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Bio-mineralization on cement-based materials consuming CO_2 from atmosphere

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HIGHLIGHTS

- One type of bacteria which can produce CA were incorporated on the surface of cement-based walls to absorb CO_2 in air. CO_2 can be transferred to minerals precipitated on surface of cement-based walls when reacting with soluble $Ca(OH)_2$ induced by CA bacteria.
- In one hand, $CaCO_3$ deposited on surface can fill micro-pores and cracks. The micro-pores and cracks can be repaired.
- In the other hand, efflorescence could be reduced obviously.
- The whole process not only absorbs greenhouse gas CO_2 in the atmosphere but also does not produce any harmful substances, thus having the superior environment-friendly features. This way is also cheap compared to traditional methods because the CO_2 can be obtained everywhere from air.

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ABSTRACT

Cement-based materials is one of the most widely used materials in the world. It consists of buildings walls directly contacting CO_2 in air in many cases. This research focuses on how to absorb and transfer CO_2 (greenhouse gas) to minerals on surface layer of cement-based walls in one hand, and in the other hand, to improve the micro-crack restoring capacities and efflorescence resistance of cement-based walls. A bio-mineralization technology was applied in this study to achieve above-mentioned purpose. Carbonic anhydrase microbe was added into cement-based materials during making building walls. The microbe can increase the absorbing of CO_2 and turn it to HCO_3^- in alkaline pore solution of cement-based materials; calcite will be produced in micro-cracks and pores because of the reaction of HCO_3^- with Ca^{2+}. Experimental results showed that the cement-based wall of 10,000 m^2 can absorb and transfer CO_2 about 300–400 kg to calcite at first 7 days, the cracks with width of 50–100 μm can be completely self-healed and the efflorescence can be reduced as much as 42%. A method to quantitatively evaluate efflorescence on surface of cement-based walls was also put forward based on image processing.

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1. Introduction

Cement-based materials are one of the most widely used materials in the world and are often used for external walls in many kinds of buildings. However, the cement-based external walls crack easily during the service life, which lead serious harm to the durability. And the efflorescence on surface of walls may spoil the appearance and limit the application [1–3]. By now, the common method to solve the two problems is applying protective layer on surface of the external walls. But the processes are often expensive and complex.

Some microbes in the nature can conduct the inter-conversion between CO_2 and $CaCO_3$. The conversion from CO_2 to $CaCO_3$ can be used to catch CO_2 in atmosphere. Dreybrodt [4] thought in the H_2O–CO_2–$CaCO_3$ system, the slow reaction $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ was considered as one of the rate-limiting steps for the precipitation rate of calcite from supersaturated solutions. Carbonic anhydrase (CA) can catalyze the inter-conversion of CO_2 and HCO_3^- to improve the absorption of CO_2 [5,6]. Therefore, CA can aid in the capture of $CO_2$and the precipitation of $CaCO_3$, following the equations [7]:

$$H_2O + CO_2 \rightarrow HCO_3^- + H^+$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H^+ + HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$

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Ramachandran [8] proposed that the microbial mineralization can be used to repair cracks in concrete in 2001. But the high alkali environment in concrete will restrict the activity of bacteria and make the repair effectiveness invalid [9]. Some studies [10,11] showed carrier such as agar can prevent bacteria from high alkali environment. And the excellent coating performance of agar could be used to repair micro-defects on the surface of paste.

In this study, bacteria which can produce CA were incorporated on the surface of cement-based walls to absorb CO_2 in air. CO_2 can be transferred to minerals precipitated on surface of cement-based walls when reacting with soluble $Ca(OH)_2$ induced by CA bacteria. The micro-defects could be repaired because of the precipitation of $CaCO_3$ and the efflorescence could be reduced by consumption of $Ca(OH)_2$ on surface of cement-based walls. This way is also cheap compared to traditional methods because the CO_2 can be obtained everywhere from air.

2. Materials and methods

2.1. Materials

2.1.1. Bacterial strain

Bacillus mucilaginous L3 (China Center of Industrial Culture Collection, CICC) which can produce carbonic anhydrase was used in this study. The best incubation time was about 24 h, and the OD400 was 0.8. After incubated for 24 h in specific liquid medium, the fresh bacterial strain were harvested by high-speed (8000 r/min) centrifugation at 4 °C for 10 min. Then the bacterial strains were resuspended in the sterile deionized water. The final concentration of bacterial suspension was about 10^9 cells/mL.

2.1.2. Preparation of the specimens

In this study, cement specimens were prepared for the restoration of surface micro-pores and cracks. Cement specimens were prisms designed with a water to cement ratio of 0.4 by using ordinary Portland cement II 42.5. The size of prisms specimens is 40 mm × 40 mm × 160 mm. After standard curing for 28 d, cracks were pre-made by bending test on the surface of cement paste. The width of cracks were among 50–100 μm.

