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Effect of ion chelating agent on self-healing performance of Cement-based materials

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HIGHLIGHTS

- Ion chelating agent improves the pore size distribution and mechanical property of cement-based materials.
- Self-healing performance of mortar on freeze-thaw damage is obviously enhanced by ion chelating agent.
- Surface crack of width more than 0.3 mm of the mortar with ion chelating agent can be self-healed.

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ABSTRACT

Ion chelating agent, a novel crystalline additive, is used to improve the self-healing performance of cement-based materials on freeze-thaw damage and surface crack for prolonging service life of the construction. The pore size distribution, internal structure and compressive strength of mortar with ion chelating agent before and after freeze-thaw as well as self-healing were investigated by nuclear magnetic resonance, scanning electron microscope and mechanical property test. The width of surface crack of the mortar during self-healing was measured. The results show that the microstructure and mechanical properties of mortars are improved by ion chelating agent. After 28 days of curing, harmful pores (larger than 0.1 μm) proportion of mortar with 0.5 wt% ion chelating agent of the cement (C2) declines by 42.3%, compressive strength increases by 26.8%, and much needle-like crystals exists in pores comparing with the control mortar (C0). After 100 freeze-thaw cycles, the compressive strength loss, mass loss and harmful pores proportion of C2 reduce by 38.0%, 29.2% and 28.7% relative to C0. After curing in water for 28 days, the compressive strength recovery ratio of C2 is 51.8%, and lots of needle-like crystals are formed in pores and micro-cracks. Energy dispersive spectrometer analysis indicates that the main components of these needle-like crystals are calcium carbonate, CSH and ettringite. Besides, the surface crack of 0.32 mm width for C2 is self-healed and X-ray diffraction analysis shows that the self-healed product in the crack is calcium carbonate.

1. Introduction

The concrete is widely used as building structure materials, which are due to high strength, better durability and wide availability of raw materials [1]. However, the damages including internal micro-cracks and surface cracks of concrete are inevitable under the conditions of external load, freeze-thaw and temperature gradients with extension of service time. The damages will further accelerate the occurrence of chemical erosion and steel corrosion of the concrete, and negatively impact the durability of concrete structure [2–4]. Thus, as for the self-healing and controlling of concrete damages, the increasing attention has always been attracted. Indeed, the cement-based materials have limited self-healing ability for further hydrated and swelling of unreacted particles [5,6], and the self-healing phenomenon has been firstly reported by the French Academy of Science in 1836 [7]. However, the self-healing ability of cement-based materials is weak, which can only make the narrow crack width less than 60 μm be healed [8]. Therefore, in order to improve the self-healing ability for internal micro-cracks and surface cracks of cement-based materials, many innovative self-healing techniques have been explored [9]. Three kinds of typical techniques have been applied to achieve self-healing in cementitious materials: (1) microcapsule [10], (2) microbes [11] and (3) crystalline additive [12]. The microcapsule technique is that once a crack occurs in the concrete, the pre-embedded microcapsules rupture and release healing agent to heal the crack [13–17]. The technique of microbes uses the bacterial

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spores to react with nutrient solution and generate calcite for repairing the cracks [18,19]. But the difficult manufacture of microcapsule, short survival time of microbes as well as their negative influence on concrete mechanical properties is main problems for their engineering application.

The crystalline additive is used to repair the cracks by promoting un-hydrated cement and other active components to form the crystalline products in concrete [20,21]. The self-healing technology of crystalline additives has many advantages, such as convenient operation, long effective period and performance improvement of concrete. Roig-Flores [22] evaluated the self-healing of surface cracks of concrete with crystalline admixtures under different curing environments. The results showed that the self-healing efficiency of concrete under water immersion was the most excellent than that under water contact, humidity chamber and air exposure, the highest self-healing rate of initial crack width around 0.25 mm of concrete was 95% after 42 days under water immersion. Sisomphon [23,24] investigated surface cracks self-healing of mortar with Xypex admixture C-1000NF crystalline additive and calcium sulfoaluminate based expansive additive. They found that the surface cracks with the width of 0.20–0.25 mm of mortar with crystalline additive were completely closed after curing for 28 days in wet environment, and the compound of calcium sulfoaluminate based expansive additive and crystalline additive improved the self-healing ability of mortar. Jiang [25] demonstrated that the self-healing capacity of mortar surface crack was increased by adding silica-based materials, chemical expansive agents, swelling minerals and crystalline components, and the crack self-healing rate of the maximum crack width around 0.3 mm on mortar with crystalline components was 0.80 after 28 days under water immersion. The researches about crystalline additive mainly focus on surface crack self-healing of cement-based materials. Little research is reported on the influence of crystalline additive on microstructure and freeze-thaw damage self-healing of cement-based materials. Besides, the self-healing ability of cement-based materials with existing crystalline additive is weak.

