

THE ROLE OF OXYGEN ON THE PASSIVATION MECHANISM OF GALVANIZED STEEL REBARS

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ABSTRACT

The protection of galvanized steel reinforcement against corrosion promoted by aggressive species penetrated inside concrete structures is related also to the formation of a compact and impervious calcium hydroxyzincate layer on the metallic surface.

The aim of this work was to establish if the formation of calcium hydroxyzincate is related only to the reduction of water, as it is often reported in the literature, or, as recently hypothesised, mainly to the reduction of oxygen.

With this purpose, the corrosion behaviour of zinc plates submerged 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 rates measurements.

The obtained results were confirmed by further data collected on galvanized rebars embedded in concrete and stored in different curing environments.

It clearly appears that it is not water but oxygen the main oxidizing agent for the rapid formation of an effective passivation layer on the zinc coating.

Keywords: zinc coating, galvanized rebars, corrosion in concrete, passivation.

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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 deicing 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].

In spite of the good initial results, some laboratory tests, later, showed contradictory corrosion behaviours. These controversial results are likely to be caused either by the different metallurgical structures of the galvanized rebar surface or by the different exposure environments able to greatly influence the still unclear zinc passivation mechanism.

The zinc amphoteric metal undergoes a severe attack either in acid or in basic media [3]. Particularly in an alkaline medium the 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 that then precipitate as $Zn(OH)_2$ (or ZnO) by forming a continuous passivating layer.

In the presence of $Ca(OH)_2$, as in the concrete pore solution, the protective layer is no longer formed only by zinc oxide and hydroxide but, above all, by a well packed, protective, and very resistant to chloride aggression layer of calcium hydroxyzincate [7-9]. The pH, too, seems to largely influence not only the type but also the morphology of the corrosion products developed [10, 11].

The zinc coating microstructure also influences to a large extent its corrosion resistance. In fact the passivation of the galvanized steel in concrete by the formation of calcium hydroxyzincate (CAHZ) needs at least 10 μm thickness layer of pure zinc (η phase) on the galvanized rebar [12]. If the η phase layer is not thick enough, as in galvanized steel of special composition [13] or grey galvanized coating [14], 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 concrete.

The literature concerning zinc corrosion in concrete generally focuses attention on the zinc oxidation mechanism often neglecting the influence of the different oxidising agents. Nevertheless, the bibliography often suggests that the formation of the protective layer due to the zinc oxidation in the alkaline concrete environment takes place with the contemporary water reduction and the following hydrogen evolution [10, 15, 16]. On the other hand some authors assert that the protective layer formation is strongly related to the presence of oxygen at the concrete/rebar interface [14, 17]. In actual fact, in the past, the presumed disbonding at the galvanized rebar/concrete interface caused by hydrogen evolution has been underlined, paying little attention, on the contrary, to the role of oxygen on the kinetic of formation of the CAHZ passive layer, overall in

real concrete.

The aim of this work was to establish if the formation of calcium hydroxyzincate is related only to the reduction of water or, as recently hypothesised, mainly to the reduction of oxygen.

With this purpose the corrosion behaviour of zinc plates submerged in calcium hydroxide saturated solutions, to simulate the concrete pore environment, was 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 on the passivation kinetic. The corrosion resistance was monitored by potential and corrosion current measurements.

The results obtained 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. It gives further insight to the zinc passivation mechanism in concrete in order to identify the causes of the controversial results obtained in previous experiments where galvanized steel reinforcement was used in concrete structures. On the other hand 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.

EXPERIMENTAL

Tests in saturated $Ca(OH)_2$ solution

Trade 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 into sample holders acting as working electrodes and allowing a surface of about 3.50 cm^2 to be exposed to the test environment. After an activating immersion into 15% NaOH solution for 5 seconds, the samples were fully submerged in $Ca(OH)_2$ 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.

The free corrosion potential of the zinc plates submerged in the four different solutions was monitored by a saturated calomel electrode (SCE) as reference.

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 Stearn and Geary law using the value of 26 mV/decade as B constant.

