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Lime mortars – The role of carboxymethyl cellulose on the crystallization of calcium carbonate

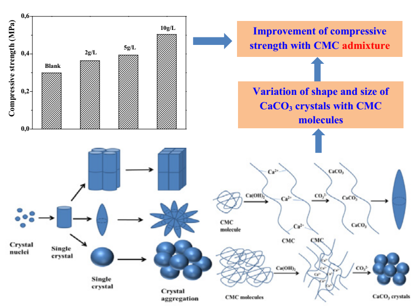
Hui Liu [a,b,c], Yunliang Zhao [b,d], Changsheng Peng [e], Shaoxian Song [b,c,e,*], Alejandro López–Valdivieso [c]

[a] Faculty of Environmental and Biological Engineering, Guangdong University of Petrochemical Technology, Maoming, Guangdong 525000, China
[b] School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, Hubei 430070, China
[c] Doctorado Institucional de Ingeniería y Ciencia de Materiales, Universidad Autonoma de San Luis Potosi, Av. Sierra Leona 530, San Luis Potosi C.P. 78210, Mexico
[d] Hubei Key Laboratory of Mineral Resources Processing and Environment, Luoshi Road 122, Wuhan, Hubei 430070, China
[e] The Key Lab of Marine Environmental Science and Ecology of Ministry of Education, Ocean University of China, Qingdao 266100, China

HIGHLIGHTS

- CMC additive can improve the compressive strength of lime mortar.
- The morphology and size of $CaCO_3$ crystals in lime mortar can be controlled by CMC.
- Polymorph of $CaCO_3$ crystals are always calcite due to the presence of CMC.
- CMC molecules slow down the growth rate and crystallinity of $CaCO_3$ crystals.

GRAPHICAL ABSTRACT



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ABSTRACT

Aerial lime-mortars are widely used in the conservation interventions, in which polymers could improve their mechanical strength. In this work, the effects of carboxymethyl cellulose (CMC) on the crystallization of calcium carbonate ($CaCO_3$) in lime mortar have been studied in order to explore the mechanism of the improvement. The experimental results have shown that CMC molecules played as templates to control the morphology and size of $CaCO_3$ crystals. Without CMC, the crystals appeared in the form of cylinder, while CMC addition changed the crystalline shape to be fusiform at the low concentration and spherical at the high concentration. The crystal size increased with CMC addition to the maximum value then declined, leading the lime mortar structure to be more compact, thus improving the compressive strength of lime mortar. These results might be attributed to the restraint effect of CMC molecules to slow down the growth rate and crystallinity of $CaCO_3$ crystals. It was also found that CMC did not affect the polymorph of $CaCO_3$ crystals, which is beneficial to maintain the compressive strength of lime mortar.

1. Introduction

The aerial lime-mortars widely used in the ancient buildings have aroused wide attentions of many scholars in recent decades, due to their great compatibility with the ancient buildings [1–3]. As we all know, the strength of aerial lime-mortar is mainly attributed to carbonation reaction of lime. During the carbonation process, calcium carbonate ($CaCO_3$) is formed from $Ca(OH)_2$ by absorbing the CO_2 in the air [4–6]. Because carbonation of Ca

* Corresponding author at: School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, Hubei 430070, China.
E-mail addresses: liuhui236@126.com (H. Liu), yunliang286@163.com (Y. Zhao), cspeng@ouc.edu.cn (C. Peng), shaoxian@uaslp.mx (S. Song), alopez@uaslp.mx (A. López–Valdivieso).

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$(OH)_2$ in lime mortar is a long-term continuous process, carbonation has a real, not apparent, influence on the mechanical resistance of the aerial lime mortars and on its evolution.

The $CaCO_3$ crystals have different polymorphs and morphologies, whose anhydrous phases include amorphous calcium carbonate (ACC), spherical vaterite, needlelike aragonite and rhombohedral calcite [7]. Calcite is the thermodynamically most stable $CaCO_3$ polymorph [8], which is also the most common polymorph of $CaCO_3$ crystals in Chinese ancient buildings built by lime mortars [9,10]. But these polymorphs and morphologies would be changed by the variation of temperature, pH and additives etc. [11–15]. Organic additives, especial high polymers, had a significant influence on the morphology and size of $CaCO_3$ crystals [16]. These variations of crystal polymorph and morphology may influence the mechanical behaviors of lime mortars.

Lime is regarded as the only calcium source of calcium carbonate crystallization in the lime mortars, so the carbonation process of $Ca(OH)_2$ has been focused by many scholars [5,6,17,18]. The effect of storage conditions on the carbonation of powdered $Ca(OH)_2$ [17] and kinetics of the reaction of $Ca(OH)_2$ with CO_2 at low temperature [19] were investigated. The model also had been built to obtain a better understanding of the carbonation process of lime mortars [20]. In addition, the carbonation processes in different types of mortars, with and without pozzolana or air-entraining additives were also discussed [5].