The ion chelating agent made by our laboratory is a novel crystalline additive. It first forms a water-soluble chelate with calcium ions, then migrates to pores and cracks in wet environment, and reacts with unhydrated cement or other active substances to produce self-healing crystallization products. The self-healing process is shown in Fig. 1. The ion chelating agent can prolong service life of construction by improving the self-healing property of concrete.

In this paper, the effect of ion chelating agent on self-healing performance of cement-based materials was investigated. The pore size distribution, internal structure and compressive strength of mortar with ion chelating agent before and after freeze-thaw as well as self-healing were investigated by nuclear magnetic resonance, scanning electron microscope and mechanical properties test. Surface crack width of the mortar during self-healing was measured. Self-healing production component in internal and surface crack of the mortar were analyzed.

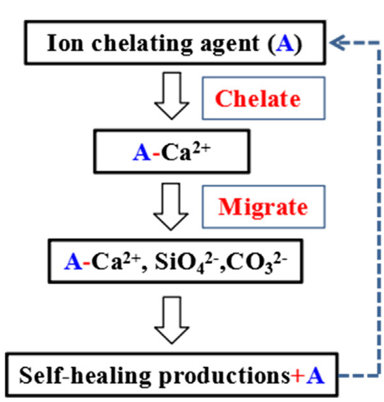

Fig. 1. Self-healing process of ion chelating agent.

2. Experimental

2.1. Materials

The ordinary Portland cement (CEM I 42.5 N) was provided by Huaxin Cement Co. Ltd, Wuhan, China, and the chemical composition of cement is given in Table 1. Medium size sand with a soil and water amount less than 1% was used. The ion chelating agent was prepared by reaction of 100 parts maleic anhydride, 100 parts deionized water, 30 parts hydrogen peroxide solution with a volume concentration of 30% and 100 parts sodium hydroxide solution with a concentration of 0.10 mol/L at 90–95 °C according to Ref. [26], whose amount of chelating calcium ion is 813 mg/g.

2.2. Specimen preparation

The formulation designs of mortars are shown in Table 2. In the process of preparing mortars, the ion chelating agent was added in mixed well with cement and sand after being dissolved in water. The mixing sequence was 90 s in (140 ± 5) r/min and followed by 90 s in (285 ± 10) r/min by a cement mortar agitator. And mortars were casted in molds with a size of 70.7 mm × 70.7 mm × 70.7 mm. The filled containers were vibrated for 30 s on a vibrating table. The mortars were demolded after 24 h and subsequently placed in a standard curing room with a controlled temperature of (20 ± 2) °C and a RH 95%. Five pieces of each kinds of mortars were tested for compressive strength and pore size distribution after 28 days of standard curing. And twenty pieces for each kinds of mortars were used for freeze-thaw cycle test after 24 days of standard curing and 4 days of soak.

2.3. Freeze-thaw cycles and self-healing of mortars

The mortar specimens were placed in (−20 ± 2) °C cooler for 4 h, then the samples were moved to (20 ± 2) °C wet curing box for 4 h, keeping a freeze-thaw cycle for 8 h. When the freeze-thaw cycles reached 25, 50, 75 and 100 times respectively, several mortar specimens were taken out from the set-up of freeze-thaw cycles, then the mass and the compressive strength were measured.

After freeze-thaw cycles for 100 times, the mortar specimens were put into water for 28 days as a self-healing process. The compressive strength and pore size distribution were measured before and after self-healing process.

Table 1
Chemical composition of cement (wt.%).

SiO_2	Al_2O_3	CaO	MgO	SO_3	Fe_2O_3	Loss
24.06	6.34	59.89	0.98	2.24	3.56	1.3

Table 2
Mix design of mortars by mass ratio.

Mix	Cement	Water	Sand	Ion chelating agent
C0	100	50	300	0
C1	100	50	300	0.3
C2	100	50	300	0.5
C3	100	50	300	1.0

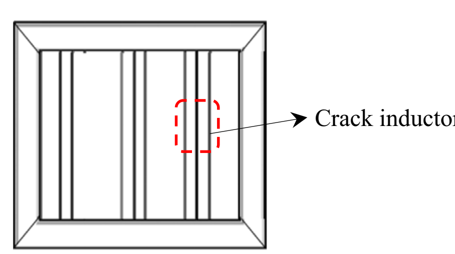

Fig. 2. Mold for specimen precast cracks.