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, while, to better evaluate the alkaline conditions made by the cement hydration, the pH of the cement suspensions was measured according to a literature methodology [18]. The total alkali content of the cement used resulted 0.93% (as Na₂O equivalent), while the soluble alkali content resulted 0.69%, giving rise to a pH value of 12.94.

Each cylindrical specimen was reinforced with 6 galvanized steel rebars (8 mm diameter and 9 cm long). The zinc coating was 100 μm thick, obtained by molten zinc immersion, with an outer pure zinc layer about 20 μm thick. The galvanized rebars, just before embedding in the casting concrete, were submerged for 5 sec in 15% NaOH solution to dissolve the ZnCO₃ layer possibly formed during atmospheric storage. The electric contacts of the rebars with the measurement apparatus were assured according to a previously reported methodology [19].

In each cylindrical specimen the rebars were alternately embedded with concrete covers of 1.5 and 4 cm respectively.

Two different curing environments were adopted:

1. air curing for the concrete specimens with w/c = 0.66;
2. nitrogen atmosphere for almost 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 hours after the cast.

The free corrosion potential of the galvanized rebars embedded in the concrete specimens exposed to the different environments was monitored. The kinetic of the corrosion process was followed by polarisation measurements by using the same methodology already described in the solution tests. A stainless steel rebar was embedded as counterelectrode at the centre of each concrete specimen.

RESULTS AND DISCUSSION

Tests in saturated Ca(OH)₂ solution

Figure 1 shows the free corrosion potential evolution of the plates immersed in the four different Ca(OH)₂ saturated solutions (cases 1-4).

Both zinc plates submerged in the two solutions previously de-aerated with nitrogen (cases 1 and 2) show initial potentials of about -1350 mV (SCE), which are typical values for the zinc activation state. However, while the potential in the solution of case 1, with continuous bubbling of nitrogen, is always lower than -1250 mV (SCE) even after 10 days of full immersion, in case 2, where oxygen substituted nitrogen after 2 days of immersion, a sharp increase suddenly appears in the potential values, just after this substitution, which reaches the passivation stable value of -600 mV (SCE).

By submerging the zinc plates in the lime solution already saturated with atmospheric air or oxygen (cases 3 and 4 respectively) there is an analogous potential rise. In the case of the solution in equilibrium with the atmosphere, the

potential gradually increases within 48 hours from the activation value of -1200 mV (SCE) to a passivation one of -600 mV (SCE); on the other hand, in the case of the oxygen saturated solution there is a very rapid potential change from the value of -1060 mV (SCE) at the immersion time to the value of -600 mV (SCE) after only 15 minutes.

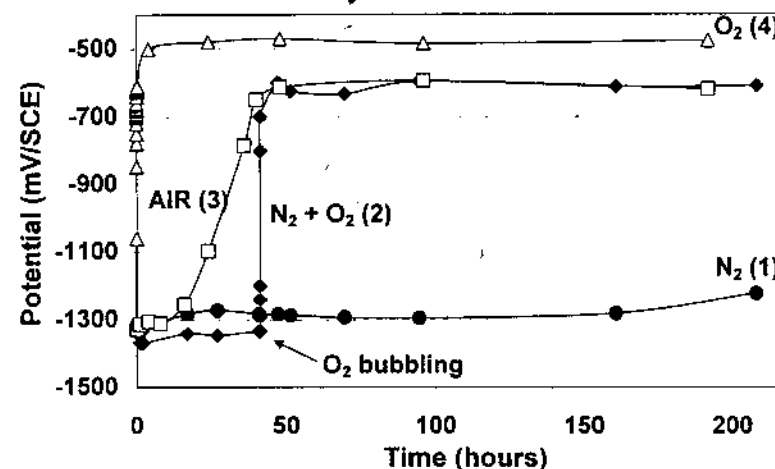


Fig. 1: Free corrosion potential evolution of the zinc plates submerged in Ca(OH)₂ saturated solution (cases 1, 2, 3, 4)

