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Quantification of chemical and biological calcium carbonate precipitation: Performance of self-healing in reinforced mortar containing chemical admixtures

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ABSTRACT

Cracks increase permeability affecting the durability of concrete. As they develop gradually, it is difficult to determine when to repair them. Self-healing materials can repair themselves gradually as cracks form. In this study, the isolated and combined effect of two self-healing agents for concrete, both based on calcium carbonate precipitation, was studied. Lightweight aggregates were impregnated with chemical and biological solution to be added as healing agents in concrete mixtures. The influence of two common chemical admixtures on the performance of the self-healing agents was also studied. All self-healing agents were able to seal cracks between 0.08 and 0.22 mm in width. The estimated effect of chemical agents on the mean healing was higher than that of biological agents. In addition, thermogravimetric analysis suggests the precipitates are different. Admixtures had no significant influence on the performance of self-healing agents.

1. Introduction

Concrete is a ceramic material susceptible to developing cracks when it is under tensile stress. Ceramic materials are generally characterized by ionic-covalent like bonds. The limited atomic mobility of this kind of bond imparts intrinsic brittleness to ceramics [1]. Moreover, these bonds make the material very strong to compressive stresses, but weak to tensile stresses. To compensate for this weakness, steel reinforcement is used in concrete due to its tensile strength and ductility. It should be noted that the role of steel in reinforced concrete is not to prevent concrete to deform or crack, but to take tensile stresses and control crack width.

Cracks below 0.05 mm in width are not usually a problem since concrete has the ability to seal them in a process called autogenous healing, and fully recovering it's mechanical and transport properties [2]. Autogenous healing is believed to be produced by swelling of the cement paste, hydration of the remaining unhydrated cement, precipitation of calcium carbonate ($CaCO_3$) crystals, and crack filling by impurities in water or by debris from the crack surface [3]. Of all these mechanisms, calcium carbonate precipitation (CCP) is the only one that can be intentioned and engineered to improve the self-healing capacity of concrete and is the primary focus of this research. In this research the effects of two different self-healing agents (chemical and biological) and two polar organic molecules (plasticizer and air-entrainer) were studied.

CCP has 4 key factors that could be managed to increase or decrease its effectiveness: (1) calcium ion (Ca^{2+}) concentration, (2) dissolved inorganic carbon (DIC) concentration, (3) pH (pK2 (HCO_3^-/CO_3^{2-}) = 10.3 at 25 °C), and (4) the availability of nucleation sites [4]. In addition, some organic molecules and bacteria can modify these factors increasing or decreasing CCP and can create different $CaCO_3$ polymorphs, such as calcite, vaterite, and aragonite [5].

Organic molecules can affect CCP by inhibition through Ca^{2+} sequestration, by acting as nucleation sites, or by modifying $CaCO_3$ precipitate to form other crystalline phases or amorphous phases. Negatively charged acidic functional groups that can sequester Ca^{2+} are carboxylic acids (R–COOH), hydroxyl groups (R–OH), amino groups (R–NH_2), sulfate (R–O–SO_3H), sulfonate (R–SO_3H),

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and sulfhydryl groups (–SH) [6]. These functional groups can also act as nucleation sites if the Ca^{2+} concentration is high [7]. Surfactants can also control the formation of the crystal phase by influencing the nucleation, crystal growth, and aggregation [8]. Likewise, amorphous phases are formed when the concentration of organic molecules is high and it can be stabilized against compaction and recrystallization [7].

The fact that some chemical admixtures for concrete have functional groups similar to those mentioned above might indicate that they can affect CCP and the healing process itself. For this reason, the effect of two chemical admixtures on CCP was studied: a common air-entrainer (surfactant) based on sodium naphthalene sulfonate formaldehyde condensate, and a common plasticizer based on calcium lignosulfonate.

Dupraz et al. [6] found that one of the fundamental controls of CCP is the "Alkalinity Engine" that can rely on an intrinsic (bacterial metabolism) and/or extrinsic (the environment) component. Since concrete has a pH above 9, due to the presence of calcium hydroxide, an intrinsic approach to increase pH with bacteria metabolism is not necessary. However, bacteria were also included in this study because they have been proven to increase the amount of precipitate [9].

CCP requires free calcium (Ca^{2+}), which can be externally provided in the form of calcium salts like calcium chloride or calcium lactate. Nevertheless, an internal source of calcium might be available in the hydrated cement paste in the form of calcium hydroxide, calcium silicate hydrates, or calcium aluminate hydrates, among others. In fact, calcium hydroxide naturally becomes calcium carbonate in a process known as carbonation. Carbonation is a form of concrete deterioration since it can reduce pH below the threshold needed to maintain the passivation of steel thus potentially speeding up the onset of corrosion. Even, bacteria's spores have calcium in its protective membrane [10] and could be a source for CCP.

