



Effect of mill scale on the long-term corrosion resistance of a low-alloy reinforcing steel in concrete subjected to chloride solution

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HIGHLIGHTS

- The corrosion resistance of steel is influenced by the mill scale.
- Typical pitting corrosion is highlighted for pickled steels.
- Pickled low-alloy steel has increasing corrosion resistance after long-term exposure.

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ABSTRACT

This study investigated the corrosion performance of reinforcing steels in concrete exposed to flowing 3.5 wt% NaCl solution for 4 years. Two kinds of steels were selected: low-carbon (LC) steel and low-alloy (LA) steel with alloying element Cr. Both steels were prepared with two surface conditions: as-received one (with mill scale) and pickled one (removal of the mill scale). The microstructure of the steel-concrete interface was observed to investigate the effect of steel type and surface condition on the corrosion pattern. The results reveal that the corrosion resistance and the corrosion pattern of steels were largely influenced by the feature of the mill scale.

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1. Introduction

Steel corrosion due to carbonation or chloride attack is one of the major causes of deterioration of reinforced concrete (RC) structures [1,2]. As steel corrosion products are approximately 2–6 times volume of original steel [3–5], with corrosion progresses, the expansive products are formed at the steel-concrete interface and cause concrete cover cracking by generating pressures on the surrounding concrete. Once penetrating into the cover, these cracks will accelerate the ingress of aggressive agents and cause further deterioration and even spalling of concrete. Therefore, corrosion-induced cover cracking is usually defined as the end of service life of RC structures [6] and research in this issue is of significant importance.

One way to improve the sustainability and prolong the service life of RC structures is to utilize reinforcing steel that has been microstructurally designed to resist corrosion [7,8]. Recently, a

new type of reinforcing steel, namely alloy steels, have emerged and are expected to use in RC structures exposed to marine environment [9–18]. These steels were rolled with different amounts of Cr and other alloying elements to improve the corrosion resistance of steels [9,12,19,20]. However, contradictory results were obtained in the literature [10,13,14], indicating that alloy steels may not always perform better than conventional low-carbon (LC) steel in some situations. Trejo and Monteiro [10] reported that alloy steel exhibited unexpected lower critical chloride threshold level and higher corrosion rate than LC steel embedded in concrete exposed to chloride contaminated environment. Balma et al. [13] also found that alloy steel performed equally bad as conventional LC steel in chloride contaminated concrete.

Another important factor affecting steel corrosion is the steel surface condition (with and without mill scale) [15,21–23]. Consequently, the influence of mill scale that exists on the surface of reinforcing steels should be considered when studying corrosion process and developing concrete cracking models [24]. Although it was reported that the presence of mill scale was detrimental to the corrosion resistance of LC steels [25–27], the mill scale of LC

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steels was not removed due to the high cost of removal process and the possible environmental pollution [8]. Thus, it is important to know the effect of mill scale on the corrosion resistance of alloy steels and to determine the feasibility of the removal of the mill scale when alloy steels may be utilized in RC structures.

In addition, it is accepted that concrete is a porous material and contains voids, so that corrosion products may diffuse into it without applying stresses on the concrete cover [6]. Furthermore, the concept of the “porous” or “diffusion” zone at the steel-concrete interface was introduced to describe a region of concrete around the reinforcing steels which can accommodate expensive corrosion products, delaying stress development in the concrete [28–30]. Accordingly, it is directly related to the corrosion pattern of steels (penetration of corrosion products) and to the model predictions of time-to-cracking of concrete cover. It should be noted that the transformed medium (TM) by Chitty et al. [31] and L’Hostis et al. [32], the corrosion accommodating region (CAR) by Michel et al. [30] and corrosion-filled paste (CP) by Wong et al. [3] and Zhao et al. [24] all refer to this region. Despite this, the corrosion pattern of alloy steels at the porous steel-concrete interface after long-term exposure to marine environment is still open to discuss.

Therefore, the objective of this study was to investigate the influence of mill scale of LC steel and a novel low-alloy (LA) steel on the long-term corrosion resistance in concrete partially submerged into flowing 3.5 wt% NaCl solution for 4 years by means of electrochemical techniques. Furthermore, the distribution of corrosion products of both LC and LA steels at the steel-concrete interface was evaluated.