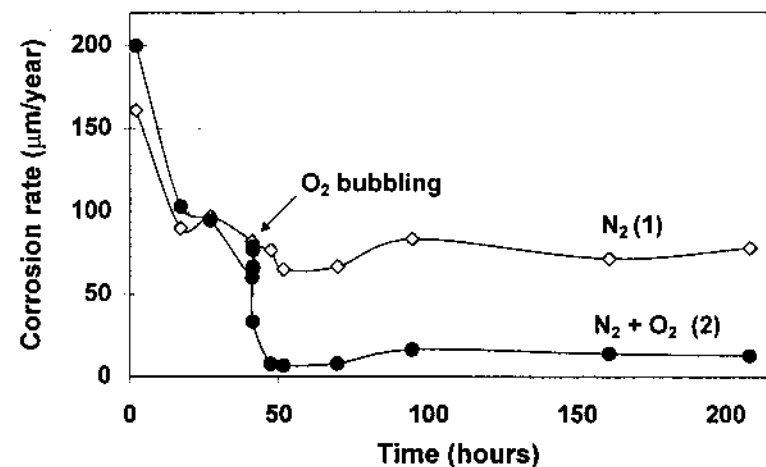


Fig. 2: Corrosion rate of the zinc plates submerged in Ca(OH)₂ saturated solution (cases 1 and 2)

Figure 2 shows the corresponding variation of the corrosion rates in cases 1 and 2. In both cases in the presence of nitrogen, the activation state of zinc is confirmed by the initial high corrosion rate of about 200 $\mu\text{m}/\text{year}$. The corrosion rates slowly decrease with time to reach the stable value of about 70 $\mu\text{m}/\text{year}$ nevertheless the potential remains at activation values. When the nitrogen flux is substituted by oxygen in case 2, after 2 days of complete immersion, the corrosion rate further decreases to rapidly reach values of about 10 $\mu\text{m}/\text{year}$.

Even in cases 3 and 4 the corrosion rates initially show values of a few hundred $\mu\text{m}/\text{year}$ which subsequently fall, more slowly in the case of air saturated solution and more rapidly in the case of oxygen saturated solution, down to values lower than 10 $\mu\text{m}/\text{year}$.

SEM observations carried out in order to scan the corrosion state of the zinc plates surface showed in case 1 a completely mordanted surface as a consequence of continuously de-aerated lime solution exposure (Photo 1). In case 3, where the zinc sample was continuously in contact with an oxygen saturated calcium hydroxide solution, the zinc surface showed no roughness except for the one due to the polishing treatment (Photo 2).

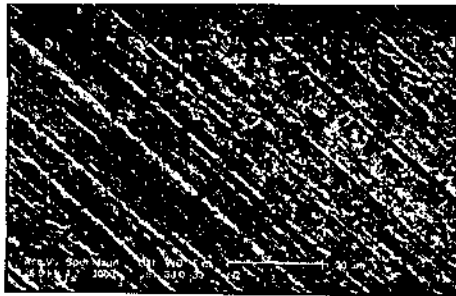


Photo 1: SEM observation on zinc plate surface after the exposure in continuously de-aerated solution (case 1)

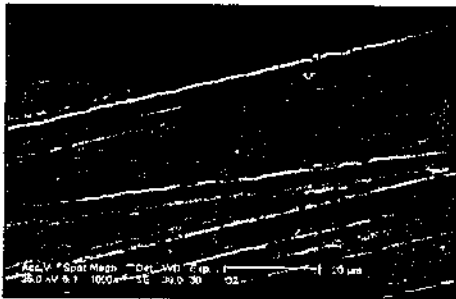


Photo 2: SEM observation on zinc plate surface after the exposure in continuously oxygenated solution (case 3)

Concrete tests

Figure 3 shows the corrosion potential change with time of the air cured concrete specimens, where the reported potential values were obtained by averaging the measures on three samples of the same type. The potentials kept constant at values of about -1350 mV (SCE) from the cast time as long as the specimens were stored in their moulds. After demoulding, the potentials rose to values of -700 mV (SCE) in a few hours.

