

Effect of the Type of Surface Treatment and Cement on the Chloride Induced Corrosion of Galvanized Reinforcements

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Abstract. The effect of a new passivation treatment, obtained by immersion of the galvanized reinforcements in a trivalent chromium salts based solution, on the chlorides induced corrosion has been investigated. To investigate also the effect of cement alkalinity on corrosion behaviour of reinforcements, concretes manufactured with three different European cements were compared. The obtained results show that the alternative treatment based on hexavalent chromium-free baths forms effective protection layers on the galvanized rebar surfaces. The higher corrosion rates of zinc coating in concrete manufactured with Portland cement compared to those recorded for bars in concrete manufactured with pozzolanic cement depends strongly on the higher chloride content at the steel concrete interface.

1. Introduction

Due to the rising costs of restoration and maintenance, preventive measures to reduce the corrosion risks in reinforced concrete structures are required. The most effective approach to obtain a durable structure is to manufacture a concrete with low w/c as required, for instance, by ENV 206 and to adopt an adequate concrete cover as recommended, for instance, by Eurocode 2. However, in real concrete structures cracks induced by loading, shrinkage, creep, thermal and flexural stress and mechanical shocks greatly increase the concrete surface permeability, since they represent preferential paths for penetration of aggressive ions, such as sulphates and chloride ions in polluted area and coastal zone [1-3], promoting concrete deterioration and corrosion of embedded reinforcements. In these cases, hydrophobic coatings/admixtures, due to their ability to make concrete less susceptible to water saturation [4-5], or stainless steel or the less expensive galvanised steel reinforcement, can be used as a preventive method to slow down steel corrosion and prolong the service life of structures [6-8].

However, open issues on galvanized steel reinforcement's remains the efficacy of the protective action in concrete containing chlorides and the compatibility with the high alkalinity of European cements [9].

Moreover, the traditional procedures of the passivation process for hot dip galvanized rebars are given by ASTM Standard and consist in the immersion of galvanized rebars in a hexavalent chromium aqueous solution. Chromate ion is a substance with well-known carcinogenic properties that causes environmental wastage and serious health problems to plant operators working with the treatment



solution. On account of hexavalent chromium hazard, the European standards limit its utilization and, therefore, alternative, equally effective and harmless agents, which could replace chromates in the passivation surface treatment, are needed.

The purpose of this work is to investigate the effect of a new passivation treatment, obtained by immersion of the galvanized reinforcements in a trivalent chromium based solution, on the corrosion behavior induced by chlorides of galvanized rebars embedded in concrete specimens. To investigate also the effect of cement alkalinity on corrosion behaviour of galvanized reinforcements, two different European cements were used and compared: Portland cement (CE I 52.5R) and pozzolanic cement (CE IV/B 32.5R).

2. Experimental

A passivation treatment was carried out by immersion of the reinforcements in a trivalent chromium salts based solution. The corrosion resistance of galvanized rebars passivated with this treatment were compared with those of conventional (hexavalent chromium based) passivated galvanized steel reinforcements in concrete specimens exposed to chlorides.

With this purpose, three different types of galvanized steel reinforcements were used:

- bare galvanized rebars without any passivation surface treatment (type BA);
- conventional galvanized steel bars with a hexavalent chromium based passivation treatment (type C6): this treatment was obtained by immersion of galvanized rebars in an aqueous solution containing hexavalent chromate ions (Cr VI) according to ASTM A767/A767M-09;
- galvanized steel rebars passivated by immersion in an aqueous solution containing exclusively trivalent chromium ions (type C3). This treatment was followed by hot drying and then immersion in aqueous solution containing both organic (acrylic polymer) and inorganic (silicates) substances. These are able to form, by drying at 60°C, a thin polymeric film on the surface of the galvanized rebar.

Two different European cements were used: Portland cement (CE I 52.5R) and pozzolanic cement (CE IV/B 32.5R). Hexavalent chromium content and alkalinity with respect to Na₂O and K₂O of the cements are given in Table 1.

Table 1. Alkali and Chromium content of the cements.

