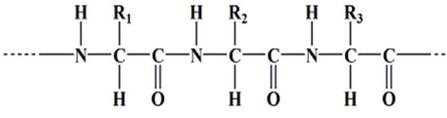
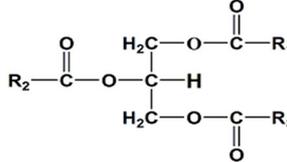
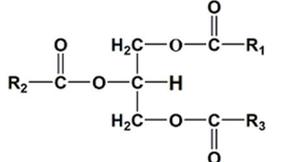
Organic additives

As we all know, the lime mortars have been prepared using natural organic additives to improve their properties in ancient times. It has been found that the natural organic additives in traditional lime mortars were polysaccharides and other saccharides (SR, brown sugar, and plant extracts), proteins (egg white and animal blood), and greases (tung oil and plant oil), whose major components of natural organic additives are shown in Table 1^[14,63]. All of the natural organic additives have the specific structure and functional groups. Some scholars^[12,64,65] have characterized and imitated the traditional lime mortars, discovering that the natural organic matters in lime mortars played an important role in improving the properties of mortars. Lime mortars with natural organic matters could form denser and more compact microstructure, which resulted in higher compressive strength and higher durability.

It can be found that most of natural organic additives used in Chinese traditional lime mortar are macromolecule compounds [Table 1], for example, SR. SR is the most common organic additive used in Chinese traditional lime mortars, whose major composition is amylopectin. As shown in Table 1, amylopectin is a highly branched polymer consisting of α -1, 4 linear and α -1, 6 branched glycosidic linkages^[66]. With the understanding of traditional lime mortars and properties of SR, the mechanism of organic additives influences the lime mortars can be hypothesized as follows.

The high pH of lime mortars promotes the amylopectin hydroxyl group ionization^[67,68]. This creates opportunities for the interaction between the Ca^{2+} or CaOH^+ with the starch, thus forming a complex with

Table 1. The major components and molecular structures of natural organic additives

NOA	Property	Major component	Molecular structure
Sticky rice	Polysaccharide	Amylopectin	
Brown sugar	Disaccharide	Sucrose	
Egg white	Protein	Polypeptide	
Animal blood	Protein	Polypeptide	
	Grease	Glyceride	
Tung oil	Grease	Triglyceride of eleostearic acid	

Ca^{2+} . As a result, a crosslink between polymer chains can be formed by Ca^{2+} on the surface of lime [Figure 1]. Consequently, Ca^{2+} can form a crosslink between the polymer chain and the lime particles. The amylopectin molecule has a large molecular weight and a long polymer chain, which may exceed the minimum distance of close approach between two particles. In this way, amylopectin can provide multiple sites to connect the lime particles together by Ca^{2+} , leading to the compact and link structure, high compressive strength, and outstanding durability of lime mortars.

Starch has been used to develop environmentally friendly material to replace conventional petroleum-based plastics^[69-71]. However, it suffers from poor mechanical properties and high moisture sensitivity. A promising method to improve these weaknesses is to disperse nanosized fillers into the starch matrix to form nano-biocomposite^[72]. Starch remains insoluble and keeps its granule structure. Thus, it must be dissolved by melting or heating before it can be used as a composite matrix. The CSH produced by the pozzolanic reaction between lime and metakaolin possesses a similar layered silicate structure. It mainly consists of two CH plates with a basal spacing around 1 nm^[73,74]. Two possible starch-CSH composites can be formed^[75,76], as shown in Figure 2: (A) Micro composite (the biopolymer does not penetrate into the

