

Evaluation of Hexavalent Chromium-Free Passivation Treatment of Galvanized Bars for Reinforced Concrete

by T. Bellezze, L. Coppola, and R. Fratesi

Synopsis: The zinc coating of galvanized rebars is often subjected to a passivation surface treatment by immersion in a hexavalent chromium aqueous solution in order to improve the corrosion resistance of the reinforcements when stored in air as well as when embedded in concrete. The chromate ion causes serious health problems to the operators working with the solution. Therefore, a hexavalent chromium-free passivation treatment of galvanized rebars is desirable.

Two free-hexavalent chromium surface passivation treatments of galvanized rebars were obtained by immersion either in a trivalent chromium based solution or in a cobalt and titanium salts solution both harmless to the workers. Conventional (hexavalent chromium based) passivated galvanized steel bars and galvanized rebars passivated with the two above alternative treatments were embedded in very porous concrete specimens manufactured with three different cements. These reinforced concrete specimens were exposed to wetting and drying cycles in a 3% sodium chloride aqueous solution. Free corrosion potential, corrosion rate, and visual observations of galvanized rebars indicated that the two hexavalent chromium free passivation treatments can give comparable or better protection than the conventional chromating treatment, independent of the type of cement used.

Keywords: corrosion; durability; galvanized materials; passivity

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INTRODUCTION

Corrosion of rebars represents the most important cause of deterioration in reinforced concrete structures. In fact, chlorides and carbon dioxide can penetrate inside the concrete and destroy the passive film protecting the steel. In these conditions corrosion of rebars can occur provided that oxygen and humidity are available at the steel surface.

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 as low w/c as required, for instance, by ENV 206 [1] and to adopt an adequate concrete cover, as recommended, for instance, by Eurocode 2 [2]. However since in real concrete structures microcracks - due to restrained thermal and moisture changes - are always present, additional protections for concrete, in form of flexible coating [3], and/or for reinforcements, in the form of resin coating [4], galvanized [5] or stainless steel [6], are needed, particularly in very aggressive environments.

Recently, an increase in the use of galvanized rebars, has been reported in concrete constructions [7]. The low cost and the effectiveness in protecting the steel from corrosion in aggressive environments are the reasons for the wide use of this reinforcement.

In order to improve the corrosion resistance of galvanized rebars a passivation surface treatment is required. In particular, this treatment inhibits the white rust - $Zn(OH)_2$ - formation on the zinc surface when the bundles of bars are stored in the air on the job-site. The procedures of the passivation process for hot dip galvanized rebars are given by ASTM Standard [8]. The passivation treatment consists in the immersion of galvanized rebars in a hexavalent chromium aqueous solution. This treatment favors the formation of a surface layer - containing chromium oxide and zinc chromate - on the zinc coating. The surface layer is responsible for a better corrosion resistance of galvanized

rebars since it inhibits the white rust formation on the reinforcement when exposed to the atmosphere as well as when embedded in concrete.

On the other hand, chromate ion – a substance with well-known carcinogenic activity – causes serious health problems to plant operators working with the solution where galvanized rebars are immersed. Moreover, the chromation process needs a final rinsing step and then a treatment of the waste water is required. In consideration of the hexavalent chromium hazard, the European standards limit its utilization [9]. Therefore, alternative, equally effective and harmless agents which could replace chromates in the passivation surface treatment are needed [10-12].

The specific purpose of the present paper was to evaluate the possibility of obtaining a protective surface coating by immersion of galvanized rebars in hexavalent chromium free solution, harmless for plant operators.

Two different passivation treatments were obtained by immersion of the reinforcements in:

- i) a trivalent chromium based solution
- ii) a cobalt and titanium salts solution

Performances – in terms of corrosion resistance of reinforced concrete specimens exposed to chlorides – of galvanized rebars passivated with the two above treatments were compared with those of conventional (hexavalent chromium based) passivated galvanized steel reinforcements.