(%)	CE I 52.5R	CE II/B- 32.5R
K ₂ O	0.90	0.77
Na ₂ O	0.52	0.33
CrVI (ppm)	1.8	0.7

Three concrete mixtures were manufactured with a relatively high water-cement ratio (w/c = 0.66). This value was intentionally chosen in order to obtain a very porous cement matrix which would favor the subsequent penetration of depassivating agents (chlorides) into concrete.

Four different sets of cylindrical concrete specimens (diameter 160 mm, height 125 mm) were cast, each containing two groups of six galvanized steel bars 10 mm in diameter with an 80 µm thick zinc coating (Figure 1). The main difference between the two groups of bars in each specimen was the concrete cover: 15 mm or 35 mm for group 1 or 2, respectively. Galvanized rebars were partially embedded in concrete with their upper ends emerging over the top surface of the concrete specimens. A stainless steel counter electrode was located in the centre of each specimen.

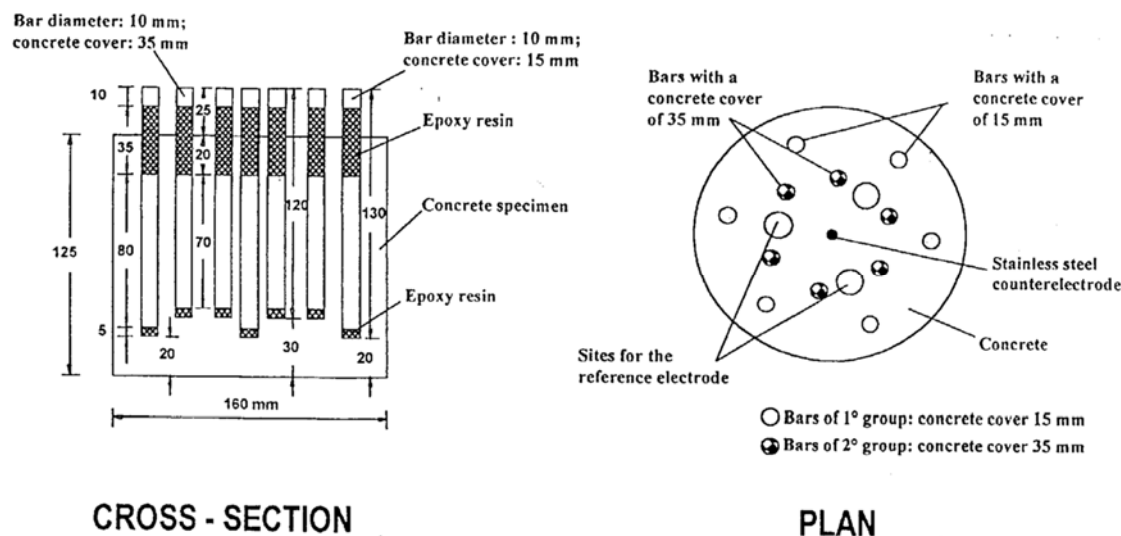


Figure 1. Schematic representation of cylindrical concrete specimens

After a 2-days wet curing at 20°C, concrete specimens were demoulded and kept for 40 days in a chamber at 20°C and 85% R.H. Then they were exposed to 17 wetting/drying cycles in 3% sodium chloride aqueous solution. Each cycle consisted of 4-day immersion in NaCl aqueous solution followed by air drying for 14 days at room temperature.

Corrosion rate and free corrosion potential measurements of galvanized steel reinforcements were carried out both before and after starting the wetting/drying cycles. The Saturated Calomel Electrode (SCE) was used as reference electrode for free-corrosion potential measurements while the polarization resistance technique was used to evaluate the corrosion rate of galvanized rebars (R_p). The R_p was obtained through a galvano-dynamic polarization method (scan rate = 0.5 $\mu\text{A/s}$; $\Delta V = \pm 5$ mV) by calculating the average of the slopes relative to anodic and cathodic branches, registered separately in order to have in both cases an initial condition of zero current density. The corrosion rate v_{corr} ($\mu\text{m/year}$) was obtained from R_p values using a B constant value equal to 26 mV [10]. All corrosion rate measurements were done by means of an AMEL electrochemical workstation managed through a National Instruments acquisition board and a software suitably developed in LabWindows environment.