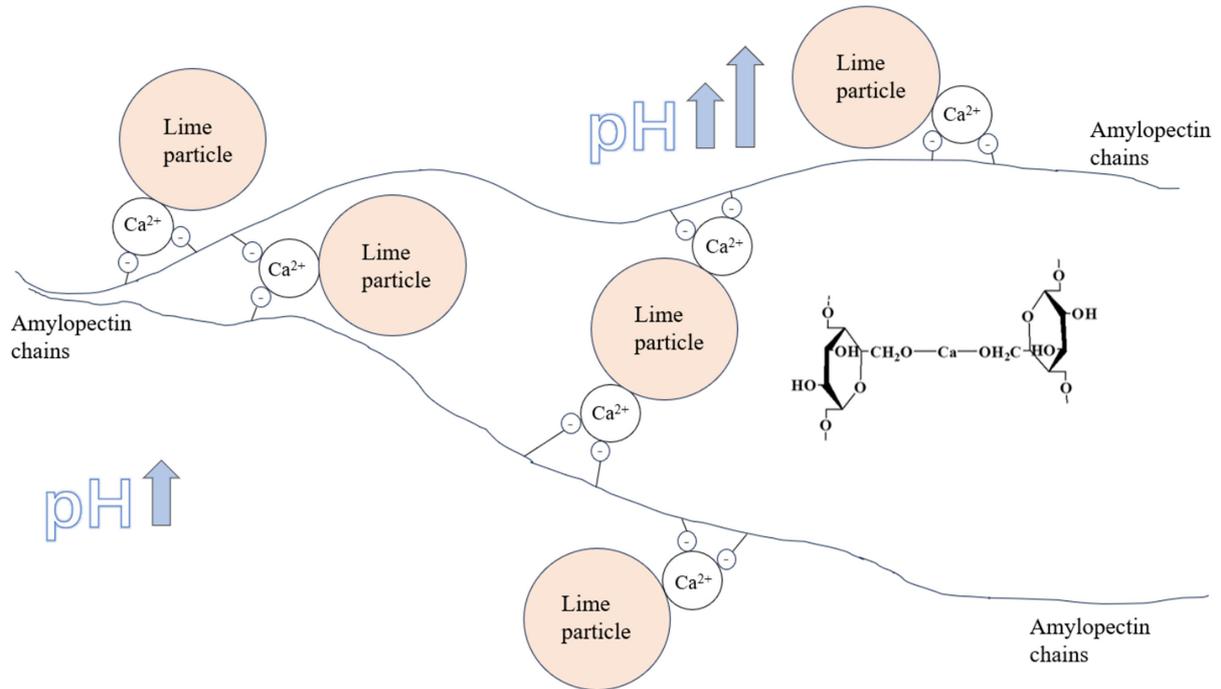


Figure 1. Bridging effect of Ca^{2+} between amylopectin and lime particles.

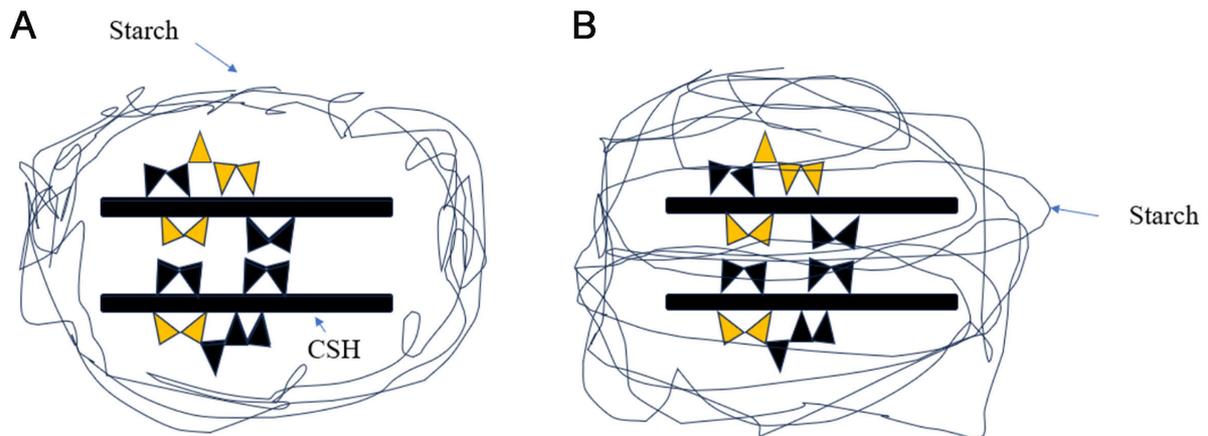


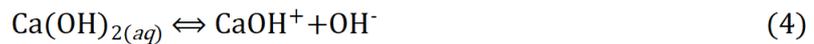
Figure 2. Sketch of two possible biocomposites with CSH: (A) Microcomposite; (B) Intercalated nanocomposite. CSH: Calcium silicate hydrate.

interlayer of CSH); (B) Intercalated nanocomposite (the polymer penetrates into the inter-lamellar space). The organic polymer chains devote this material much tougher than the purely inorganic material. Besides, macromolecule organics can play the main increasing thick function in preparing lime mortars. Therefore, organic/inorganic lime mortars can exhibit outstanding properties. In addition, the organic admixture can influence the carbonation reaction of lime mortar, which will be described in detail in Section “Organic additives”.

