Cement and Concrete Composites 69 (2016) 9–17

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Preliminary study on mitigating steel reinforcement corrosion with bioactive agent

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ARTICLE INFO

Article history:
Received 3 April 2015
Received in revised form
11 January 2016
Accepted 10 February 2016
Available online 20 February 2016

Keywords:
Corrosion
Reinforcing steel
Lightweight aggregate
Encapsulation
Bioactive agent
Cinnamaldehyde

ABSTRACT

Corrosion causes over $100 billion in damage annually. Cinnamaldehyde, a bioactive agent derived from cinnamon bark, can mitigate the corrosion of metals but has a negative effect on hydration when incorporated in cementitious systems. In order to avoid these negative consequences while harnessing anti-corrosive properties, cinnamaldehyde was incorporated in a cementitious mixture through the use of lightweight aggregate (LWA). The same method was used for penetrating corrosion inhibitors in an attempt to reduce the time required for the inhibitor to reach and protect reinforcing steel. The setting time, compressive strength, heat evolution (via semi-adiabatic calorimetry), and autogenous shrinkage of the experimental mixtures were measured and an accelerated corrosion test (ACT) was used to quantify performance in a corrosive environment. Experimental mortars showed prolonged setting times, reduced compressive strength, heat evolution, and autogenous expansion. However, the experimental mortars showed an increase in time to cracking when exposed to a corrosive environment.

1. Introduction

The corrosion of reinforcing steel in concrete reduces the service life of a structure [1,2]. This phenomenon commonly begins when a structure is exposed to aggressive media (e.g., chloride ions from deicing salts or seawater) which depassivates the steel and leads to the formation of expansive deterioration products, primarily iron oxides [3]. As iron oxides accumulate and expand during corrosion, pressure builds, which eventually leads to cracking and spalling of the concrete cover [4,5]. Cracks are particularly undesirable because they immediately reduce many mechanical properties, most importantly compressive strength, and provide aggressive media access to the reinforcing steel, which accelerates the cycle of deterioration [6,7]. Additionally, corrosion of reinforcing steel can suffer from mass loss and therefore create a reduction of its cross-sectional area; this can result in a reduction of the mechanical properties of the steel [3,8].

Several methods have been adopted for corrosion mitigation. Epoxy coatings can slow the interaction of chloride ions with rebar [8,9]. Two other options include galvanized reinforcement, which provides protection through sacrificial corrosion, and stainless steel rebar, which is highly corrosion resistant but cost prohibitive to use [8,10]. Another form of protection is the use of waterproofing membranes, whereby a barrier segregates the rebar from chloride ions [8,11]. In cathodic protection, either current is impressed to polarize the reinforcement or a sacrificial anode is placed to protect the rebar [12]. Corrosion inhibitors such as calcium nitrite act as an anodic inhibitor when added to the concrete mix, forming a protective oxide film on the rebar [13]. Penetrating corrosion inhibitors are surface applied and travel into the concrete to protect the steel reinforcement [14,15]. Although these and many other corrosion mitigation methods are currently on the market, $100 billion is expended annually worldwide to maintain and repair corrosion related damage [16,17]. Therefore, new and innovative corrosion prevention methods are a necessity.

Research has demonstrated that natural bioactive agents such as cinnamaldehyde mitigate corrosion by forming a protective film on the surface of metals [18,19]. Cinnamaldehyde, a derivative of cinnamon bark [20], has been used as a flavor enhancer in food and in the medical field for generations to alleviate health concerns such as diabetes [21]. When incorporated in a cementitious matrix, bioactive agents can coat cement particles and inhibit the hydration of the cement reducing compressive strengths at all ages [22,23].

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http://dx.doi.org/10.1016/j.cemconcomp.2016.02.011
0958-9465/

Table 1
Sand and LWA distribution.

Sieve No.	Mesh size	Percent retained (%)
8	0.0937 in. (2.36 mm)	14.6
16	0.0469 in. (1.18 mm)	16.0
30	0.0234 in. (600 μm)	26.2
50	0.0117 in. (300 μm)	34.2
100	0.0059 in. (150 μm)	9.0

Larger LWA particle sizes (retained on sieve No. 8 and No. 16) were used to prevent the internal agents from remaining on the surface of the LWA. The total distribution remained constant throughout all mixtures.

This experimental program introduces a novel approach to incorporating these bioactive agents without interfering with the properties of the concrete; this is by encapsulation in lightweight aggregate[1] (LWA) [24,25]. Conventionally, LWA is pre-wet with water and over time an internal drop in humidity due to cement hydration causes the liquid absorbed by the LWA to be released. Therefore, if the corrosion inhibitor is soaked in LWA instead, it will be released once the early-age properties have developed [26]. After release, the bioactive agent should migrate towards the reinforcing steel and protect against corrosion. The same concept can also be applied to the use of conventional penetrating corrosion inhibitors. When penetrating corrosion inhibitor is applied to the surface of a structure, the time for it to reach and protect the rebar may be shortened if the inhibitor is encapsulated in the LWA.