EXPERIMENTAL PROGRAM

Materials

- Four 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/A767 M-90 followed by a water rinsing and drying at room temperature;
 - innovative galvanized steel rebars passivated by immersion in an aqueous solution containing exclusively trivalent chromium ions (type C3). The passivation treatment was followed by hot drying and further immersion in aqueous solution containing both organic (acrylic polymer) and inorganic (silicates) substance. These are able to form, by drying at 60°C, a thin polymeric film on the surface of the galvanized rebar;

- innovative galvanized steel bars passivated by immersion in an aqueous solution based on titanium and cobalt salts (type TC) followed by drying at room temperature.
- Three different European cements all meeting ENV 197-1 [13] were used:
 - portland cement (CE I 52.5R)
 - composite portland cement (CE II/B-M 32.5R) with 20-35% of mineral additions
 - pozzolanic cement (CE IV/B 32.5R) with 45-64% of natural and/or artificial pozzolans

In order to evaluate the influence of the passivation treatment on the corrosion resistance of galvanized rebars, cements with a hexavalent chromium content much lower than 25 ppm were chosen. In fact, bare galvanized steel bars embedded in concrete manufactured with cements having a C_r^{6+} content higher than 25 ppm have a good corrosion resistance, independently of the passivation surface treatment. Hexavalent chromium content and chemical compositions of the cements used are given in Table 1.

- Sand with a fineness modulus of 2.65 and gravel (4-8 mm) were used with a proportion of 32.3 and 67.7% by mass, respectively.

Concrete Mixtures

Three concrete mixtures (Table 2) with the above mentioned cements 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 will favor the penetration of depassivating agents (chlorides) into concrete.

Reinforced Concrete Specimens

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 a zinc coating 80 μm thick (Fig. 1). The main difference between the two groups of bars in each specimen was the concrete cover: 15 mm or 35 mm for the 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 as shown in Fig. 1.

A stainless steel counter electrode was located in the centre of each specimen.

After a 2-day wet curing at 20°C, concrete specimens were demolded 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.

Measurements

Corrosion rate and free corrosion potential measurements of galvanized steel reinforcements were carried out both before and after starting the wetting/drying cycles. Polarization resistance technique was used to evaluate the corrosion rate of galvanized rebars. This method calculates the corrosion current (v_{corr}) through the Stern and Geary formula. In the calculation of v_{corr} a 26 mV/decade value for the coefficient B was used.

A Saturated Calomel Electrode (SCE) as reference electrode was used to carry out free-corrosion potential measurements.

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

RISULTS AND DISCUSSION

Corrosion Potentials and Corrosion Rate During the Curing Period

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.

Potentials of bare galvanized rebars move from values of -1300/-1400 mV vs SCE to more noble values (-500/-700 mV vs SCE) after a 4-day curing. On the other hand, potentials of passivated galvanized reinforcements start from values between -800/-1000 mV vs SCE and attain a range of -600/-900 mV vs SCE depending on the passivation treatment. Moreover, these data seem to indicate that potentials of both bare and passivated galvanized rebars don't depend on the type of the cement used.

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. Similar results were obtained for galvanized rebars embedded in

concrete specimens with the other two cements (CE II/B-M and CE IV/B). Therefore, for the sake of brevity, only results of concrete specimens with portland cement are shown.

The corrosion rate trend during the curing time depends on the passivation surface treatment (Fig. 2). Bare galvanized rebars (BA) attain – just after demoulding of the concrete specimens corresponding to a curing time of 0 days - the highest corrosion rate values (about 200 $\mu\text{m}/\text{year}$). However, after 3 days the corrosion rate is significantly lower (about one order of magnitude) than the initial value. This particular behavior of the bare galvanized rebar could be ascribed to the zinc passivation in the alkaline aqueous phase of the capillary pores in the cement matrix. The formation of a layer of zinc oxidation products during the passivation process of the zinc rebars is responsible for both the sharp decrease of v_{corr} and the more noble potentials attained by galvanized reinforcements.

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.

For both the two alternative surface passivated galvanized rebars (type C3 and TC) the corrosion current initially increases up to a maximum value. These results indicate that the passivation treatment improves the corrosion behavior during the first 2-3 days after casting, in addition to the improvement in the air on the job-site. Then, after about three days, the corrosion rate trend is very similar to that of the untreated galvanized steel bar. This behavior could be ascribed to the good protection initially offered by the passivation treatment to the zinc coating (low initial corrosion rate) and then to the failure of the surface passivated layer which was defective in some points (increase in corrosion current). Hence, the breakdown of the passivation layer favor the formation of calcium hydrozincate identified by SEM [14]. This product is considered to be responsible for the protection of the zinc coating and thus for the consequent decrease of the corrosion rate.

