



Investigation of the major reduction reaction occurring during the passivation of galvanized steel rebars

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ABSTRACT

The corrosion behaviour of zinc plates immersed in calcium hydroxide saturated solutions in the presence of oxygen, air and nitrogen, respectively, was studied. The corrosion resistance was monitored by potentials and corrosion rate measurements. The results obtained were confirmed by further data collected on galvanized rebars embedded in concrete and stored in different curing environments. The results clearly show that oxygen is the main oxidizing agent and indeed not water for the rapid formation of an effective passivation layer on zinc coating.

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1. Introduction

Galvanized rebars were first used in reinforced concrete structures exposed to tropical marine environment. The increased service life obtained in this way [1] extended their use also to other aggressive environments such as in the presence of de-icing salts.

The zinc coating on rebars embedded in concrete acts as a threefold protective effect: a barrier effect avoiding direct contact between the coated reinforcing steel and the aggressive environment, a sealing effect on coating discontinuities due to the zinc corrosion products and finally, the active sacrificial galvanic effect in the damaged or discontinuous areas of the coating [2].

Zinc is an amphoteric metal which undergoes severe attack either in acid or in basic media [3]. In alkaline medium particularly, zinc dissolves as zincate ion, $Zn(OH)_4^{2-}$. As reported by many authors [4–6] this dissolution continues until the solution becomes oversaturated by these ions which then precipitate as $Zn(OH)_2$ (or ZnO) thereby forming a continuous passivating layer.

In the presence of $Ca(OH)_2$, as in the concrete pore solution, the protective layer is formed not only by zinc oxide and hydroxide but also by a well packed and protective layer of calcium hydroxyzincate (CAHZ) [7–12]. The pH seems to largely influence not only the type but also the morphology of the developed corrosion products [13,14].

The zinc coating microstructure also influences its corrosion resistance to a large extent [15]. In fact the passivation of the

galvanized steel in concrete by the formation of calcium CAHZ needs at least a 10 μm thickness layer of pure zinc (η phase) on the galvanized rebar [16]. If the η phase layer is not thick enough, as in galvanized steel of special composition [17] or grey galvanized coating [18], the zinc necessary for the formation of CAHZ is supplied by the Zn–Fe alloy layers. The Zn–Fe alloys are then quickly destroyed thereby eliminating the protective features of the galvanized coating on steel rebars in the concrete.

The literature concerning zinc corrosion in concrete [19] generally focuses on the zinc oxidation mechanism often neglecting the influence of the different oxidizing agents. Nevertheless, the bibliography often suggests that the formation of the protective layer due to zinc oxidation in the alkaline concrete environment takes place with water reduction and subsequent hydrogen evolution [13,19,20]. On the other hand, some authors claim that the formation of the protective layer is strongly related to the presence of oxygen at the concrete/rebar interface [11,18,21]. Moreover, previously only the presumed disbonding at the galvanized rebars/concrete interface caused by hydrogen evolution has been underlined, paying little attention to the role of oxygen on the kinetic of formation of the CAHZ passive layer.

To establish if the formation of calcium hydroxyzincate is related only to the reduction of water or mainly to the reduction of oxygen, the corrosion behaviour of zinc plates immersed in calcium hydroxide saturated solutions to simulate the concrete pore environment, is studied in the presence of oxygen, air and nitrogen, respectively. In this way, it was possible to separate the possible oxidizing agents in order to understand their individual influence

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on the passivation kinetics. The corrosion behaviour was monitored by potential and corrosion current measurements.

The obtained results were confirmed by further similar measurements carried out on galvanized rebars embedded in concrete and stored in different curing environments.

The study is mainly of theoretical interest and gives further insight on the zinc passivation mechanism in concrete. However, the results could have practical implications for evaluating the most favourable environment to better develop the passivation potentiality of galvanized rebars, thus increasing the service life of reinforced concrete structures.

2. Experimental

2.1. Tests in saturated $\text{Ca}(\text{OH})_2$ solution

Commercial grade (pure, 98%) zinc plates (30 mm diameter, 1 mm thick) polished with emery paper by decreasing the grade to 1200 mesh were used for the solution tests. The plates were inserted inside sample holders acting as working electrodes with a surface of about 3.50 cm^2 exposed to the test environment. After an activating immersion in 15% NaOH solution for 5 s, the samples were fully immersed in $\text{Ca}(\text{OH})_2$ filtered saturated solution (700 cm^3) under four different conditions:

1. Continuous de-aeration by constant nitrogen flux.
2. Nitrogen flux de-aeration followed by oxygen bubbling.
3. Atmospheric equilibrium.
4. Oxidation by continuous oxygen bubbling.

