Pergamon

Cement and Concrete Research, Vol. 26, No. 2, pp. 215-224, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in the USA. All rights reserved
0008-8846/96 $15.00 + .00

SSDI 0008-8846(95)00215-4

ANALYSIS OF THE PROTECTIVE EFFICIENCY OF GALVANIZING AGAINST CORROSION OF REINFORCEMENTS EMBEDDED IN CHLORIDE CONTAMINATED CONCRETE

A. Bautista and J.A. González
Centro Nacional de Investigaciones Metalúrgicas (CSIC)
Avda. Gregorio del Amo nº 8, 28040 Madrid, Spain. Fax: 34 1 534 7425

(Refereed)
(Received July 12, 1995; in final form November 21, 1995)

ABSTRACT

Galvanizing concrete embedded steel reinforcements is one of the methods for avoiding their corrosion. However, whether they can guarantee predicted service lives for structures exposed to highly chloride containing media remains controversial. This paper analyses the protective efficiency of galvanized steel embedded in concrete specimens of variable cement/water/sand ratios immersed in sea water. The results are compared with those obtained for bare steel under the same conditions. The influence of concrete porosity on the corrosion rate is discussed.

Introduction

The aqueous phase held in concrete pores is a highly alkaline medium (pH 12–14) that passivates steel reinforcements and hence protects them against corrosion. However, steel embedded in real structures has frequently been found to undergo corrosion, mainly of two origins:

(*a*) Carbonation of the medium by reaction of atmospheric CO_2 with the liquid phase held in concrete pores, which is saturated with $Ca(OH)_2$, and with hydrated compounds of concrete that are in equilibrium with the liquid phase; this decreases the pH of the pore solution to about 8 and breaks steel passivity, thereby giving rise to generalized reinforcement corrosion.

(*b*) The presence of chloride ions at concentrations above a critical threshold as the result of mixing the cement with sea water, immersing the structure in chloride containing water or exposing it to a marine atmosphere; this causes local acidification and eventually failure of the structure concerned through localized corrosion. The chloride content in concrete should not exceed 0.1% by weight (1) as higher concentrations can lead to steel corrosion in the presence of enough atmospheric oxygen and moisture. When chlorides are not initially present in the concrete, but penetrate it through its pore network, the pore type and degree of porosity may hinder or boost attack on the embedded steel.

One of the most widely used measures for avoiding corrosion of concrete embedded reinforcements involves galvanizing, which is relatively inexpensive. This protects steel by two mechanisms, the efficiency of which can by diminished by some conditions, namely:

(*a*) Zinc may act as a sacrificial anode in corrosion. Its action would be time-limited by a high corrosion rate owing to the typically small thickness of the galvanized coatings (60–100 µm).

(*b*) Provided the pH of the pore solution is between 12.2 ± 0.1 and 13.3 ± 0.1, zinc is covered with a thin, compact film of calcium hydroxyzincate [$Ca(Zn(OH)_3)_2 \cdot 2H_2O$] that passivates it and avoids reinforcement corrosion (2). On the other hand, if the pH of the pore solution exceeds 13.2, Zn is in the active state and undergoes generalized corrosion. Finally, at a pH of 11–12, Zn is covered with a porous, scarcely adhesive film of ZnO that provides no protection (3,4). The pH of concrete is determined by the alkali content of the cement, which should therefore be carefully chosen in order to ensure adequate corrosion resistance of the galvanized steel to be embedded (5,6). Therefore, to concrete composition is ascribed the differential behaviour of real structures.

The joint use of galvanized and bare reinforcements is counterproductive as it increases the corrosion rate through formation of galvanic couples (7).

The galvanized coating consists of superimposed layers of different chemical composition (the outermost layer usually consists of pure Zn and those underneath of Zn–Fe alloys of variable composition) (5). Galvanized coatings lacking the pure Zn layer (grey galvanizing) are less effective in protecting reinforcements (7). Aluminium–zinc coatings, which were formerly used successfully for preventing atmospheric corrosion of steel in urban and industrial atmospheres, are less efficient than traditional galvanizing procedures in such a highly alkaline medium as concrete (8). Even so, the composition of the electrolyte held in concrete pores is seemingly more influential on the corrosion process than is the type of the galvanized coating (9).