Many natural organic additives come from the foods, animals or plants, so it is not good to injure the animals or plants or to compete with human beings for the foods. Another reason is that there are many cheap and different kinds of artificial macromolecule compounds in the markets with the rapid development of economy. Hence, it is a better way to find appropriate artificial macromolecule compounds to replace natural organics in the lime mortars.

CARBONATION IN LME MORTAR

It is well known that the strength of lime mortar mainly comes from the carbonation reaction of lime. In the carbonation process, Ca(OH)_2 reacts with CO_2 in the air to form CaCO_3 ^[24,25]. The content of CO_2 in the atmosphere is about 400 ppm. According to the chemical equilibrium diagram of CO_3^{2-} , when pH is more than 12, the primary ions in the equilibrium system are CO_3^{2-} and a small amount of HCO_3^- [Figure 3]. Lime mortar is a highly alkaline environment, in which CO_3^{2-} ions are consumed to form CaCO_3 crystals. At the same time, the equilibrium of HCO_3^- and CO_3^{2-} moves to the right, leading to the formation of lots of CO_3^{2-} ions used for carbonation of Ca(OH)_2 . Meanwhile, the equilibrium equations of Ca(OH)_2 are given in Equations 3-5:



Even though there are CaOH^+ ions in the system, the equilibrium moves to the right with the consuming of Ca^{2+} ions (Equation 5), resulting in continuous formation of Ca^{2+} ions. Therefore, in the lime mortar, carbonation reaction takes place certainly with the extending of time because of the existence of CO_2 and Ca(OH)_2 . The carbonation reaction in lime mortar occurs continuously for a long time, and many factors have the ability to influence the carbonation reaction.

In general, the order of carbonation process of calcium hydroxide was: hydrated amorphous calcium carbonate (ACC), anhydrous ACC, crystal stone, aragonite, and finally stable calcite^[77]. Calcite was the most stable CaCO_3 crystal form in thermodynamics^[78,79], and it was also the most common CaCO_3 crystal form in ancient buildings built with lime mortar^[14,80]. However, these morphologies and polymorphs were not constant, which can be varied depending on the prime factors (content of reactants, temperature, mixing and stirring rate) and the secondary factors (pH, type, and content of additives)^[81-83]. Organic additives had significant effects on the morphology and size of CaCO_3 crystals^[16]. For example, the addition of SR and anionic polyacrylamide helps CaCO_3 crystals to show as calcite. These changes in crystal morphology and morphology can affect the mechanical properties of lime mortar.

Climatic conditions

As a matter of fact, the climatic conditions [temperature, relative humidity (RH), and the content of CO_2] are determinants that affect the carbonation process in the lime mortars. How the ambient RH and temperature (RH of 30%, 60%, 100% and temperature at 10, 20, 40 °C) influence the carbonation in lime mortars has been studied^[84,85]. The samples are analyzed at different temperatures and RH after drying at the end of a 10-day period; CO_2 level corresponds to air, which has low level of pollution (0.03% of CO_2). According to the results of Dheilily *et al.*, higher RH is beneficial to carbonation of lime, especially the 60% RH^[84]. It cannot be ignored that excessive RH (100%) will delay its carbonation process, and due to excessive humidity, CO_2 in the air cannot enter the pores of the mortar to complete the carbonation process.