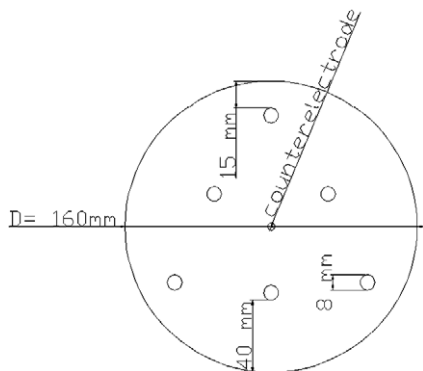


Fig. 1. Rebar arrangement in the cylindrical concrete specimen.

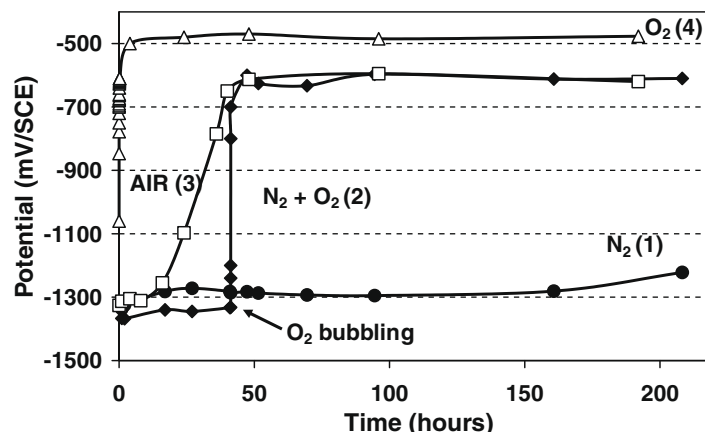


Fig. 2. Free corrosion potential evolution of the zinc plates immersed in $\text{Ca}(\text{OH})_2$ saturated solution (cases 1–4).

The free corrosion potential of the zinc plates immersed in the four different solutions was monitored by a saturated calomel electrode (SCE) as reference and the polarisation resistance was measured by the galvanodynamic method by calculating the average value between the anodic and the cathodic branch. The corrosion rate was calculated by the Stern and Geary law using the value of 26 mV/decade as B constant.

2.2. Concrete tests

Cylindrical concrete specimens (16 cm diameter, 19 cm high) were manufactured by using high pH cement (CEM I 52.5R, pH 12.94) with water to cement ratios (w/c) equal to 0.45–0.66–0.80. The alkali content of the cements was determined by double extraction with distilled water. To better evaluate the alkaline conditions due to cement hydration, the pH of the cement suspensions was measured according to a literature methodology [22]. The total alkali content of the cement turned out to be 0.93% (as Na_2O equivalent), while the soluble alkali content resulted in a value of 0.69%, giving rise to a pH value of 12.94.

Each cylindrical specimen was reinforced with six galvanized steel rebars (8 mm diameter and 9 cm long). The zinc coating was $100 \mu\text{m}$ thick, obtained by molten zinc immersion, with an outer pure zinc layer about $20 \mu\text{m}$ thick. The galvanized rebars, prior to embedding in the casting concrete, were immersed for 5 s in 15% NaOH solution to dissolve the ZnCO_3 layer quite possibly formed during atmospheric storage. The electric contacts of the rebars with the measurement apparatus were assured according to a previously reported methodology [23]. In each cylindrical specimen the rebars were alternately embedded with concrete covers of 1.5 and 4 cm, respectively (Fig. 1).

Two different curing environments were adopted:

1. Air curing for the concrete specimens with $w/c = 0.66$.
2. Nitrogen atmosphere for 8 days followed by oxygen saturated atmosphere curing inside a glove box, for the specimens with $w/c = 0.45$ and 0.80 .

The concrete specimens were demoulded in the respective curing environment 24 h after the cast. The free corrosion potential of the galvanized rebars embedded in the concrete specimens exposed to the different environments was monitored. The kinetics of the corrosion process was followed by polarisation measurements using the same methodology already described in the solution tests. A stainless steel rebar was embedded as counter electrode at the centre of each concrete specimen (Fig. 1).

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