Even though many investigations have been performed to study the carbonation process of lime mortar, there are few reports about the effect of organic admixtures on the carbonation of lime. In ancient Chinese buildings, the organic lime mortar which is composed of lime, sand and organic additives (sticky rice, egg white, brown sugar, tung oil or animal blood) has been widely used [9,16,21–24]. The analysis results of ancient Chinese buildings show that the inorganic component of the mortar is calcium carbonate (mainly is calcite), and the organic component is mainly natural polysaccharide, protein or fatty acid [9,10,25]. The researches have verified that organic additives have a positive effect on the mechanical behaviors of lime mortar [26,27]. What's more, the organic additives can determine the morphology, polymorph and growth of $CaCO_3$ crystals, which may result in better mechanical behaviors of lime mortar. Therefore, it is important to know the influence of organic additives on the carbonation of lime mortar.

In the light of above results, polysaccharide is a kind of important organic additives to improve the mechanical behaviors of organic lime mortar. Carboxymethyl cellulose (CMC) is an artificial polysaccharide prepared by replacing the hydrogen atoms of the hydroxyl groups with the carboxymethyl groups. It has good properties (e.g., bonding, thickening, and water retention) due to its long molecular chains and abundant hydroxyl and carboxyl substituent groups along the cellulose chains [28,29]. The polar carboxyl groups render the cellulose soluble and chemically reactive and can be protonated or deprotonated depending on the solution pH. The properties of CMC depend on the degree of substitution (DS) of carboxymethyl groups. Namely, the higher DS, the better properties. The study shows that CMC molecules can improve the compressive strength of lime mortar due to its good properties [30], but the influences of CMC on the carbonation process of lime and on the morphology and polymorph of $CaCO_3$ crystals are still unclear. In the present work, the roles of CMC concentration and reaction time on the crystallization of calcium carbonate in the lime mortars are investigated.

2. Experimental

In order to delineate the mechanisms of interactions between CMC and lime during the carbonation process of lime mortars, the effects of CMC concentration and reaction time on the crystallization of $CaCO_3$ crystals were investigated. Meanwhile, the lime mortars with CMC were also prepared to develop a kind of organic-inorganic adhesive materials to restore the ancient buildings.

2.1. Materials

Lime ($Ca(OH)_2$, Analytical reagent (AR)), urea ($CO(NH_2)_2$, AR) and sodium carboxymethyl cellulose (CMC, Chemically Pure) used in the experiment were from the Sinopharm Chemical Reagent Co. Ltd., China. The CMC had the viscosity of 0.8–1.2 Pa·s at the concentration of 20 g/L at 25 °C. The sands used in preparation of lime mortars were purchased from ISO standard sand Co. Ltd. (Xiamen, China). The Chinese standard sand, from Xiangtan in Fujian province, is the natural quartz sand. The components and granularity were shown in Table 1. Deionized water used in all experiments was made with a Milli-Q Direct 16 system, and the resistivity was determined to be 18.25 MΩ cm.

2.2. The preparation and carbonation of lime suspensions with CMC

To obtain the suspension of lime, 0.5 mol $Ca(OH)_2$ powders were added in 3 L of deionized water. The mixtures were stirred evenly and then were allowed to settle for 30 min. After that, the supernatant liquids were collected and used.

In the meanwhile, 0, 0.2, 0.4, 0.8, 2.4 and 3.2 g/L of CMC solutions were prepared. A certain amount of CMC solids were added slowly and evenly into the deionized water stirred constantly to make the CMC dissolve totally.

$CaCO_3$ crystals were prepared by the following equations which displayed the synthesis process of calcium carbonate ($CaCO_3$) using $Ca(OH)_2$ and $CO(NH_2)_2$. Firstly, lime suspension (1500 mL) and different concentration of CMC solutions (500 mL) were mixed by magnetic stirrer (200 rpm) for 30 min. Then 0.5 mol $CO(NH_2)_2$ were added into the mixture as carbon dioxide (CO_2) source to form the crystallization of calcium carbonate ($CaCO_3$). After that, the solutions were transferred to 500 mL of reagent bottles. Then the bottles were sealed with covers and placed into a 70 °C thermostatic box for 24 h and 120 h. The crystals formed in the bottles were collected, rinsed with deionized water and dried for the measurements and analysis.

During the preparation process of $CaCO_3$ crystals, the $CO(NH_2)_2$ was used to supply the CO_2 due to its decomposition at high temperature and no influence on the morphology/nucleation of $CaCO_3$ [31,32]. Because the urea solution will begin to hydrolyze to form NH_3 and CO_2 when the temperature reaches to 60 °C. After 80 °C, the hydrolysis rate will be faster. Hence, the reaction temperature of 70 °C has been chosen to prepare the $CaCO_3$ crystals. What's more, the host-guest composition belongs to the secondary factor in $CaCO_3$ crystallization process, which is not the most important factor [12]. In addition, according to the prior works [16,33], it can be known that there is no influence of the urea concentration on the morphology/nucleation of $CaCO_3$ crystals.

Table 1
The components and granularity of Chinese standard sand (wt%).

SiO_2 content	Loss on ignition	Silt content	Granularity	
			Diameter of square mesh sieve	Cumulative sieve residue
>96	≤0.40	≤0.20	0.65 mm	<3
			0.40 mm	40 ± 5
			0.25 mm	>94