Mortar specimens were prepared for the experiment of efflorescence resistance. Mortar specimens (300 mm × 300 mm × 30 mm) were made by using ordinary Portland cement II 42.5, sand and tap water. The fineness modulus of sand was 2.1–2.6 with an average particle size of 0.25–0.35 mm. The water to cement ratio by mass was 0.3 and the sand to cement ratio by mass was 1.0. Four series of specimens were made. The experimental wallboard contains two layer and the surface layer is the structure layer. And the thickness of structure and surface layer is 4.5 mm and 12.5 mm respectively. Group C are specimens without any additions. Group S1 are specimens with CA bacteria added into surface layer of mortars. Group S2 are specimens with CA bacteria added into structure layer of mortars, Group S are specimens with bacteria added into surface and structure layer of mortars at the same time. The mortars of structure layer was prepared first with a water-to-cement weight ratio of 0.3. Then the bacteria were added into mortar during mixing process. About 6 h later, surface layer was casted into the structure layer and the surface layer was prepared same like structure layer. The amount of bacteria added in each group was 6% of cementitious material by mass. Bacteria suspension replaced equal amount of water for keeping a consistent water to cement ratio.

2.2. Methods

2.2.1. Absorption of CO_2

For studying the absorption of CO_2 in CA, sterile deionized water and bacterial suspension (10^9 cells/mL) were prepared in same volume. CO_2 (99.2%) was passed through two solutions continuously with a constant velocity of 5 mL/s. The conductivity was tested in each group until it stabilized. The conductivity tests of two groups were conducted under the same conditions with the temperature of 25 °C and relative humidity of 50%.

2.2.2. Deposition of calcium carbonate in solution

In order to research the deposition of calcium carbonate in solution, two types of solution were prepared. Solution 1 was sterile deionized water and solution 2 was bacterial suspension (10^9 cells/mL). Then appropriate amount of $Ca(NO_3)_2$ was added into two groups to guarantee the same concentration of Ca^{2+} in two groups. The initial concentration of Ca^{2+} in two groups was 6800 mg/L. The initial pH of the two solutions were adjusted to 11. Two groups were exposed to atmosphere at temperature of 30 °C. The concentration of Ca^{2+} in solutions was tested every day by method of EDTA titration.

2.2.3. Restoration of surface micro-pores and cracks

The surface of cement specimens were sealed using paraffin wax except the tested surface with cracks. The tested surface was brushed by 2% agar solution completely to form an agar layer. When the agar was cooled to about 50 °C, the fresh bacterial suspension were sprayed upon to the agar layer uniformly. Bacteria were immobilized by agar layer which was covered onto surface of cement paste. After that, $Ca(OH)_2$ and $NaHCO_3$ solution was sprayed on the surface of cement specimens. Then the cement specimens were cured at 30 °C exposed to atmosphere. The process was repeated once daily for 3 days. Film-covering procedures in different groups were similar but different raw materials were used. The experiment procedures of film-covering on the surface of specimens are shown in Table 1. The film-covering method is showed in Fig. 1.

2.2.4. Efflorescence resistance of cement-based walls

Specimens were de-mold after standard curing for 24 h, then tap water was sprayed to keep the surface covered by a layer of water film for 24 h. The thickness of water film was about 5–10 mm. A continuous airflow with constant velocity of 5 m/s was conducted on the surface of mortar specimens to speed up the drying of the water film as shown in Fig. 2. When water film was dried completely, the experiment processes above was repeated continuously 2–3 times for simulating the rainfall environment. Control specimens were treated in the same way but no bacteria was added.

Table 1
Experiment procedures of film-covering on specimens surface.

Type	Bacteria concentration × 10^9/(cells mL^{-1})	Concentration/g L^{-1}		
		Agar	$Ca(NO_3)_2{\cdot}4H_2O$	$NaHCO_3$
I	0	0	0	0
II	0	20	0	0
III	2.3	0	118	42
IV	0	20	118	42
V	2.3	20	118	42

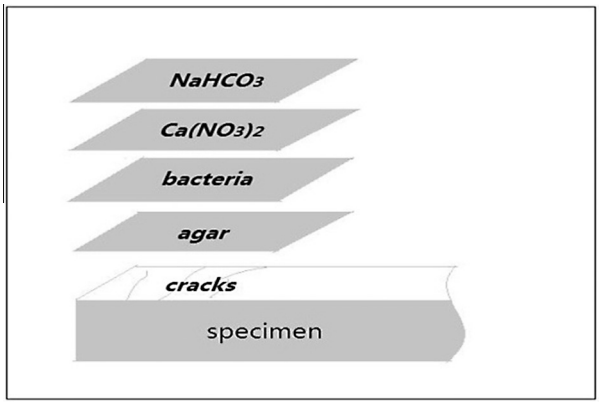

Fig. 1. Film-covering method on the surface of specimen.

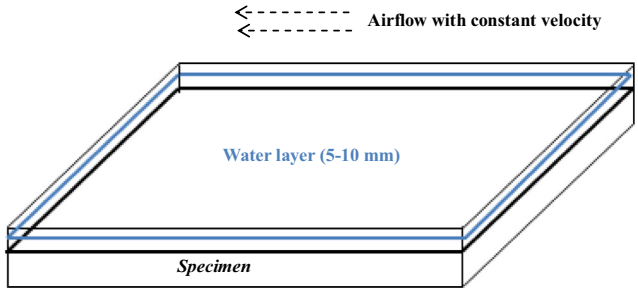

Fig. 2. Schematic diagram of accelerated test of efflorescence resistance of cement-based walls.

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