At the end of the wetting/drying cycles (after about 1 year) all the concrete specimens were autopsied in order to visually assess the possible effects of corrosion of the galvanized steel reinforcements. Observation of the galvanized rebars cross-sections was carried out with naked eye and by optical microscopy, in order to detect the corrosion products morphology and the zinc coating depth destroyed by chlorides, if any.

Furthermore, the chloride concentration profile in concrete was determined. Free chloride concentration in mortars at different depths was determined after drilling the specimens. The free chloride concentration expressed as percentage on the total weight was measured following the procedure reported in UNI 9944:1992. Each powdered sample (5 g approximately) was put in 20 ml of demineralized water (powder/water ratio equal to 1:4 by weight). The obtained suspension was stirred for 24 hours to dissolve free chlorides from the solid sample. Then, it was filtered, diluted in 100 ml of demineralized water and analyzed to determine the content of chloride ions expressed as wt% of the mass of concrete.

3. Results and discussions

3.1. Electrochemical measurements

Free corrosion potentials (E_{corr}) and corrosion rates (v_{corr}) of galvanized rebars embedded in concrete specimens during the curing period (at room temperature and 85% R.H.) were measured. The data seem to indicate that potentials and corrosion rates of rebars do not depend on the type of cement used, while the corrosion rate trend during the curing time depends on the passivation surface treatment. As an example, Figure 2 shows the corrosion rate of galvanized bars embedded in concrete specimens manufactured with Portland cement (CE I 52.5R) during the curing period. Bare galvanized rebars (BA) reach the highest corrosion rate values (about 200 $\mu\text{m}/\text{year}$), just after the demoulding of concrete specimens, corresponding to a curing time of 0 days. However, after 3 days, the corrosion rate was significantly lower (about one order of magnitude) than the initial value. This particular behavior could be ascribed to the zinc passivation in the alkaline aqueous phase of the cement matrix pores. The formation of a layer of zinc oxidation products during the passivation process of the galvanized rebars is responsible for both the sharp decrease in v_{corr} and for the more noble potentials reached by galvanized reinforcements [11, 12].

Corrosion rate values of conventional (hexavalent chromium based) passivated galvanized steel bars are very low (about 8-10 $\mu\text{m}/\text{year}$) and constant during the whole curing time. Concerning with the galvanized rebars passivated with the alternative treatment (type C3), the corrosion current initially increases up to a maximum value. Then, after about 3 days, the corrosion rate trend becomes very similar to that of bare galvanized steel bar. This behaviour could be ascribed to the good protection initially offered by the surface treatment of the zinc coating (low initial corrosion rate) followed by the failure of the surface protective layer in some areas (increase in corrosion current). Hence, the breakdown of the protective layer favours the formation of zinc passivating products responsible for a better protection of the zinc coating and for the subsequent corrosion rate decrease.

These results seem to indicate that there are no significant differences in terms of E_{corr} and v_{corr} , after about four days of curing, between conventional passivated (by means of hexavalent chromium bath) galvanized steel bars and galvanized rebars passivated with the alternative treatment based on trivalent chromium solution.

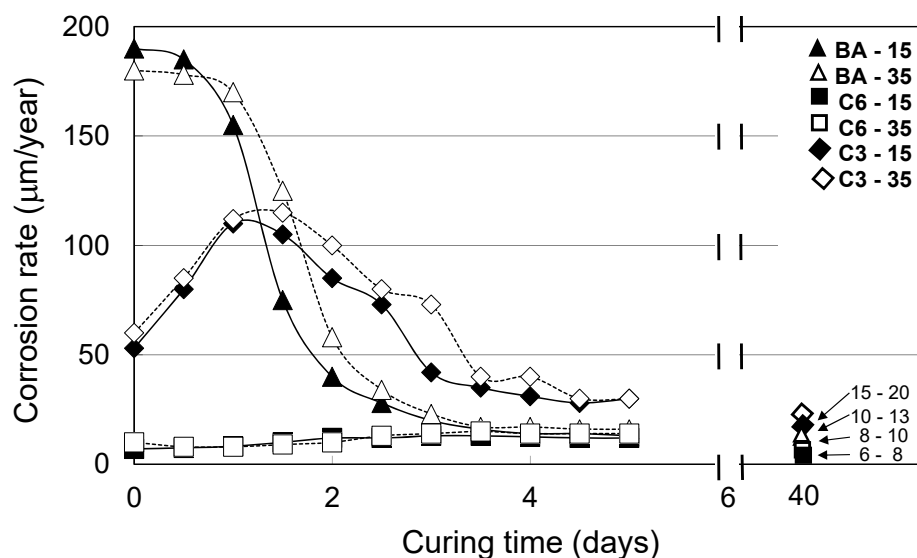


Figure 2. Average corrosion rates of galvanized bars embedded in concrete specimens manufactured with Portland cement (CE I 52.5 R) during the curing time at room temperature and 85% R.H