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 (hexavalent chromium based) passivated galvanized steel bars and galvanized rebars passivated with the two alternative treatments based on the trivalent chromium solution or the cobalt and titanium salts solution.

Corrosion Potentials and Corrosion Rate During the Wetting/Drying Cycles in NaCl Aqueous Solution

Free corrosion potentials and corrosion rate of galvanized rebars embedded in concrete specimens exposed to wetting/drying cycles in 3% sodium chloride aqueous solution were measured. However, since no significant informations were obtained by potential data, only corrosion rate values of galvanized rebars are shown.

Figures 3, 4 and 5 show corrosion rates as a function of the number of wetting and drying cycles for galvanized rebars of the group 1 (cover 15 mm) in concrete specimens manufactured with CE I 52.5, CE II/M 32.5R, and CE IV/B 32.5, respectively. It is interesting to note that bare galvanized rebars have a sharp increase in the corrosion rate value after 7-8 wetting/drying cycles. On the other hand, 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, and more importantly, after 17 wetting and drying cycles corrosion rates of the two hexavalent chromium free passivated galvanized rebars (type C3 and TC) are lower than those recorded for both bare galvanized bars (type BA) and conventional (hexavalent chromium based) passivated galvanized steel reinforcements (type C6), independently of the cement type.

Similar results were obtained for galvanized rebars with a concrete cover of 35 mm (Fig. 6-8). Again, the two alternative passivation treatments (type C3 and TC bars) give comparable or better corrosion protection than both bare galvanized rebars and conventional chromating treatment, independent of the cement used.

These data indicate that surface passivation treatments improve the corrosion resistance of galvanized rebars with respect to that of bare galvanized steel reinforcements. Moreover, type TC and C3 bars showed at the end of the 17 wetting and drying cycles a better corrosion resistance behavior than that of the conventional passivated steel reinforcements (type C6), independent of the cement type.

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 surface of galvanized rebars, the reinforcements were divided into four groups:

- **group A:** bars with the zinc coating slightly and partially etched without red rust and with small dark grey spot due to uncovering of Zn-Fe intermetallic compounds as a consequence of the external zinc layer dissolution (Fig. 9-11).
- **group B:** reinforcements with the zinc coating fully etched, with dark grey spots, without red rust.
- **group C:** rebars with the zinc coating fully etched and the presence of spots of red rust.
- **group D:** galvanized rebars with heavy presence of red rust.

Classification of rebars according to the above mentioned four groups is shown in Table 3. Again, the visual observation confirms that type C3 and TC bars showed, at the end of the 17 wetting/drying cycles, a better corrosion resistance than that of both conventional passivated steel bar (type C6) and bare galvanized reinforcements.

Independent of both the type of galvanized rebars and the concrete cover, reinforcements embedded in concrete specimens manufactured with portland (CE I 52.5R) and portland composite cement (CE II/B-M 32.5R) showed higher corrosion rates (Tab. 3) than those recorded for bars in concrete manufactured with the pozzolanic cement (CE IV/B 52.5R). These results, in terms of v_{corr} can be ascribed to the lower chloride content in concrete manufactured with the pozzolanic cement independent of the concrete cover (Fig. 12). For instance, the percentage (by mass of concrete) of chloride at 35 mm depth is about 0.4, 0.55 and 0.70 in concrete with pozzolanic cement, portland composite 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 steel/concrete interface.

Finally, Figure 12 indicates that the chloride content in concrete specimens is significantly high and this reflects the heavy corrosion detected in many galvanized rebars.

CONCLUSIONS

No significant differences in terms of E_{corr} and v_{corr} exist after 40 days of curing in 20°C and 85% R.H. environment between conventional (hexavalent chromium based) passivated galvanized steel bars (type C6) and galvanized rebars passivated with two alternative surface treatments based on a trivalent chromium solution (type C3 bars) or a cobalt titanium salts solution (type TC bars).

After 17 wetting/drying cycles in a 3% NaCl aqueous solution corrosion rates of the two hexavalent chromium-free passivated galvanized rebars (type C3 and TC) are lower than those recorded for both untreated galvanized bars (type BA) and conventional (hexavalent chromium based) passivated galvanized steel reinforcements independent of the cement type.

