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Surface treatment of concrete bricks using calcium carbonate precipitation



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HIGHLIGHTS

• A new surface treatment method using mineral precipitation is proposed for porous materials.

• Durability and strength of the concrete can be significantly increased by the proposed method.

• The mineral precipitation produced by the proposed method has been identified as calcite.

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ABSTRACT

A new surface treatment method using mineral precipitation is proposed in this study for treating concrete and similar porous materials to enhance their durability and mechanical properties. The major innovation of this method is that a green solvent dimethyl carbonate (DMC) is used to replace expensive bacteria and their nutrients in the microbiologically induced calcite precipitation (MICP) method so that the drawbacks of the MICP method can be overcome. In the basic environment of concrete, DMC can be hydrolyzed slowly to produce carbonate which is then used to form calcium carbonate precipitant. The resulted calcium carbonate particles can then seal/fill the surface cracks/voids of the porous material, and therefore, enhance the durability and strength of the material. As verification, this method was used to treat concrete bricks. Testing data show that the water absorption of the concrete bricks can be significantly reduced and the compressive strength can be significantly increased by this method. The mineral precipitated on the surface of the treated specimens identified by scanning electron microscope imaging was confirmed as calcite by X-ray diffraction (XRD) analysis.

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1. Introduction

Masonry blocks including concrete or clay bricks can deteriorate in harsh environments. Because most deterioration mechanisms of masonry blocks are associated with water transport, the durability of these materials can be significantly enhanced by reducing their permeability. To this end, a variety of organic materials such as water-repellents, pore-blockers, and coatings are commonly used to treat the surfaces of masonry blocks. For example, DePasquale et al. [1] introduced water based systems containing silanes as water-repellent for rendering masonry surfaces. However, surface treatment with organic materials suffers a few drawbacks. Firstly, the thin organic layer formed on the surface of the treated materials is incompatible with the inorganic substrate. The mismatch in material properties between the organic film and the inorganic substrate can result in severe stress concentration along the interface between them, leading to potential debonding of the coating layer from the applied surface of the substrate. Secondly, the organic coating materials are vulnerable to ultraviolet radiation and can be easily oxidized in open air. Thirdly, organic materials used for coating can cause unpleasant effects on public health [1–4].

To overcome the shortcomings of using organic materials to reduce the water absorption of the masonry blocks, a new method, microbiologically induced calcite precipitation (MICP) has been proposed recently. In this method, bacteria are used to assist the enzymatic hydrolysis of urea [5,6]. Bacteria can produce urease as part of metabolism. The produced urease catalyzes the hydrolysis of urea to produce carbonate and ammonium, leading to high PH value in the surroundings [2]

$$CO(NH_2)_2 + 2H_2O \xrightarrow{\text{Urease}} 2NH_4^+ + CO_3^{2-}$$
(1)

The produced carbonate then combines with calcium ions to produce calcium carbonate precipitate







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$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3(s).$$

(2)

To treat the surface using MICP, a water-based medium consisting of bacteria, nutrients for bacteria, urea and calcium ions are applied to the surface to be treated, as shown in Fig. 1. The applied medium can penetrate into the cracks and pores and produce calcium carbonate precipitants which fill vacant spaces in the treated material and block the pathway of water to enter into the material. As a result, the water absorption of the treated material is reduced, as well as the potential of harmful chemicals entering into the material. The durability of the material is thus significantly increased [3,7].

Sarda et al. showed that MICP can reduce the water absorption on the surfaces of bricks up to 45% [8]. Dhami et al. conducted a similar treatment on ash bricks and then tested their water absorption, frost resistance and compressive strength. They found that calcite deposition is beneficial to durability by reduction in permeability and improve specimens overall compressive strength [9]. Raut et al. applied the MICP method on standard clay bricks using a medium especially optimized for urease production (OptU). They monitored the calcite precipitation for a period of 28 days and found that the new method improves the compressive strength by 83.9% and decreases the water absorption by 48.9% [10].