Free corrosion potentials and corrosion rates of galvanized rebars embedded in concrete specimens exposed to wetting/drying cycles in a 3% sodium chloride aqueous solution were measured. Since no significant information was obtained by potential data, only corrosion rate values of galvanized rebars are shown. As an example, the results of corrosion rates of galvanized bars embedded in the concrete specimens manufactured with pozzolanic cement, CE IV/B 32.5, as a function of the number of wetting and drying cycles, are shown in Figure 3. It is interesting to observe that the corrosion rate values of bare galvanized rebars increase sharply after 7-8 wetting/drying cycles while the corrosion rates of passivated galvanized steel bars increase gradually after a higher number of wetting/drying cycles. This means that the passivation surface treatments are able to improve the corrosion resistance of galvanized steel bars since they delay the onset of the corrosion process. Moreover, after 17 wetting and drying cycles, corrosion rates of the hexavalent chromium free passivated galvanized rebars (type C3) is lower than those recorded for both bare galvanized bars (type BA) and conventional (hexavalent chromium based) passivated galvanized steel reinforcements (type C6), regardless of the cement type.

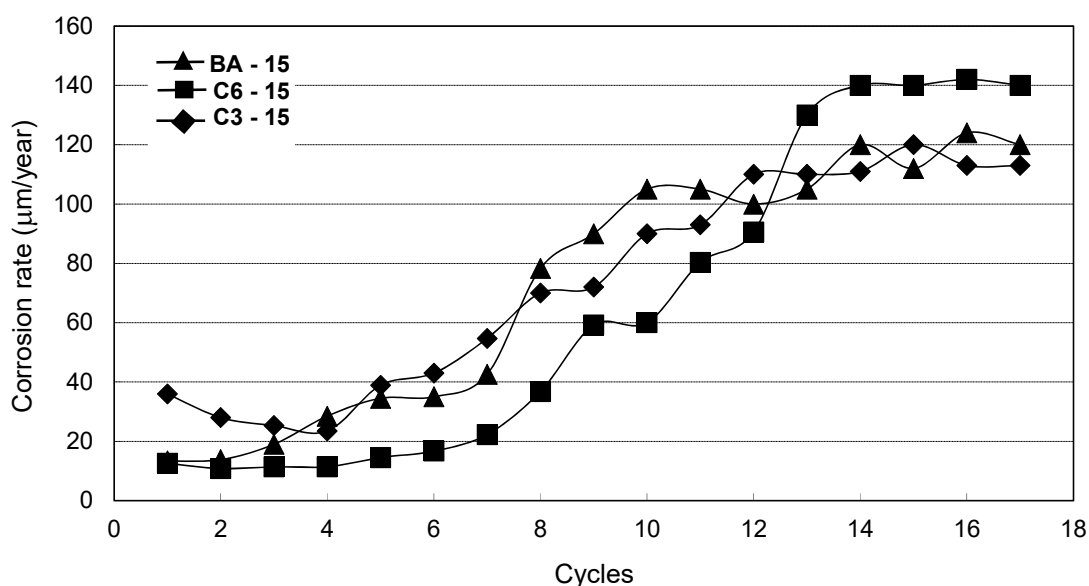


Figure 3. Average corrosion rates of galvanized bars embedded (concrete cover = 15 mm) in the concrete specimens manufactured with pozzolanic cement (CE IV/B 32.5 R) as a function of the number of wetting and drying cycles.

Similar results were obtained for galvanized rebars with a concrete cover of 35 mm. Again, the alternative passivation treatments (type C3) give comparable or better corrosion protection than both bare galvanized rebars and conventional chromating treatment, regardless of the cement used.

3.2. Autopsy of Reinforced Concrete Specimens

At the end of the wetting/drying cycles reinforced concrete specimens were autopsied.