Jonkers and Schlangen [9] proposed a two-component self-healing system based on the addition of bacteria and calcium lactate. The mechanism is based on the metabolic conversion of suitable organic compounds to calcite, e.g. represented by the bio-conversion of calcium-formate with portlandite present in the paste matrix.

The relative size of bacteria with respect to cement paste pores suggests that it cannot be directly embedded in the concrete matrix because there would not be enough space for bacteria to live. An attempt to overcome this problem was proposed through the immobilization of bacteria in porous glass beads (Siran TM) [11]. Another attempt to protect bacteria was proposed by Wang et al. [12] encapsulating silica gel or polyurethane with bacteria in glass tubes. Yet another approach used diatomaceous earth to host bacteria [12] and observed that cracks in the range from 0.15 to 0.17 mm in width were completely healed. Recently, porous lightweight aggregates were used to immobilize bacteria and calcium lactate [13]. After 100 days of immersion in water, it was obtained full crack healing for cracks up to 0.46 mm in width, which compared favorably to the 0.18 mm in width sealed in control specimens.

This research focuses on the performance of alternative self-healing agents that improve CCP and how such performance is influenced by common components present in concrete. The self-healing agents were based on calcium lactate, representing chemical CCP, and bacteria, representing biological CCP. The concrete's admixtures were calcium lignosulfonate (plasticizer) and naphthalene sulfonate formaldehyde condensate (air-entrainer).

2. Materials and methods

Reinforced mortar flexural specimens, each with different self-healing agents and chemical admixtures, were prepared, cured, cracked, and left to self-heal immersed in water at room temperature for 100 days. The mortar specimens were prepared using Ordinary Portland Cement, water, and siliceous sand. Three types of self-healing agents were prepared (Table 1): chemical agent (C) calcium lactate solution, biological agent (B) bacteria and yeast-extract solution, and both combined (CB). The agents were embedded in lightweight aggregate (LWA) according to Wiktor and Jonkers [13].

2.1. Bacteria selection and grow

Bacillus pseudofirmus LMG 17944 (Belgian coordinated collections of microorganisms, Ghent), a spore-forming facultative alkaliphilic bacteria, was used for this study. These bacteria grow in a pH range from 7.5 to 11.4 and can withstand large sudden increases in external pH [14].

Bacterial stocks were stored at −80 °C in glycerol. Bacteria were cultured for 4 h in liquid nutrient media according to the supplier's recommendations. The medium was comprised of 5 g peptone, 3 g meat extract, 10 mg $MnSO_4 \times H_2O$, 0.5% NaCl in 1 L MilliQ ultra-pure water. pH was adjusted to 9.7 with a solution of 0.42 g $NaHCO_3$ and 0.53 g Na_2CO_3 in 100 mL MilliQ ultra-pure water. This culture (batch 1) was used to inoculate a second culture (batch 2) to enhance spore formation according to [15]. Cultures were aerobically incubated in Erlenmeyer flasks on a shaker table at 250 rpm and 37 °C. The growth of bacteria was monitored using Optical Density set at 600 nm. Bacterial concentration was estimated with the most probable number method cultivation–dilution technique.

Bacteria were centrifuged for 20 min at 6000 rpm and re-suspended twice in sterile MilliQ ultra-pure water. The final concentration of bacteria was 1.5×10^9 cells/mL and it was stored at 4 °C (batch 3) until the preparation of the self-healing agent.

2.2. Preparation of self-healing agent

Self-healing agent consist in impregnated LWA with the chemical and/or biological solution. LWA used was expanded clay sieved between ASTM standards n°4 and 16 (4.75 mm and 1.18 mm). The Table 2 shows the main properties of the LWA used [16].

For the CB agent, the LWA particles were vacuum-impregnated with a solution of 50 g/L calcium lactate pentahydrate that corresponds to maximum solubility and 1 g/L yeast extract (according to Wiktor and Jonkers [13]), followed by a final impregnation step with bacteria at 4 °C from batch 3 (Section 2.1). After each impregnation treatment, LWA was oven-dried for 5 days at 37 °C. Impregnated LWA containing 2% by weight calcium lactate and 1.3×10^8 cells/g particles was obtained. The preparation of agents

Table 1
Nomenclature of mortar specimens used in this study.

Chemical admixture	No agent	Calcium lactate	Bacteria	Calcium lactate + bacteria
Self-healing agent				
No admixture	Control	C	B	CB
Plasticizer	P	CP	BP	CBP
Air-entrainer	AE	CAE	BAE	CBAE