There is wide consensus that galvanizing provides effective protection against corrosion due to concrete carbonation (6,7,10,11), which shifts the pH of the pore solution to a region where Zn cannot be attacked; however, whether the effect is preserved in a chloride containing concrete remains controversial. The large number of reinforced concrete structures that are immersed in or near sea water, and the vast economic losses arising from their corrosion, have created the need for perfect knowledge of the protection methods of steel in these media and their actual efficiency. This paper analyses the protective efficiency of galvanized steel embedded in concrete of different cement/sand/water ratios that was partly immersed in artificial sea water.

Experimental

Materials. We used galvanized and bare corrugated carbon steel reinforcements that were 8 cm long and 6 mm diameter.

Concrete specimens were shaped in cubes of 7 cm side by using Portland P-450 cement of a high initial resistance. Specimens were prepared in 9 different compositions by combining three cement/sand ratios (1:8, 1:3 and 1:1) and as many water/cement ratios (0.4:1, 0.6:1 and 0.8:1). Three specimens per composition (an overall 27) were made. The first and second specimen in each batch were used to embed 5 reinforcements of bare carbon steel and galvanized steel, respectively; the third specimen contained no reinforcement and was used for chloride penetration tests. All of them were cured at 20 ± 2°C and 90% RH during the first 24 days. Then, they were submerged in artificial sea water prepared according to ASTM-D 1141-75 for 1 year (12).

Measurement Methods. The corrosion rate of carbon steel and galvanized steel was evaluated gravimetrically by weighing reinforcements before and after exposure (an average value for the period was thus obtained), as well as electrochemically, by measuring the polarization resistance (13), which was substituted into the Stern–Geary equation to determine the corrosion rate at different times over the testing period.

Chlorides were determined by Mohr method using cylinders of 0.8 cm diameter and 0.5 cm height that were dry extracted by drilling the specimens to a depth of 3–3.5 cm.

Concrete porosity at each composition was determined gravimetrically from the difference between the wet and dry weight of each specimen.

Results

Figure 1 shows the average corrosion rate obtained under each set of experimental conditions after a year exposure period. As can be seen, galvanizing reinforcements and using a high cement/sand ratio in the concrete both had a high protective effect against corrosion.

Figure 2 shows temporal changes in the corrosion rate throughout the exposure period under each of the 18 different experimental conditions studied. As can be seen, the corrosion rate of carbon steel increased continuously during the 12 months the specimen was immersed in sea water, whichever the composition of the encasing concrete. Galvanized steel reinforcements behaved somewhat differently; in fact, their corrosion rate decreased during the first few months of exposure to an extent dependent on the composition of the encasing concrete, and then increased during the last few months to values that were always below those for carbon steel.

As can be seen from Fig. 3 the corrosion potential for the reinforcements exhibited the opposite trend to the corrosion current. Thus, the specimens with a cement/sand ratio of 1:8 had a higher corrosion current and a more negative corrosion potential than the other cement-richer

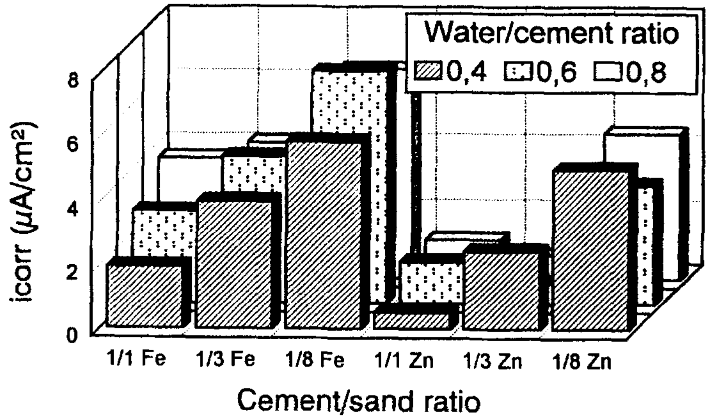

FIG. 1.

Average corrosion rate of galvanized and bare steel reinforcements embedded in concrete of variable cement/sand/water ratios after a 12-month period of partial immersion in artificial sea water.