On the basis of the observation of the corrosion products present on the galvanized rebar surfaces, the reinforcements were divided into four clusters. Cluster A: bars with the zinc coating slightly and partially etched without red rust but with small dark grey spots due to exposure of Zn-Fe intermetallic compounds as a consequence of the external zinc layer dissolution. Cluster B: reinforcements with the zinc coating fully etched, with dark grey spots, without red rust. Cluster C: rebars with the zinc coating fully etched and with the presence of spots of red rust. Cluster D: galvanized rebars with presence of red rust.

The classification of rebars according to the above mentioned four groups is shown in Table 2. Again, the visual observation confirms that type C3 bars showed a better corrosion resistance than both conventional passivated steel bars (type C6) and bare galvanized reinforcements at the end of the 17 wetting/drying cycles.

Table 2. Corrosion rates at the end of wetting and drying cycles and visual rating of the corroded surface on galvanized steel bars.

Type of cement	Type of bar	BA		C6		C3	
	Concrete cover (mm)	15	35	15	35	15	35
CE I 52.5R	Corrosion rate* ($\mu\text{m}/\text{year}$)	124	107	142	135	120	122
	Visual rating	D	D	D	D	D	C-D
	Corrosion rate* ($\mu\text{m}/\text{year}$)	87	80	92	53	38	40
CE IV/B 32.5R	Visual rating	D	D	D	B	A-B	A

*After 17 wetting/drying cycles in a 3% NaCl aqueous solution.

Regardless of the type of galvanized rebars and the concrete cover, reinforcements embedded in concrete specimens manufactured with Portland (CE I 52.5R) showed higher corrosion rates (Table 2) than those recorded for bars in concrete manufactured with the pozzolanic cement (CE IV/B 32.5R). These results can be ascribed to the lower chloride content in concrete manufactured with the pozzolanic cement, regardless of the concrete cover (Figure 4). For instance, the percentage (by mass of concrete) of chloride at 35 mm depth is about 0.40 and 0.70 in concrete with pozzolanic cement, and Portland cement, respectively. Thus, these results confirm that the higher corrosion rate in Portland cement, i.e. the higher reactivity of the zinc coating, depends strongly on the higher chloride content at the rebar/concrete interface. Figure 4 indicates that the chloride content in the concrete specimens is significantly high and this explains the heavy corrosion detected in many galvanized rebars.

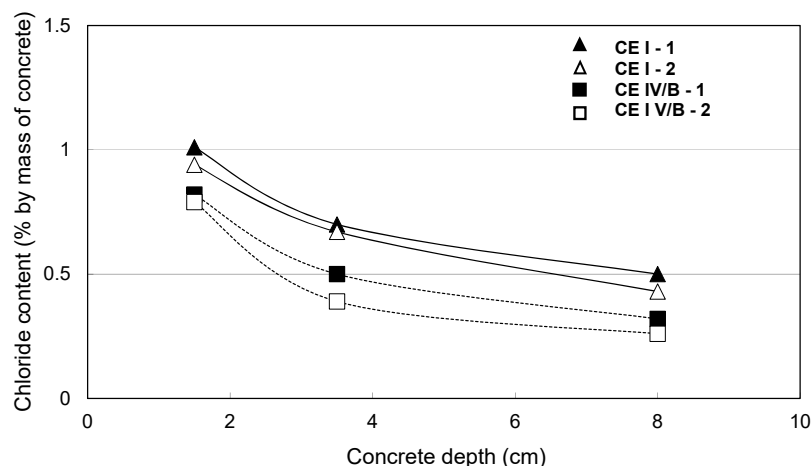


Figure 4. Chloride content at various depth in the concrete specimens.

4. Conclusions

The results obtained from this work show that:

- the alternative treatment based on hexavalent chromium-free baths forms an effective protective layer on the galvanized rebar surfaces. Therefore, it represents an innovative and promising process for increasing durability of reinforced concrete structures;
- the corrosion behaviour of galvanized reinforcements does not depend on the type of cement used;

- the higher corrosion rates of zinc coating in concrete manufactured with Portland cement compared to those recorded for bars in concrete manufactured with pozzolanic cement depends strongly on the higher chloride content at the steel concrete interface.

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