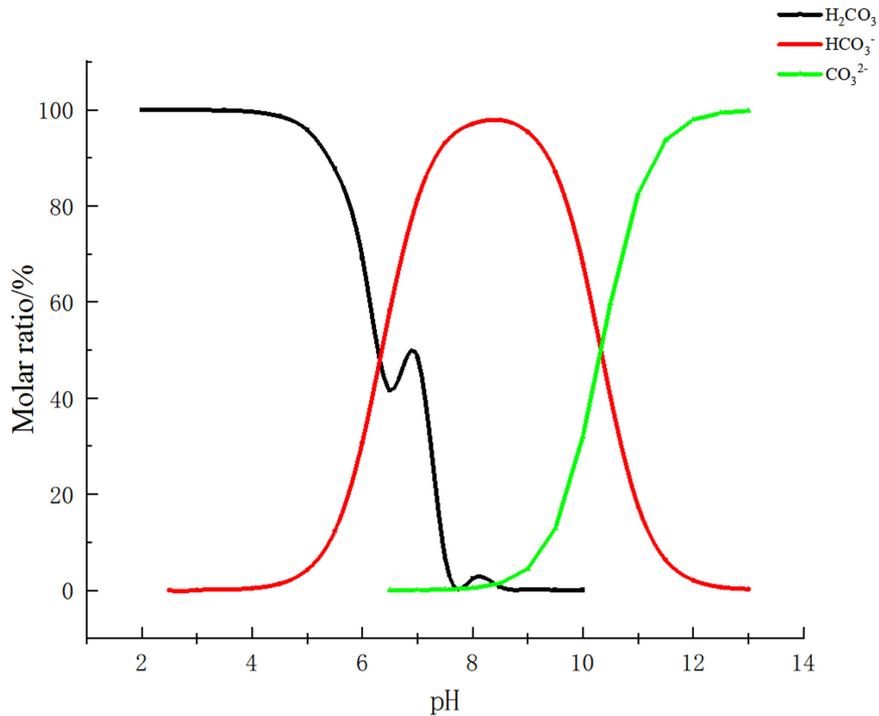


Figure 3. The chemical equilibrium diagram of CO₃²⁻ ions: [CO₃²⁻]_{TOT} = 16 μM.

It can be found that a higher temperature results in a lower carbonation degree. Therefore, high temperature is not good for the carbonation in lime. In addition, the variation of temperature also induces polymorphic formation of CaCO₃, which was investigated by Ergenç and Fort^[86], Oliveira *et al.*^[87], and Kitano^[88]. The experimental results indicate that it cannot change polymorph of CaCO₃ (calcite) at temperatures below 25 °C. At around 30 °C, aragonite is also formed, but no vaterite. As temperatures increase successively, vaterite also appears, but the proportion of calcite decreases. However, between 70 and 90 °C, only aragonite and small amounts of vaterite are formed at 100 °C, suggesting that high temperature, especially above 50 °C, makes it easy to form metastable polymorphs (aragonite and vaterite) of CaCO₃. These metastable crystals are not in favor of mechanical properties of lime mortar because of their susceptibility to temperature. It is well known that moisture is a key factor for the carbonation of lime (Equations 3 and 4). In addition to RH and temperature, the concentration of CO₂ is another critical influence factor. Actually, the degree of carbonation in lime mortar must increase with increasing CO₂ concentration.

Organic additives

The organic additives can influence the carbonation process in lime, thereby controlling the growth of calcium carbonate. Carmona-Carmona *et al.* reported that some properties of the mortars could be enhanced by adding the natural organic additives to lime mortars^[89].

Yang *et al.* have reported that after adding glutinous rice, the compressive strength and compatibility of lime mortar were significantly improved^[80]. Higher water retentivity, lower shrinkage, lower water vapor permeability, and lower water absorption of lime mortar are obtained by adding 3% SR than lime mortar without additives. Moreover, the flexural, compressive and adhesive strength increase by around 58%, 56% and 100%. In addition, SR can also control the growth of CaCO₃ crystals [Figure 4]. In the lime mortar of the control group, it can be observed that the crystal shape is regular, but the overall structure is loose [Figure 4B]. However, it can be found that when SR is added to lime mortar, the CaCO₃ crystal becomes