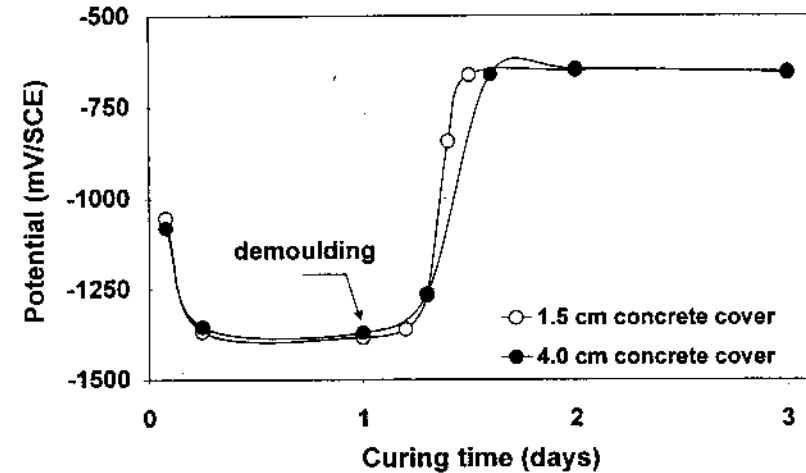


Fig. 3: Corrosion potential change with time of the rebars embedded in the air cured concrete specimens (case 1)

On the contrary, the specimens stored in the glove box (fig. 4) showed during their exposure to the nitrogen atmosphere, potential values gradually changing from the initial value of -1400 mV (SCE) to the practically steady value of about -1000 mV (SCE). When the nitrogen flux was replaced by oxygen after about 8 days exposure, within 1 hour the potential reached the passivation value of about -700 mV (SCE) for $w/c = 0.45$ and -550 mV (SCE) for $w/c = 0.80$, regardless of the cover thickness. This difference related to w/c could probably be due to the greater porosity of the cementitious matrix with the higher w/c allowing a greater amount of oxygen to flow through the concrete cover.

At the beginning, the corrosion rate always reached the value of 150 $\mu\text{m}/\text{year}$. In the case of the specimens demoulded in air, the corrosion currents decreased with time down to values of a few $\mu\text{m}/\text{year}$ (fig. 5).

In the case of the specimens cured in a nitrogen atmosphere inside the glove box (fig. 6), the corrosion currents stabilized within a few days at the value of 40 $\mu\text{m}/\text{year}$; when oxygen replaced nitrogen the corrosion currents suddenly rose to 100 $\mu\text{m}/\text{year}$, showing a fast passivation process before stabilizing to a few $\mu\text{m}/\text{year}$ values, regardless of the cover thickness and the w/c .

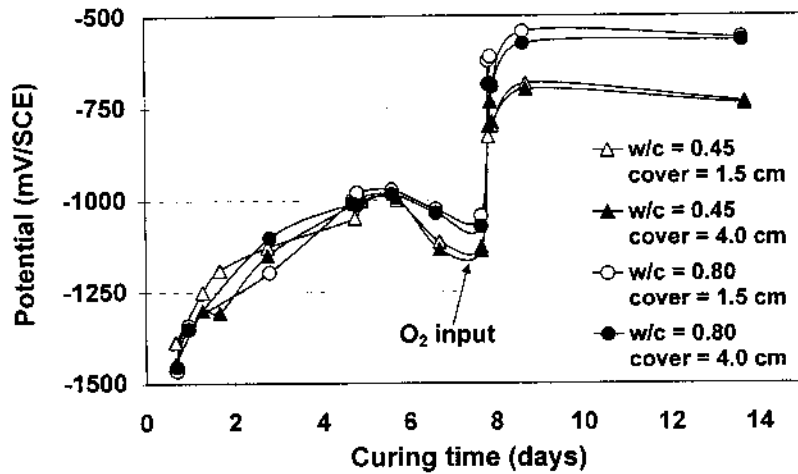


Fig. 4: Corrosion potential change with time of the rebars embedded in the concrete specimens cured in the glove box (case 2)