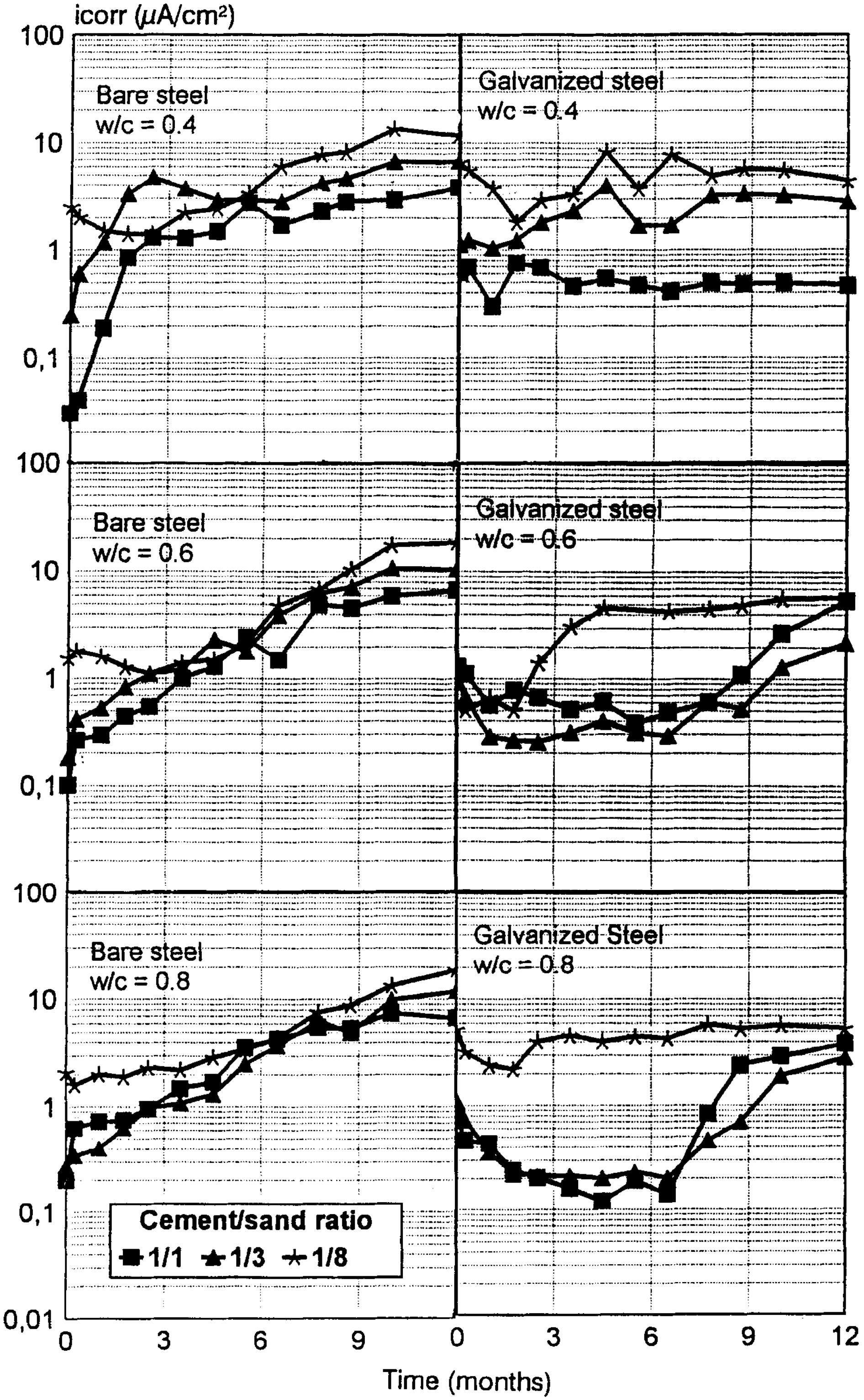

FIG. 2.

Variation of i_{corr} for reinforcements during the 12-month exposure period.