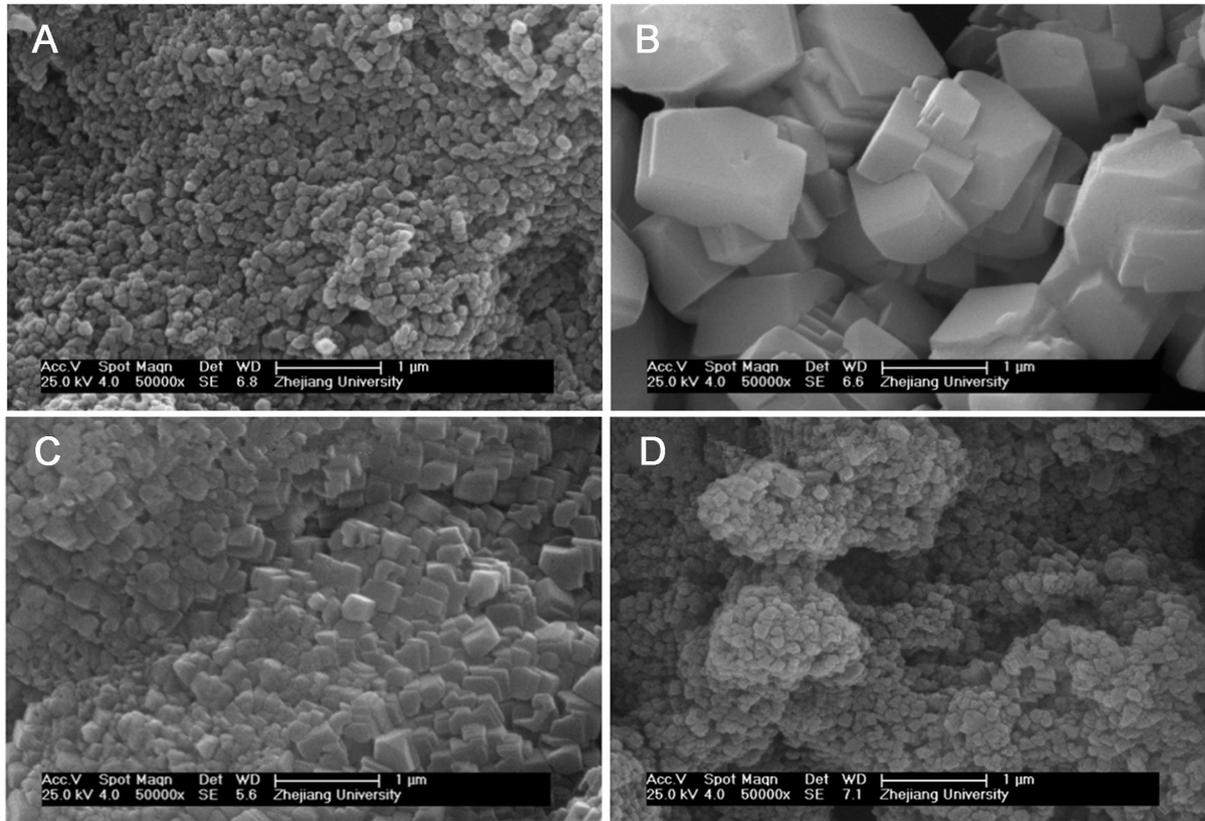


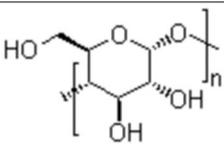
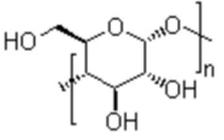
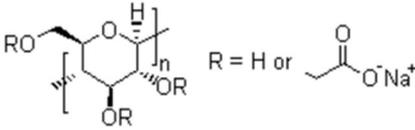
Figure 4. SEM images of lime mortars^[80]: (A) Traditional lime mortar from Nanjing city wall; (B) Lime mortar without SR; (C) Lime mortar with 1% SR; (D) Lime mortar with 3% SR. SEM: Scanning electron microscope; SR: sticky rice.

smaller, the shape becomes irregular, and the crystal particles begin to stick together to form a dense structure [Figure 4B and C]. This is the reason for improved strength. What is more, the size and polymorph of calcite in lime mortar with 3% SR are similar to the calcite in historical samples [Figure 4A]. The content of additives affects the size of CaCO_3 crystals, while the reaction time affects the morphology and size of CaCO_3 crystals. It is worth noting that although the morphology and size of CaCO_3 crystals are affected by the content of additives and reaction time, the morphology of CaCO_3 crystals remains calcite^[17].

Some other studies on the effect of natural and artificial polysaccharides on the crystallization of CaCO_3 also have been investigated^[90-92]. The molecular structures of these polysaccharides are shown in Table 2. It can be seen that both dextrin and starch have the same glucose monomer, but the molecular weight of dextrin is less than that of starch. Starch is composed of amylopectin (75%~80%) and amylose (20%~25%), and amylopectin has the active hydroxyl groups and branches-like structure^[93]. These active groups and special structures may be the key factors to affect the crystallization of CaCO_3 . The carboxymethyl cellulose (CMC) not only has the glucose monomer but also has the carboxyl groups, which decides that the CMC has a different effect on the crystallization of CaCO_3 than the dextrin and starch.

Zheng *et al.* studied the effect of dextrin, potato starch, and corn starch on the carbonation of calcium hydroxide^[94]. It could be found that all additives had a distinct influence on the morphology and size of CaCO_3 but no effect on the polymorph of calcite [Table 3]. All of the crystals were the most stable calcite, which was the main source of strength in traditional lime mortars. However, the influence of dextrin on the

Table 2. The molecular structures of polysaccharides^[90,92]

Organic additives	Molecular structure	Molecular weight	Functional groups
dextrin		504.4	-OH
Starch		60,000-20,000	-OH
CMC		6,400	-OH and -COO

CMC: Carboxymethyl cellulose.

