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Application of wire beam electrode technique to investigate the migrating behavior of corrosion inhibitors in mortar

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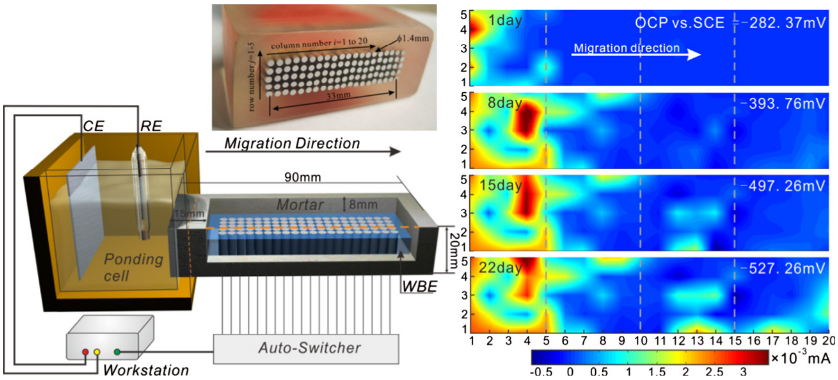
HIGHLIGHTS

- Wire beam electrode technique can evaluate the migration of inhibitor under mortar.
- Preferential absorption of MCIs were directly detected by using WBE technique.
- The so-called pore-blocking effect of MCI could be distinguished by using WBE technique.

GRAPHICAL ABSTRACT

The migration rate and inhibitive effect on rebar corrosion of migrating corrosion inhibitors (MCIs) in mortar were studied using wire beam electrode technique with high temporal and spatial resolution. The MCIs readily diffused through the mortar but exhibited preferential adsorption on the bare metal surfaces rather than on the rust layer on rebars. The ingress of MCIs in mortar increased the general corrosion resistance. This increase was mainly attributed to the sealing effect on mortar pores (pore-blocking effect) rather than on chemical absorption.



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ABSTRACT

The migration rate and inhibitive effect on rebar corrosion of migrating corrosion inhibitors (MCIs) in mortar were studied using wire beam electrode technique with high temporal and spatial resolution. The MCIs readily diffused through the mortar but exhibited preferential adsorption on the bare metal surfaces rather than on the rust layer on rebars. The ingress of MCIs in mortar increased the resistance on general corrosion much more than localized corrosion. This increase was mainly attributed to the sealing effect on mortar pores (pore-blocking effect) rather than on chemical absorption.

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1. Introduction

The prevention of reinforcement corrosion is commonly achieved in the design stage by adopting high-quality concrete, adequate cover, and admixing inhibitors in fresh concrete. However, a surface-applied inhibitor, also called migrating corrosion inhibitor (MCI), is a very attractive option for matured concrete structures that show signs of corrosion because of its cost-effectiveness and ease of application [1,2]. MCIs are mainly composed of alkanolamines and amines or amino carboxylate [3], which are highly volatile ingredients that help MCIs penetrate the concrete cover of reinforcing steels through liquid capillary suction and gaseous phase diffusion [4]. The migration rate and inhibitive effect on a corroded rebar [5,6] are both important to evaluate MCIs. Many works [1,4] have proved the migration rate of MCIs via concentration profiles in concrete. However, the conclusions on the inhibitive efficiency of MCIs are highly controversial [7]. Ngala et al. [7] determined that for ethanolamine-based inhibitor-treated specimens, the corrosion rate of already-corroded steel only decreases in noncarbonated concrete with low levels of chloride (0.3% by cement wt.), at higher levels of chloride (>0.6%), or in carbonated specimens. The ethanolamine-based inhibitor is also nearly ineffective. Ormellese et al. [8] found that ethylene amine can effectively enhance the pitting potential of rebar in simulating pore solution. Similar results were also obtained by El-Hacha et al. [9] and Morris and Vázquez [10]. Clearly, the inhibitive effect of MCIs depends highly on both the migration rate and corrosion state of a rebar.

Pitting corrosion is the most common corrosion type on rebars [11,12], in which pits grow and control the service life of concrete structures [13,14]. Thus, the key point is whether MCIs can effectively retard the growth of pits. As generally known, pitting tends to occur in areas with sufficient chloride ions and low pH or physical heterogeneities, such as inclusions and grain boundaries [12]; to inhibit the corrosion of rebars, MCIs must migrate into the pit cavity, rehabilitate the damaged passive film, and hinder Cl^- ion influx. Moreover, given that the squeezed rust layer formed on rebars because of the volume expansion under concrete cover [15], whether or not the MCIs could penetrate through the barrier was not clearly known.