The visual observation of the surface of galvanized rebars confirms that type C3 and type TC bar showed at the end of the 17 wetting/drying cycles a better corrosion resistance than that of both conventional passivated galvanized bars (type C6) and untreated galvanized reinforcements.

Galvanized reinforcements embedded in concrete specimens manufactured with portland cement (CE I 52.5R) and portland composite cement (CE II/B-M 32.5R) showed higher corrosion rates than those recorded for bar in concrete manufactured with the pozzolanic cement (CE IV/B 32.5R), independent of both the type of galvanized rebars and the concrete cover. These results can be

ascribed to the lower chloride penetration in concrete with pozzolanic cement and confirm that the higher corrosion rate of zinc coating in portland cement depends strongly on the higher chloride content at the steel concrete interface.

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Table 1 – Chemical composition of the cements used

Composition (%)	Portland cement CE I 52.5R	Pozzolanic cement CE IV/B32.5R	Portland Composite cement CE II/B-M 32.5R
SiO ₂ %	21.2	18	25.4
Al ₂ O ₃	2.3	4.2	4.76
Fe ₂ O ₃	5.2	3.4	4.2
CaO	60.3	63.2	61.9
MgO	0.98	3.2	2.63
K ₂ O	0.90	2.36	0.77
Na ₂ O	0.52	0.44	0.133
SO ₃	2.3	3.1	1.7
C _r ⁶⁺ (ppm)	1.8	1.1	0.7

Table 2 - Composition and properties of concrete mixtures manufactured

Ingredients-Property	
Water	210 kg/m ³
Cement	318 kg/m ³
Gravel (4-8 mm)	1185 kg/m ³
Sand (0-4 mm)	590 kg/m ³
w/c	0.66
Slump	60 mm

Table 3 - Corrosion rates at the end of wetting and drying cycles and visual rating of the corroded surface in galvanized steel bars.

Reinforced bar	Type of bar	BA		C6		C3		TC	
	Type of passivation	No passiv.		C _r ⁶⁺		C _r ³⁺		Ti/Co salts	
Type of cement	Concrete cover (mm)	15	35	15	35	15	35	15	35
CE I 52.5R	Corrosion rate* (µm/year)	124	107	14	13	120	122	99	41
	Visual rating	D	D	D	D	D	C-D	D	B
CE II/B-M 32.5R	Corrosion rate* (µm/year)	113	108	11	55	94	35	90	60
	Visual rating	D	D	D	B-C	D	A	D	B-C
CE IV/B 32.5R	Corrosion rate* (µm/year)	87	80	92	53	38	40	62	55
	Visual rating	D	D	D	B	A-B	A	C-D	B-C

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

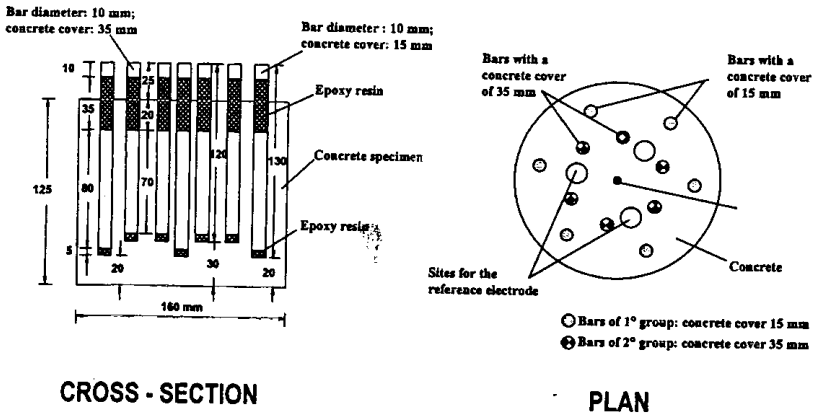


Fig. 1 – Schematic representation of cylindrical concrete specimens.