Table 3. The effect of dextrin and starch on the polymorph and morphology of CaCO₃

Additive	Molecular weight	Concentration of additives	Size (nm)	Shape
-		0	200	Regular rhombohedra
Dextrin	504.4	2% wt	No change ≈ 200	Many layers of crystals overlapped together to form a massive structure
		3% wt		
		5% wt		
Potato starch	> Corn starch	2% wt	≈ 100	Rhomboheda
		3% wt	50-100	Irregular rhombohedra with many particles Calcite of unsharp shape
		5% wt	< 10	Particles of unsharp shape aggregated
Corn starch	< Potato starch	2% wt	100	Partial rhombohedra with many particles of unsharp shape
		3% wt	> 100	Many layers of crystals overlapped together to form a massive structure
		5% wt	10-100	Particles with no shape aggregated together

crystals was less than that of starches, which was caused by the lower molecular weight and absence of special molecular structure of dextrin. Starch, with higher molecular weight and complex structure, results in an obvious effect on the morphology and size of crystals. The effect of potato starch is more obvious than the corn starch; the reason for this is that, in addition to the molecular weight, the particle size of potato starch, content of amylopectin, and gelatinization temperature or viscosity of starch paste are higher than corn starch^[95]. While some properties of the starch depend on the chain length and the number of branches of starch molecules, the molecular structures are one of the key factors affecting the carbonation of lime. To sum up, polysaccharides, especially ones with high molecular weight, played an important role in the morphology and size of CaCO₃ and even some varying polymorphs of CaCO₃ crystals, thus affecting the mechanical properties of lime mortar.

The effect of CMC with 0.45 mmol/g carboxyl content on the crystallization of CaCO₃ was investigated^[90]. The calcite was the dominant polymorph in the experiments, but the morphology was ball shaped amorphous particles with a size range of 66-970 nm at 25 °C. Hence, the presence of CMC in the reaction system could affect the crystallization of CaCO₃ to form the spherical crystals at room temperature, which is

different from dextrin and starch. These results also showed that the carboxyl groups in CMC played an important role in the growth of CaCO_3 crystals. The carboxyl groups in CMC can not only make CaCO_3 crystals smaller at similar reaction times and temperatures but also help to get spherical microparticles. Liu *et al.* reported that the CMC molecules, as a template, could control the carbonation process and crystallization of calcium carbonate in lime mortar^[96].

Biomineralization is a process of producing harden minerals composite materials comprised of both mineral and organic components by the control of organic organisms, in which the calcium carbonate is the typical biomaterial^[97]. A biomineralization process consists of four stages, which are pre-organization of organics, interfacial molecular recognition, growth modulation, and epitaxial growth. In this process, organic macromolecules are used to control the CaCO_3 crystal nucleation, orientation, size and phase of minerals to develop sophisticated microstructure. Organic additives affect the carbonation of lime mortar, which is similar to the biomineralization process, and both of them are organic-inorganic hybrids. Consequently, the mechanisms of carbonation of organic-lime mortars and bio-mineralization are almost analogical.

The biomineralization mechanism is mainly attributed to the interactions between inorganic and organic interfaces, including electrostatic or chelate interaction, geometrical lattice matching^[98,99] and stereochemical complimentary. Among them, electrostatic or chelate interaction devotes significant effect to formation of calcium carbonate, which is similar to the carbonation mechanism of lime with organic additives. Negatively charged organics can adsorb Ca^{2+} by electrostatic or chelate interaction, resulting in a higher concentration of CO_3^{2-} in part. At the same time, more Ca^{2+} ions are adsorbed to further increase the concentration until the concentration is high enough to nucleate. CaCO_3 precipitation forms when calcium and carbonate ions are sufficient to make the ion activity product (IAP) exceed the solubility constant (K_{so})^[97,100]. Hence, the saturation state (Ω) of the system is as follows^[101]:

$$\Omega = a(\text{Ca}^{2+})a(\text{CO}_3^{2-})/K_{so} \quad (6)$$

Where K_{so} of calcite at 25 °C is 4.8×10^{-9} . When $\Omega > 1$, the system is supersaturated to form CaCO_3 precipitation. And epitaxial growth affects the growth of calcium carbonate by using organic additives as a template^[99]. The specific adsorption of organic additives on specific surfaces can inhibit the growth of these surfaces^[102]. In order to reduce the high-energy surface, the direction perpendicular to the highest surface energy has the fastest crystal growth rate, while the low-energy surface has a larger exposed area. Therefore, the rapidly growing surfaces usually have a high surface energy, and eventually, they will disappear in the final shape^[102]. However, the preferential adsorption of organic additives on a specific crystal plane inhibits the crystal growth perpendicular to the crystal plane, thereby changing the final shape^[103,104]. This will help to control the formation of calcite in lime mortar, which can further affect the strength of lime mortar and improve the working performance of lime mortar for repairing architectural heritages.