This experimental program focuses on creating an innovative LWA encapsulated inhibitor that can be added to a cementitious mix in order to protect the reinforcing steel from corrosion and extend the service life in a corrosive environment. Because of the unknown impact of the internal agents (cinnamaldehyde, penetrating corrosion inhibitor, or water) incorporated via lightweight aggregate, experiments were conducted to examine the mechanical and chemical properties of these cementitious systems. Five tests were carried out to characterize the changes in compressive strength, setting time, semi-adiabatic calorimetry, air content, and autogenous shrinkage. Additionally, to assess the performance of the mortars when subjected to a corrosive environment, an accelerated corrosion test (ACT) was conducted along with characterization of electrical resistivity over time.

2. Experimental investigation

2.1. Materials and methods[2]

All mixes were prepared with commercially available ASTM C150 Type I/II cement. Local sand was used throughout and the particle size distribution was determined by sieve analysis. Sand retained on sieve sizes No. 8, 16, 30, 50, and 100 were included in all mix designs. Sieve sizes as well as their corresponding mesh size are detailed in Table 1. The three liquids that were soaked and encapsulated within the LWA were: cinnamaldehyde (C_9H_8O), a commercially available penetrating corrosion inhibitor, and water. Expanded shale LWA (Northeast Solite Corporation) was used to encapsulate the internal agents. In order to reduce the amount of cinnamaldehyde entering a mix, fine LWA particles (which retain cinnamaldehyde on the surface because of its high surface area) were removed and only LWA retained on a No. 8 or No. 16 sieve (Table 1 for sieve mesh size) were used in the production of samples.

To encapsulate the liquids into the LWA, LWA was soaked at room temperature in the appropriate liquids for at least 24 h in an airtight container. The amount of liquid encapsulated into the LWA was determined by the absorption capacity provided by the manufacturer of LWA (17.5% by mass of LWA). These LWA-soaked liquids were incorporated into the mix at a saturated-surface-dry (SSD) state. A water:cement (w/c) ratio of 0.4 (not including any water added via LWA, if applicable) and a 55% volume fraction of aggregate were used in all mix designs. Since the specific gravity between encapsulated liquids differ, therefore the volume of all encapsulated liquids remained at 75 cm^3 (4.6 in^3) in order for comparison purposes. Aggregates were either sand or a mix of LWA and sand. LWA replaced sand on a volumetric basis in order to ensure a constant particle size distribution and accurate comparison between mixtures.

A total of six mortar mixes were produced (Table 2). Mix 1 was a control where only sand, cement and water were used. Mix 2 included cinnamaldehyde-LWA inhibitor; Mix 3 was the same as Mix 2, but included water instead of cinnamaldehyde. Mix 4 contained penetrating corrosion inhibitor-LWA; Mix 5 was the same as Mix 4, but with water in place of the penetrating corrosion inhibitor. In this way, Mixes 1, 3, and 5 served as controls enabling the identification of changes in physicochemical properties due to the incorporation of LWA (as opposed to due to the cinnamaldehyde and penetrating corrosion inhibitor). In a final mix, Mix 6, penetrating corrosion inhibitor was applied to the surface in three 24 h intervals 24 h after demolding. Mix 6 was used for comparison purposes and underwent only the accelerated corrosion test where it was evaluated for electrical resistivity and mass steel loss (setting time, compressive strength, air content, semi-adiabatic calorimetry, and autogenous shrinkage were not tested on Mix 6 since penetrating corrosion inhibitor was applied to the surface and therefore made those tests not applicable).

X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were conducted on the as-received ordinary portland cement (OPC) for quality control purposes (Fig. 1). Alite (C_3S), belite (C_2S), and celite (C_3A) were detected by XRD. Five bands were identified with FTIR. Bands at 601.8 cm^{-1} and 663.5 cm^{-1} were due to Si—O vibrations; the band 881.5 cm^{-1} was due Si—O, Al—O, CO_3^{2-} vibrations; the band at 1153.4 cm^{-1} was due to S—O vibrations; and the band at 1438.9 cm^{-1} was due to CO_3^{2-}. These results are consistent with standard ready-mix ordinary portland cement.

Compressive strength tests were performed according to ASTM C109. Mortar was placed in 2 in. (50 mm) cube molds, which were then placed in a plastic bag, stored in a fog room, and demolded after 24 h. The cubes were stored uncovered at 70 °F (21 °C) and 99% humidity during curing. Three mortar cubes from each mix design were tested at ages of 3, 7, and 28 d. Setting time was determined in accordance with ASTM C191 and the air content of the mortar was measured in accordance with ASTM C185. Air contents were measured to be 3.8% (Mix 1), 2.2% (Mix 2), 3.5% (Mix 3), 4.4% (Mix 4), and 3.1% (Mix 5). This suggests that the air content is not significantly impacted by the internal agents, and was not further investigated.

Semi-adiabatic calorimetry was used to characterize potential interference in hydration reactions due to the additional liquids (cinnamaldehyde, penetrating corrosion inhibitor, and water), which would appear as an alteration of heat evolution during the exothermic cement hydration processes. Specimens were cast in 4 × 8 in. (100 × 200 mm) cylinder molds with type K thermocouples embedded in the center. The entire cylinder was insulated and the rise in sample temperature recorded for 3 d.

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[1] Lightweight aggregate is abbreviated as LWA.

[2] Certain commercial equipment, instruments, or materials are identified in this report in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.