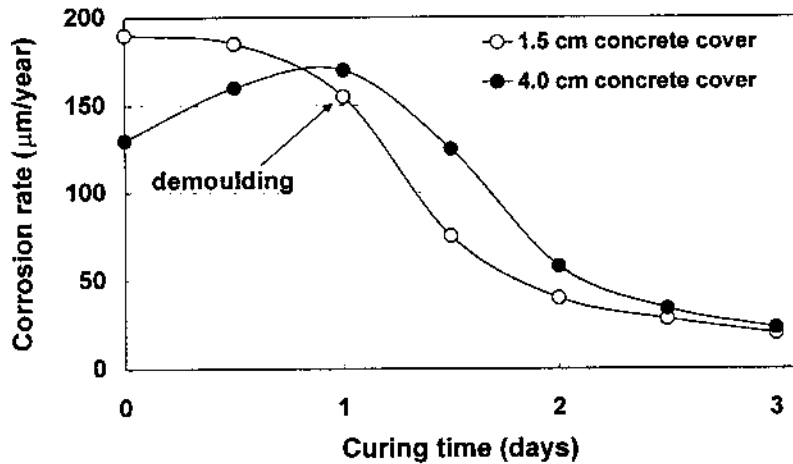


Fig. 5: Corrosion rates variation with time of the rebars embedded in the air cured concrete specimens (case 1)

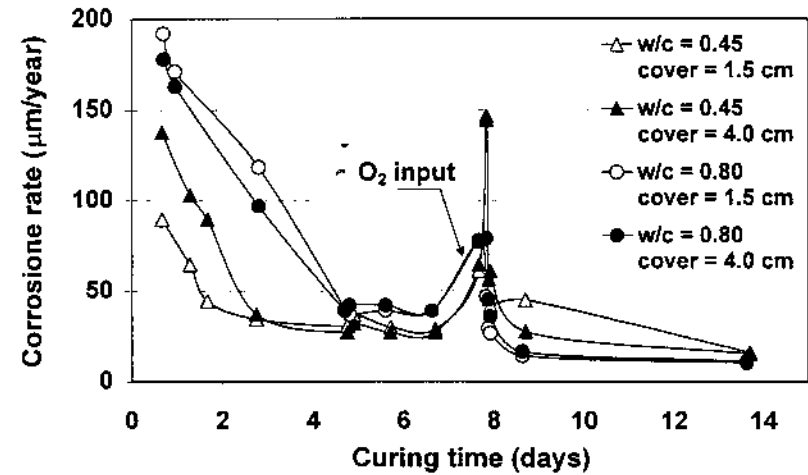


Fig. 6: Corrosion rates variation with time of the rebars embedded in the concrete specimens cured in the glove box (case 2)

The results obtained from the solution tests on zinc plates have been in this way widely confirmed by the values found on galvanized rebars embedded in concrete. It appears clear that it is not water but oxygen that is the fundamental oxidizing agent for a fast and effective zinc passivation in concrete through the very likely formation of a compact layer of calcium hydroxylzincate. In fact, only the presence of oxygen, either bubbling into a $\text{Ca}(\text{OH})_2$ saturated solution or flowing into the concrete cover, determines a fast and sharp potential change from activation values lower than -1000 mV (SCE) to passivation values higher than -600 mV (SCE) to occur and the corrosion currents to decrease from some hundreds to few units of $\mu\text{m}/\text{year}$.

However, water too can contribute to the oxidation process, although with slower kinetics. As a matter of fact, in the case of the zinc plates submerged in de-aerated solution the corrosion rate slowly decreases, even if without a corresponding change of potential; it might occur that water reduction could lead to the formation of a feeble, coarse, porous and then poorly covering passive film.

CONCLUSIONS

The results obtained by monitoring the corrosion rate of zinc plates submerged in calcium hydroxide saturated solutions in the presence of oxygen, air and nitrogen respectively, satisfactorily agree with those obtained by the measurements carried out on galvanized rebars embedded in concrete specimens and stored in different curing environments.

In both cases the results show that it is not water but oxygen the fundamental oxidizing agent for a fast and effective zinc passivation in concrete by means of

the formation of a compact passive layer, very likely constituted of calcium hydroxyzincate.

Water too can participate in the oxidizing action but it leads only to the formation of a feeble, coarse and porous passive film with slower kinetics.

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