Zheng *et al.* have reported that the crystallization process of CaCO_3 was mediated by egg-white [Figure 5]^[94]. The crystallization process is shown as follows: (A) Supramolecular interaction between some functional groups of egg white and Ca^{2+} ; (B) Uniform ACC nanoparticles were formed at the initial stage of the reaction; (C) The aggregation of some nucleation and ordered structures under electrostatic interaction and van der Waals force; (D and E) ACC nuclei begin to aggregate and form mesoscale layered CaCO_3 nanoparticle arrangement; (F) Nanoparticles are constructed, and hierarchical structures are formed by a self-assembly process; (G) The flake CaCO_3 crystals aggregate and self-assemble to form a wool spherical

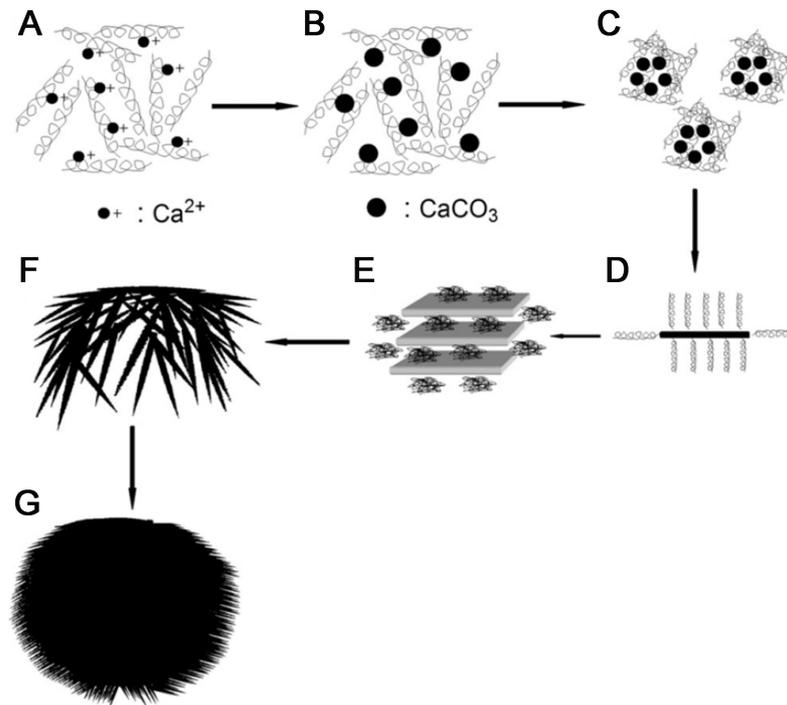


Figure 5. Crystalline hierarchical structure process of CaCO_3 . (A) Supramolecular interaction between some functional groups of egg white and Ca^{2+} ; (B) Uniform ACC nanoparticles were formed at the initial stage of the reaction; (C) The aggregation of some nucleation and ordered structures under electrostatic interaction and van der Waals force; (D and E) ACC nuclei begin to aggregate and form mesoscale layered CaCO_3 nanoparticle arrangement; (F) Nanoparticles are constructed, and hierarchical structures are formed by a self-assembly process; (G) The flake CaCO_3 crystals aggregate and self-assemble to form a wool spherical upper structure with many fibers. ACC: Amorphous calcium carbonate.

upper structure with many fibers. It can be discovered that Ca^{2+} can connect egg white molecules, which is consistent with the results shown in Figure 1. These mechanisms of biomineralization can be used in the carbonation of lime mortars with organic additives to achieve superior building materials.

Feijoo *et al.* have reported that under the same water content, adding paraffin phase change materials can reduce the porosity of the mortar, mainly by filling the smallest diameter pores^[105]. Although this hinders the carbonation process, it enhances durability. The added compounds reduce the presence of small pores and increase the durability of lime mortar against external media such as soluble salts or water. This is because larger pores are not as susceptible to the pressure exerted by these media on their walls as smaller pores. This is beneficial to the mortar and maintains strength for a long time.