Another view of inhibition efficacy of MCIs is the pore-blocking effect [16,17], which is derived from the works of Nmai [18] and Tritthart [4]. The mechanism of this effect is briefly attributed to the formation of insoluble fatty acid salt generated by the reaction of carboxylic acid ingredient with the hydroxyl in highly alkaline conditions; the formation of the insoluble fatty acid fills the concrete pores and blocks concrete porosity [17]. This effect is apparently inclined to be a physical blocking rather than a corrosion inhibitive action from an electrochemical point of view. However, the influence of physical blocking, which is rarely discussed in literature, cannot be evaluated in isolation easily [16,17].

A multi-electrode technique (also called wire beam electrode, WBE) composed of many arrayed wire electrodes is adopted in the present work to investigate in situ the localized corrosion on rebars under a concrete cover. This technique was successfully applied in studies on heterogeneous corrosion beneath coating [19], soil [20], and biofilms [21]. In our previous work [22], the expansion behavior of localized corrosion on rebars under a concrete cover without inhibitors was studied using the WBE technique. The subtle change on position and intensity of the localized corrosion can be exhibited by continuously mapping the potential, galvanic current, impedance, and corrosion rate distributions on the WBE surface [23], thereby facilitating the study on the mechanisms of migration and inhibitive effects of MCIs. Conventional electrochemical methods, such as half-cell potential, linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS), are widely used to assess the uniform corrosion rate of rebars and the inhibitive effect of MCIs. However, these methods fail to indicate the change on position and the intensity of pitting corrosion.

In this work, a mortar specimen embedded with a WBE was equipped on a customized ponding cell to simulate the migration of inhibitors. Three types of inhibitors [i.e., dimethylethanolamine (DMEA), triethylenetetramine (TETA), and $NaNO_2$] were chosen for comparative study [24]. The difference in migration behavior and inhibitive effect among the three inhibitors on pre-corroded WBE was studied with the spatial resolution of the WBE technique. Several assistive experiments, which support the mechanism proposed from WBE and help answer the influence of the pore-blocking effect, were also conducted in this work.

2. Experimental

2.1. Mortar preparation

All mortars used for casting in each test were manufactured with ordinary Portland cement with water/cement/standard sand (ISO679 EN 196-1) at a mass proportion of 0.6/1/2.5 [25]. The fresh mortar specimen was initially compacted with a laboratory vibrator, and then demolded and cured at 95% relative humidity (RH) for 28 days at 20 ± 3 °C.

2.2. Migration cell with WBE

A WBE was fabricated with 100 identical wires (1.4 mm diameter) of Q345B mild steel with a total working area of 1.54 cm^2. All wires were arranged regularly into a 5×20 rectangle array and embedded in epoxy resin at an interval of 0.3 mm from one another for electric insulation (Fig. 1) [26,27]. The chemical composition of Q345B (wt%) was as follows: C 0.18, Mn 0.42, Si 0.30, $P \leqslant 0.035$ and $S \leqslant 0.035$, Fe balance. The exposed face of the WBE was ground subsequently with 400, 800, and 1000 grit SiC paper and cleaned with deionized water and ethanol.

The WBE was placed at the center of a $90 \times 50 \times 20$ mm mold and then casted with a mortar. After demolding and curing, the left terminal of the WBE mortar specimen was tightly clamped with a plexiglass ponding cell, as shown in Fig. 2. An 8 mm-thick mortar cover was adopted to ensure an adequate oxygen supply [22,28]. A 15° tilt angle was adopted to facilitate the horizontal diffusion of MCIs through the specimen.

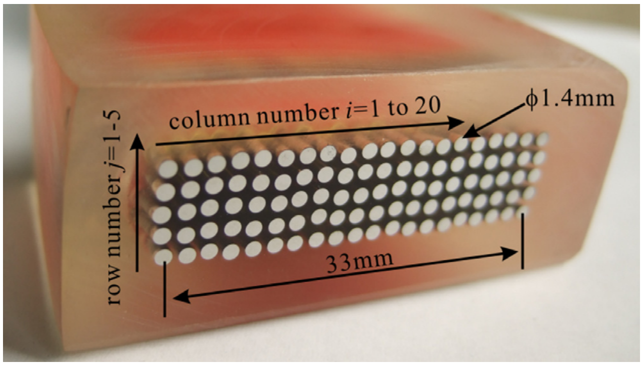

Fig. 1. Photograph of a 5×20 rectangular shape wire beam electrode (WBE).