Despite all the potential capabilities of the MICP, there are some barriers preventing practical application of this technique. The largest barrier of the MICP treatment is its high cost. A recent study by De Muynck et al. (2010) shows that the cost of the MICP treatment based on the price of the microorganisms and the price of the nutrients could be as high as \$11–19/m² [2]. The inconvenient application procedure is another major barrier that prevents the MICP from practical application in construction industry. The sealing effects of MICP are dependent on many factors such as temperature, pH, concentration of donors and acceptors of electrons, concentration and diffusion rates of metabolites. Therefore, it requires high quality control of application and high skill of the workers. The MICP method also needs considerably longer time because the production of calcium carbonate precipitate is limited by the capacity of the bacteria to produce urease. In addition, the potential impact of the MICP method on environment and public health is another major concern if this technique is implemented in public places. Ammonia, the direct product of urea hydrolysis in the MICP method is a dominant pollutant in sensitive ecosystems and contributes to acidification. It can cause eutrophication in the biodiversity of semi-natural ecosystems [11]. Although the microbe itself is not a dangerous organism, it can be a potential threat if its side effects are neglected. In addition, sometime unwanted microbes can be induced by the MICP method.



Fig. 1. Treating the surface using MICP method: (a) surface pore filled with medium; (b) calcite precipitates and seals the pore.

2. Calcium carbonate deposition by hydrolysis of dimethyl carbonate (DMC)

In order to overcome the disadvantages of the MICP method in surface treatment, this study proposes a new routine to produce calcium carbonate precipitants on masonry blocks or other porous materials' surfaces without using any expensive bacteria. In the MICP method, urea is used as carbonate source to produce calcite precipitants. However, the hydrolysis of urea in ambient temperature is too slow. Therefore, bacteria are needed to produce urease which can accelerate the hydrolysis of the urea in ambient temperature. In this study, an organic carbonate, dimethyl carbonate (DMC) is used to provide the required carbonate to generate calcite precipitants. DMC is a green reagent with low toxicity and high biodegradability. DMC can be hydrolyzed slowly into methanol and carbonate in the basic environment at ambient temperature and pressure, as given by Eq. (3)

$$(CH_3O)_2CO(l) + 2OH(aq) \longrightarrow 2CH_3OH(l) + CO_3^{2-}(aq).$$
(3)

Methanol (CH₃OH) can be later oxidized in the air to carbon dioxide and water. By using Eq. (3), carbonate can be produced in controlled manner in ambient temperature without using any urease. Carbonate ions produced by this reaction can then react with calcium ions to form calcium carbonate deposition, as illustrated in Eq. (2). Faatz et al. showed that calcium carbonate precipitants can be successfully produced using the controllable hydrolysis of DMC to provide carbonate. They also found that the by-product of DMC decomposition, methanol, does not negatively affect the carbonate deposition [7,12].

3. Materials and methods

3.1. Treatment solution

Treatment solution mainly consists of calcium chloride (CaCl₂) as calcium source, DMC as carbonate source, and water. A small portion of sodium hydroxide (NaOH) is added to tune the pH value of the solution so that DMC can be hydrolyzed at a desired speed. The hydrolysis of DMC produces carbonates which react with calcium ions to form calcium carbonate. Since calcium carbonate has a low solubility in water, it will precipitate onto the surface of the masonry block and fill the pores and holes. The pathway of water permeation and subsequently penetration of the aggressive chemicals into the brick will be blocked if sufficient amount of carbonate precipitation forms.

3.2. Masonry block specimens

Concrete bricks with size of 177.8 × 88.9 × 44.5 mm (7" × 3 1/2" × 1 3/4") were purchased from a local distributer. Each brick was cut into four similar cubic pieces in size of 88.9 × 44.5 × 44.5 mm (3 1/2" × 1 3/4" × 1 3/4"). A group of control specimens was subjected to compression test. The average value of compressive strength was 20.9 MPa.

ASTM C140 [13] procedure was followed to determine the water absorption percentage of each specimen. In this regard, three representative full-sized units are needed for absorption test. Specimens were immersed and suspended by a metal wire and completely submerged in water at a temperature of $15-26 \degree C$ ($60-80\degree F$) for 24 h. After removing and allowing them to completely drain for 2 min, the visible surface water was removed with a damp cloth. They were weighed immediately for recording their saturated weight (W_s).

The specimens were dried in a ventilated oven at 100 °C to 115 °C (212–239°F) for not less than 24 h until two successive weights at intervals of 2 h show a difference of not greater than 0.2%. Then they were weighed to record the weight as the oven-dried weight (W_d). The water absorption percentage can be obtained by following equation:

Absorption,
$$\% = [(W_s - W_d)/W_d] \times 100$$
 (4)

where W_s is saturated surface dry weight, and W_d is the oven dry weight of the specimen, respectively.

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