Organics can induce the variation of polymorph, size and morphology of CaCO_3 crystals. The formation of calcite is beneficial to the lime mortars. The cohesive “bridges” can form calcite crystals between existing sand grains to increase the stiffness of sand, thus decreasing the permeability of building materials^[106,107]. What is more, biomineralized CaCO_3 , namely, CaCO_3 formed with organics, has proved its efficacy in sealing the cracks in concrete structures^[94,108]. Therefore, organic additives can play important roles in carbonation of lime mortars to get better mortars for the restoration of architectural heritage.

Inorganic additives

Similar to organic additives, inorganic additives also affect the properties of lime mortar greatly. Ergenç *et al.* reported that the addition of ferrocyanide to lime mortar can increase the internal pore volume,

reduce the pore distortion, accelerate the flow rate of water in the porous network of the structure, increase the evaporation rate, and fully react with CO_2 in the air, thereby increasing the carbonation rate of lime^[109]. Another study by Feijoo *et al.* showed that ferrocyanide can not only improve the carbonation degree of mortar and its adhesion to the surface of porous materials, but also protect lime mortar against chloride erosion, and maintain the resistance to NaCl over time, which can effectively improve its durability and even protects the stone materials that it bonds^[110].

In addition, Ergenç *et al.* also found that the addition of nano- SiO_2 alone or together with nano- $\text{Ca}(\text{OH})_2$ is more conducive to improving the pozzolanic activity in mortar. The resulting less stable hydration leads to microcracks that ultimately weaken the compressive strength but increase the ability to deform, which provides a new theoretical basis for the development of high compatibility mortar for cultural heritage^[111].

However, it should not be ignored that although the combined addition of nano-silica and nano $\text{Ca}(\text{OH})_2$ is more conducive to improving the activity of volcanic ash in the mortar, the resulting hydration instability will produce micro-cracks and ultimately weaken the compressive strength. Inorganic substances reduce the porosity of mortar, improve the resistance to soluble salt, and even improve the carbonization degree of mortar to a certain extent. However, it should not be ignored that although the combined addition of nano-silica and nano $\text{Ca}(\text{OH})_2$ is more conducive to improving the activity of volcanic ash in the mortar, the resulting hydration instability will produce micro-cracks and ultimately weaken the compressive strength. Thus, a reasonable selection of additives can improve the performance of building heritage restoration mortar.

CONCLUSIONS

Considering that the air lime mortar is the most compatible mortar with old buildings, we discussed the effect of water-binder ratio, aggregate properties and particle size, and inorganic and organic additives on lime mortar properties and durability from the aspects of mechanical properties and carbonization mechanism of lime mortar. Additionally, we explored the lime mortar carbonation principle to draw the following conclusions:

1. The influence of aggregate type on air lime mortar properties is greater than that of water cement ratio. Limestone and volcanic material as aggregates are more suitable for the preparation of lime mortar than other siliceous aggregates. Lime compressive strength can be increased from 0.3~0.7 to 2.5 MPa by using angular aggregate instead of rounded aggregate. Different B/A ratios have a certain effect on the mechanical properties of lime mortar, but the effect is not obvious under the same curing time.
2. Organic or inorganic additives may optimize the properties of lime mortar in a variety of ways: providing multiple sites and connecting lime particles together through Ca^{2+} , resulting in dense and linked structure of lime mortar; preventing NaCl from entering its porous network from surrounding sandstone blocks; the shape of CaCO_3 crystal was changed through adsorption.
3. The lime mortar containing highly active pozzolanic materials, which is prepared at 20 °C and 60% RH with a weight ratio of 1:1 MK/lime, has better compressive strength, up to 400 times better. At the same time, adding appropriate additives, such as SO, *etc.*, can improve its durability and will greatly improve the ability to repair architectural cultural heritage.

Considering the various properties of lime mortar, the optimal conditions for repairing the lime mortar of architectural heritage are proposed. However, there is still room for further research in practical application.

DECLARATIONS

Authors' contributions

Writing - original draft: Liu H

Writing - review and editing: Chen Z

Manuscript discussion and revision: Xu L

Data curation, validation, visualization: Ge W

Availability of data and materials

Not applicable.

Financial support and sponsorship

This work was financially supported by the Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJCX22_1380).

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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