2. Experimental

2.1. Materials and specimen preparation

The mixture proportions of the concrete specimen are presented in Table 1. Portland cement (P-II 42.5R) was used for the preparation of concrete specimens and its chemical composition is given in Table 2. The coarse and fine aggregates in concrete were gravel at 10 mm maximum size and river sand with fineness modulus of 2.4, respectively. Tap water was used for concrete casting.

Two kinds of ribbed reinforcing steels with 10 mm diameter were selected: low-carbon (LC) steel and low-alloy (LA) steel. Their chemical composition is listed in Table 3, further analysis of the LA steel can be obtained in previous studies [14,15]. The microstructure of LC and LA steels is similar, showing two dominant phases (brighter ferrite and darker pearlite) (Fig. 1).

The microstructure of the mill scale on steel surface is shown in Fig. 2. Notably, imperfections can be observed for the mill scale of LA steel, whereas LC steel has a relatively uniform mill scale (Fig. 2). Fig. 3 shows the cross-sectional images of the mill scale and the steel substrate. Defects and crevices can be detected for LC steel (Fig. 3a), whereas the interface of mill scale and steel substrate of LA steel is slightly more compact (Fig. 3b). However, it is evident from the EDS results (Fig. 3b) that the content of Cr in the mill scale of LA steel is much lower than that in the steel substrate, which is in good agreement with the previous investigations [8,33].

Table 1
Mixture proportions of concrete specimens.

| Material | kg/m ³ |
|------------------|-------------------|
| Cement | 352 |
| Water | 187 |
| Fine aggregate | 705 |
| Coarse aggregate | 1057 |
| w/c ratio | 0.53 |

Table 2
Chemical composition of Portland cement.

| Oxide | wt.% |
|--------------------------------------|-------|
| CaO | 64.11 |
| SiO ₂ | 20.60 |
| Al ₂ O ₃ | 5.03 |
| Fe ₂ O ₃ | 4.38 |
| MgO | 1.46 |
| SO ₃ | 2.24 |
| Na ₂ O + K ₂ O | 0.57 |
| Loss on ignition | 1.30 |

Table 3
Chemical composition of LC and LA steels (GB1499.2-2013).

| Element | LC (wt.%) | LA (wt.%) |
|---------|-----------|-----------|
| C | 0.22 | 0.20 |
| Si | 0.53 | 0.65 |
| Mn | 1.44 | 0.57 |
| P | 0.025 | 0.027 |
| S | 0.022 | 0.008 |
| V | 0.038 | 0.032 |
| Cr | – | 0.86 |
| Cu | – | 0.06 |
| Ni | – | 0.03 |
| Fe | Bal. | Bal. |

A first group of steels was used in as-received condition and no efforts were made to remove the existing mill scale, while a second group of steels was pickled in diluted hydrochloric acid to remove the mill scale (Fig. 4). In this way, four types of steel specimens, as-received LC, as-received LA, pickled LC and pickled LA, were prepared in this study. The steel specimens were coated with insulating tape and epoxy resin in both ends, leaving the exposure length of 10 cm (Fig. 4). The interface of steel and coatings (insulating tape and epoxy resin) was carefully sealed with sealant to mitigate the possible crevice corrosion. After long-term exposure, no evident crevice corrosion was found for all steel specimens. A copper wire was electrically connected to one end of the steel for electrochemical measurements.

According to Table 1, the fresh concrete was poured into a prismatic mould (200 mm length, cross-section of 50 mm × 50 mm) where the steel was centrally placed along its longitudinal axis (Fig. 5). Therefore, the cover thickness of concrete specimens was 20 mm. Triplicate concrete specimens were prepared for each case to ensure the reproducibility of results. The concrete specimens were demoulded after 24 h, and then stored at standard curing room for 28 days prior to exposure.

2.2. Long-term exposure

After curing, both ends of concrete specimens were coated with epoxy coating to avoid the penetration of chlorides through the ends. Afterwards, concrete specimens were partially submerged into flowing 3.5 wt% NaCl solution for 4 years to simulate the marine environment (Fig. 6) [34]. NaCl solution was exchanged at regular intervals in order to ensure the constant chloride concentration. Three water pumps were employed to accelerate the flow of NaCl solution in order to simulate the tidal and splash zones in marine environment (Fig. 6).

2.3. Electrochemical measurements

Electrochemical tests were performed with three-electrode arrangement by a P4000 electrochemical workstation. Saturated calomel electrode (SCE) was used as the reference electrode. The reinforcing steel (embedded in concrete) and a stainless steel plate

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