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Role of calcium sources in the strength and microstructure of microbial mortar

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HIGHLIGHTS

- Aragonite crystal of carbonate precipitation was found when $Ca(CH_3COO)_2$ was used.
- Microbial mortar samples treated with three different calcium sources were prepared.
- The UCS of samples treated with $Ca(CH_3COO)_2$ were higher than that of the others.
- The BTS of samples treated with $Ca(CH_3COO)_2$ were higher than that of the others.

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ABSTRACT

This study investigated the uniaxial compressive strength, splitting tensile strength and water absorption ratio of microbial mortars treated with three different calcium sources ($CaCl_2$, $Ca(CH_3COO)_2$ and $Ca(NO_3)_2$). The results showed that the uniaxial compressive and splitting tensile strengths of microbial mortars treated with $Ca(CH_3COO)_2$ were about twice those of the microbial mortars treated with the other two calcium sources ('the others' hereafter). The results of mercury intrusion porosimetry analysis showed that the pore size distribution in the microbial mortar treated with $Ca(CH_3COO)_2$ was much more uniform than that of the others. The mineralogical compositions and the microstructure morphology of the microbially induced calcium carbonate precipitation were analyzed in detail. Scanning electron microscopy and X-ray diffraction revealed that the calcium carbonate cemented in the microbial mortar treated with $Ca(CH_3COO)_2$ were different from others. Besides the calcite and the vaterite crystals, aragonite crystals with an acicular mineral morphology were observed.

Calcium acetate is a more appropriate calcium source than calcium chloride for the application of MICP technology in reinforced concrete structures because it avoids the corrosion of steel bars caused by chloride ion.

1. Introduction

Microbially induced carbonate precipitation (MICP) is the product of a series of biochemical reactions. The urease in the urea hydrolysis environment is produced by microorganisms. The hydrolysis reaction creates ammonia and carbon dioxide, which are then converted to ammonium and carbonate ions in an alkaline environment (Eq. (1)) [1]. Since the microorganisms are negatively charged, they adsorb calcium ions. If there are enough calcium ions in the environment, carbonate ions will react with them to produce calcium carbonate precipitation with the cell as the crystal nucleus (Eqs. (2) and (3)) [1].

$$CO(NH_2)_2 + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \quad (1)$$

$$Ca^{2+} + Cell \rightarrow Cell - Ca^{2+} \quad (2)$$

$$CO_3^{2-} + Cell - Ca^{2+} \rightarrow Cell - CaCO_3 \downarrow \quad (3)$$

This technology has been applied in many fields, such as in surface restoration of ancient buildings [1–2], heavy metal treatment in soil [3–4], defect repair in construction materials [5–14] and improvement of the mechanical properties and permeability of the soil [15–17]. Some studies have reported that MICP can improve the strength and durability of concrete containing defects, thus providing a new method for repairing cracks in concrete [7–14].

Most researchers use calcium chloride as the calcium source in MICP technology [7–17]. It is widely known that once chloride penetrates into concrete through cracks, depassivation and electrochemical corrosion of the steel bars will occur, which

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affects the durability of the reinforced concrete [18]. Therefore, further experiments using other calcium sources such as calcium acetate and calcium nitrate are necessary to reduce the adverse effects of chloride ion on concrete durability.

Van Tittelboom et al. applied $CaCl_2$, $Ca(CH_3COO)_2$ and $Ca(NO_3)_2$ to repair the surface of cracked concrete. The treatments with these three calcium sources performed almost equally in reducing water permeability [12]. De Muynck discovered that the crystal morphology of calcium carbonate could be strongly influenced by the nutrient composition. The calcium carbonate crystal was rhombohedral when $CaCl_2$ was used as the calcium source, but spheroidal when $Ca(CH_3COO)_2$ was used. However, the mineralogical composition, which was mainly calcite, was the same. Biodeposition treatment by $Ca(CH_3COO)_2$ has been shown to have similar effectiveness to that by $CaCl_2$ [7]. Li and Qu used calcium acetate and calcium chloride as calcium sources to prepare microbial mortar for repairing concrete cracks. Their test results showed that the remediation increased the compressive strength by 15% and the calcium source had no significant effects [8].

The research group of Tsinghua University has carried out a series of studies on the application of MICP in the civil engineering field [2,4,19]. Yang and Cheng applied low-pressure grouting technology to the preparation of high-strength microbial mortar using $CaCl_2$ as the calcium source [19]. Based on the work, before applying MICP technology in the concrete field, bio-grouting experiments on both the durability and the mechanical properties of sand columns treated with three different calcium sources were conducted. And the test results were presented in this paper. The tests included uniaxial compressive strength tests, splitting tensile strength tests and water absorption ratio tests. The mineralogical composition, microstructure morphology and pore size distribution of the MICP bonded minerals were analyzed.