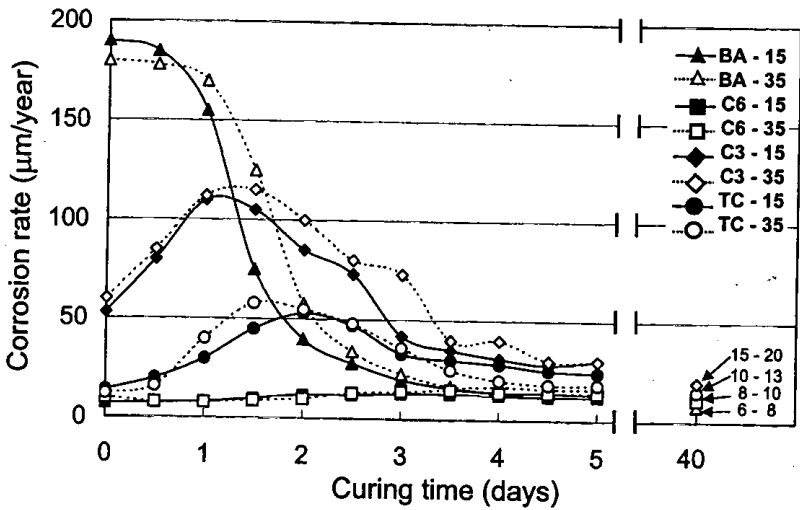


Fig. 2 – Average corrosion rates of galvanized bars embedded in concrete specimens manufactured with portland cement (CE I 52.5 R) during the curing time at room temperature and 85% R.H.

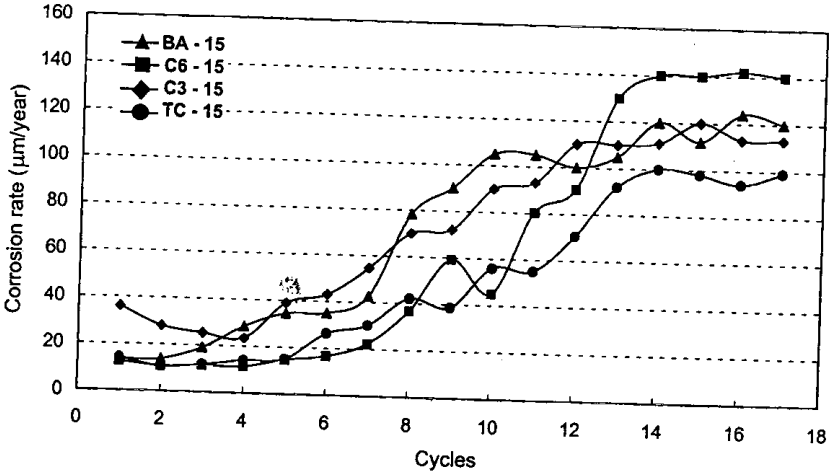


Fig. 3 - Average corrosion rates of galvanized bars embedded (concrete cover = 15 mm) in the concrete specimens manufactured with portland cement (CE I 52.5 R) as a function of the number of wetting and drying cycles.

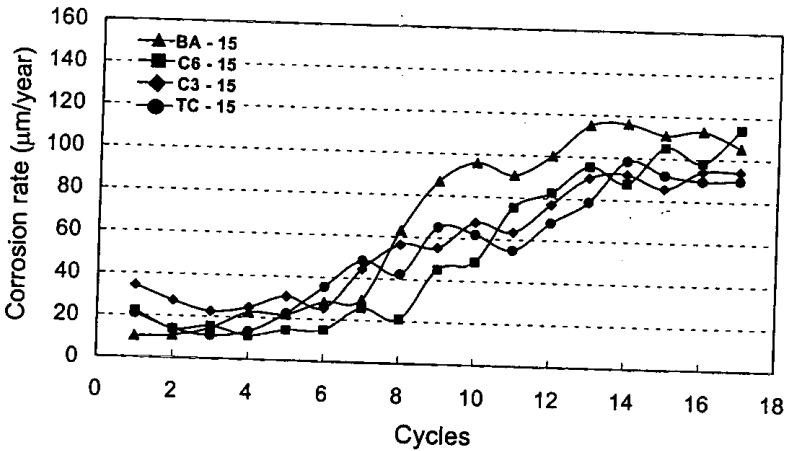


Fig. 4 - Average corrosion rates of galvanized bars embedded (concrete cover = 15 mm) in the concrete specimens manufactured with portland composite cement (CE II/B-M 32.5 R) as a function of the number of wetting and drying cycles.

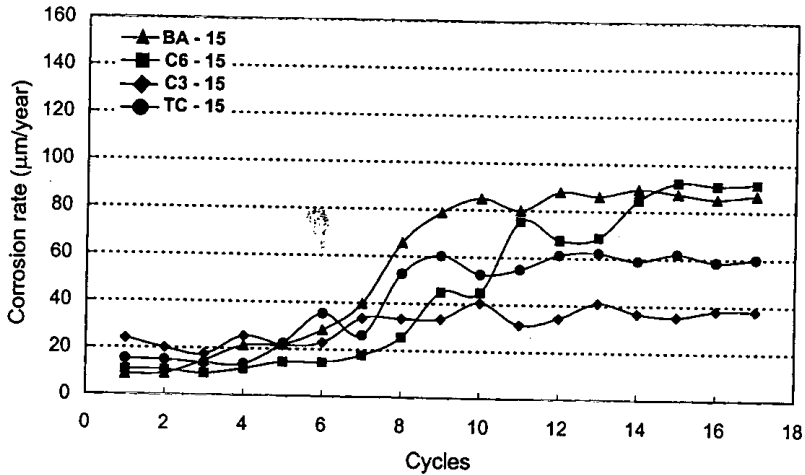


Fig. 5 – Average corrosion rates of galvanized bars embedded (concrete cover = 15 mm) in the concrete specimens manufactured with pozzolanic cement (CE IV/B 32.5 R) as a function of the number of wetting and drying cycles.

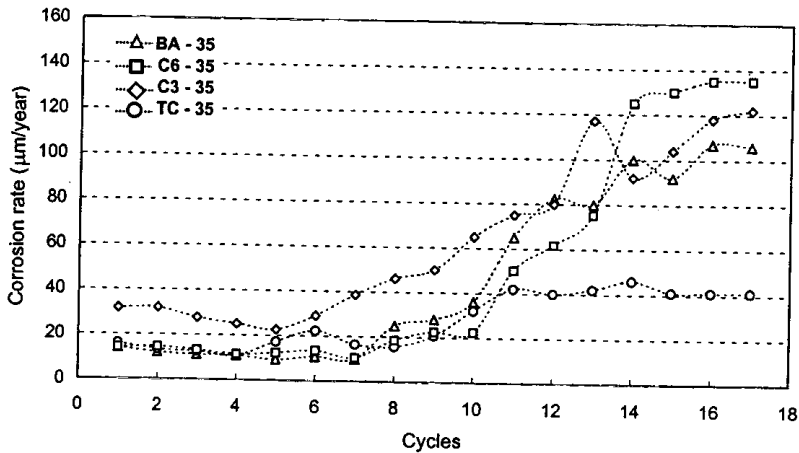


Fig. 6 – Average corrosion rates of galvanized bars embedded (concrete cover = 35 mm) in the concrete specimens manufactured with portland cement (CE I 52.5 R) as a function of the number of wetting and drying cycles.

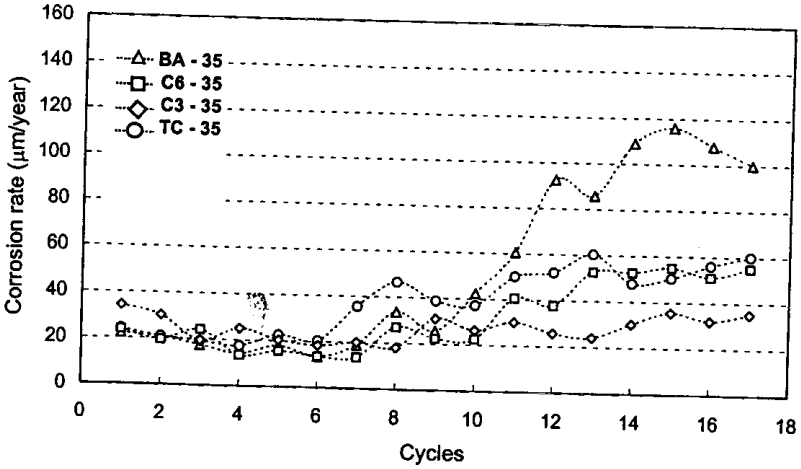


Fig. 7 – Average corrosion rates of galvanized bars embedded (concrete cover = 35 mm) in the concrete specimens manufactured with portland composite cement (CE II/B-M 32.5 R) as a function of the number of wetting and drying cycles.