2. Experimental materials and methods

2.1. Experimental materials

2.1.1. Bacteria

A wild strain of *Sporosarcina pasteurii* (American Type Culture Collection, ATCC 11859), which is a Gram-positive chemoheterotrophic bacteria with rhabditiform cells with a length of 2–3 μm. The diameter of the round spores was 0.5–1.5 μm. The cultivation and the detection methods of the strain were the same as those used by Yang and Cheng [19].

2.1.2. Culture medium

NH^{4+}-YE (the medium contained 20.0 g of yeast extract and 10.0 g of $(NH_4)_2SO_4$ per liter, and the pH value of the medium was around 9).

2.1.3. Nutrient solution

A mixed solution of the calcium source and the urea with equal molar concentrations of 0.5 M. The calcium sources were $CaCl_2$, $Ca(NO_3)_2{\cdot}4(H_2O)$ and $Ca(CH_3COO)_2{\cdot}H_2O$.

2.1.4. Bacteria fixative

50 mM calcium acetate/calcium chloride/calcium nitrate solution.

2.1.5. Filling particles

Industrial sand with a particle size of 200–380 μm.

2.2. Biogrouting and preparation of test samples

The grouting equipment and the grouting methods were the same as those used by Yang and Cheng [19]. To prepare microbial mortars with different strengths, we pumped 1–3 batches of bacteria solution, fixative solution and nutrient solution. To investigate the influence of different calcium sources on the macroscopic properties and microscopic structure of the microbial mortar, we prepared samples using three kinds of calcium source, as shown in Table 1. We prepared the microbial mortars samples of group A, B and C with the similar initial urease activities and the different pumped batches, the samples of group C and D with the same batches and different urease activities. The detailed parameters are also shown in Table 1.

The molds were removed after grouting and each microbial mortar sample was halved (diameter = 30 mm, height = 50 mm) using a stone-cutting machine. All of the samples were immersed in deionized water for 48 h like Thawadi [20] before testing to eliminate the soluble substances on the surface. Then, the samples were dried at 75 °C for 48 h. After cooling to room temperature, the weight, diameter and height of each sample were measured, and the dry density of the samples was calculated. Then the tests of water absorption, UCS and BTS were carried out.

2.3. Testing methods for the mechanical and physical properties

2.3.1. Dry density

The samples were dried at 70 °C for 36 h until their mass-loss ratios (in 24 h) were less than 0.1% and then cooled to room temperature. The dry density was then obtained by measuring the mass, diameter and height of the samples.

2.3.2. Water absorption ratio

The water absorption ratios of the samples treated with different calcium sources were obtained by taking the following steps:

(1) Measure the moisture-free weight of the sample, m1; (2) immerse the sample in water for 24 h; (3) remove the sample from the water and quickly clean the water off the surface using wet towel; (4) measure the weight of the sample, m2; and (5) calculate the water absorption ratio $W = \frac{m_2 - m_1}{m_1} \times 100\%$.

2.3.3. Mechanical properties (UCS and BTS)

The uniaxial compressive strength (UCS) test and the Brazilian splitting tensile strength (BTS) tests were carried out using a Material Test System 810 (MTS810) and an electronic universal testing machine (Sinter WDW-10KN). The uniaxial compressive strength tests were set to be displacement controlled at a loading rate of 0.05 mm/min.

Table 1
Detailed parameters of the samples.

Group		A			B			C			D		
Pumped Batches[a]		1			2			3			3		
Urease activity (mS/cm/min)		1.20			1.00 ± 0.08			1.10 ± 0.09			2.35 ± 0.15		
Biomass (OD_{600})		2.96			3.08 ± 0.25			3.24 ± 0.23			1.81 ± 0.14		
Environmental temperature (°C)		19			21 ± 1			21 ± 1			29		
Calcium source		Cl^-	NO_3^-	CH_3COO^-	Cl^-	NO_3^-	CH_3COO^-	Cl^-	NO_3^-	CH_3COO^-	Cl^-	NO_3^-	CH_3COO^-
Number of samples	Dry density [b]/water absorption[b]	7	5	11	9	7	12	11	13	6	5	6	5
	UCS [b]	0[c]	2	4	8	6	10	8	5	8	5	6	5
	BTS[d]		/		4	5	9		/			/	
	MIP		/			/			/		1	1	2
	SEM	1	1	1	1	1	1	1	1	1	3	3	3
	XRD	1	1	1		/			/		3	3	3

No tests were carried out.

[a] Pumped batches — for example, batches = 2, means to pump the bacteria solution, fixative solution and nutrient solution in turn into sand samples, and then to repeat once.

[b] The number of samples for different calcium sources in the same group before grouting were same, but after grouting there were some samples that were not suitable to do the physical and mechanical test. The samples of dry density and water absorption are the same and some of them were used in UCS.

[c] There were no qualified samples.

[d] The dry density and water absorption ratio of the BTS samples were tested and their average results were the same as the samples listed in Table 1. The BTS samples were cylindrical with a length of 30 mm and a diameter of 30 mm.