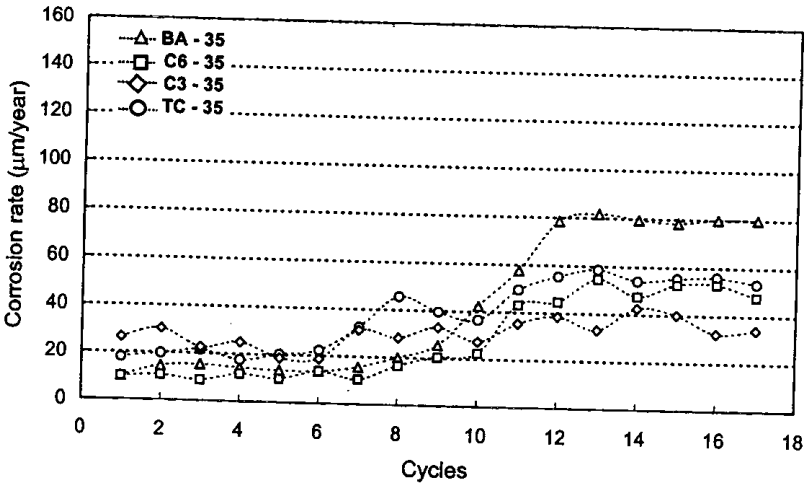


Fig. 8 – Average corrosion rates of galvanized bars embedded (concrete cover = 35 mm) in the concrete specimens manufactured with pozzolanic cement (CE IV/B 32.5 R) as a function of the number of wetting and drying cycles.



Fig. 9 - Partial cross section of a type C3 galvanized bar embedded in concrete (concrete cover: 35 mm) manufactured with pozzolanic cement (CE IV/B 32.5R).

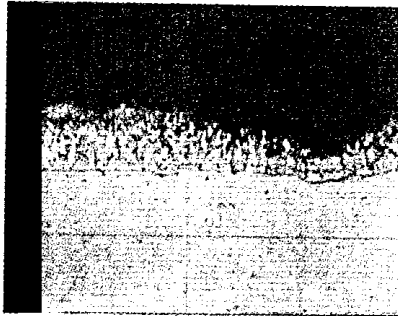


Fig. 10 - Partial cross section of a type C6 galvanized bar embedded in concrete (concrete cover: 35 mm) manufactured with pozzolanic cement (CE IV/B 32.5R).

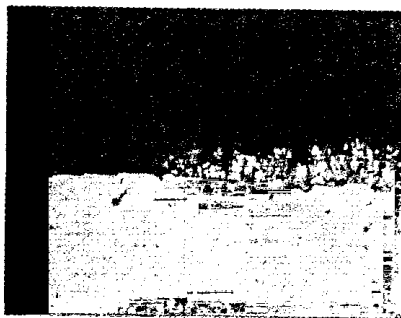


Fig. 11 - Partial cross section of a type TC galvanized bar embedded in concrete (concrete cover: 15 mm) manufactured with portland composite cement (CE II/B - M 32.5R).

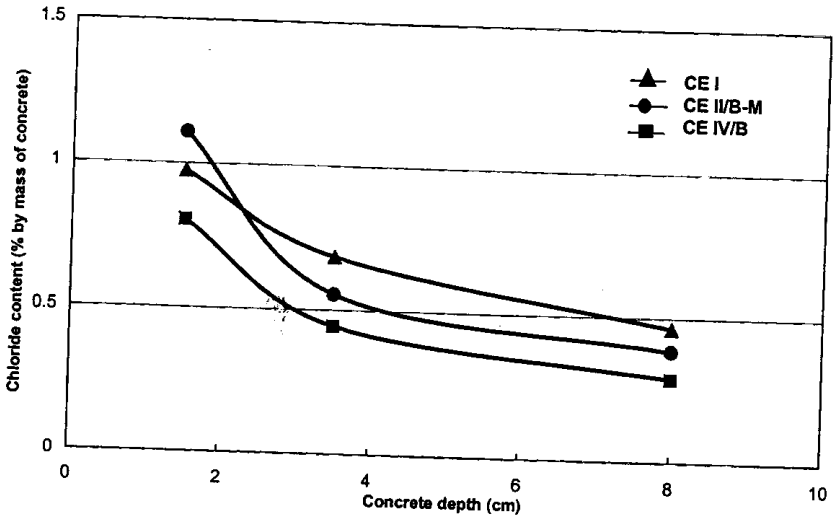


Fig. 12 - Chloride content at various depth in the concrete specimens.