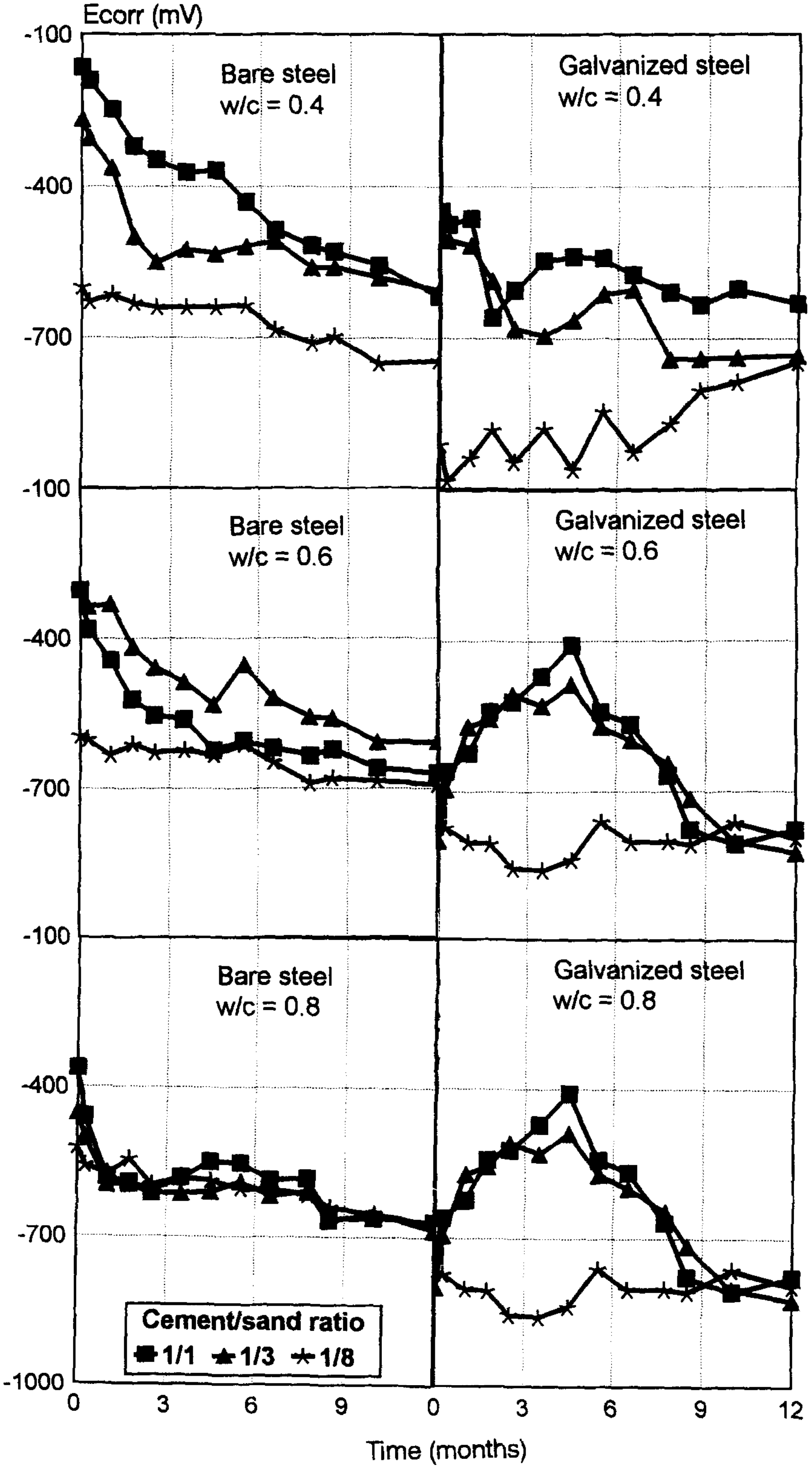

FIG. 3.

Variation of E_{corr} for reinforcements during the 12-month exposure period.

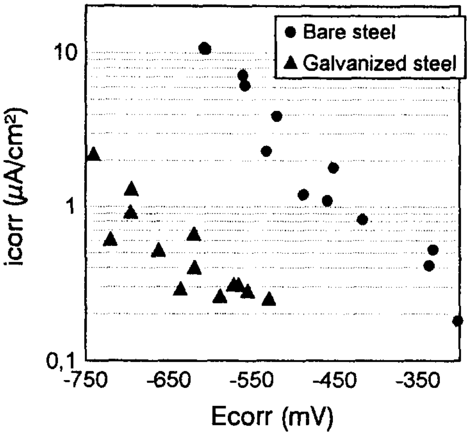

FIG. 4.

Variation of the relationship between i_{corr} and E_{corr} for galvanized and bare reinforcements embedded in concrete made in a cement/sand and water/cement ratio of 1:3 and 0,6, respectively, during the 12-month exposure period.

compositions, whether they contained carbon steel or galvanized steel reinforcements. Also, the corrosion potential and current were roughly linearly related throughout the exposure period for all the conditions. This is illustrated in Fig. 4 for two of the specimens studied: galvanized and bare steel embedded in concrete of the same composition (*viz.* cement/sand = 1:3 and water/cement = 0.6).

Figure 5 shows the variation of the amount of chloride measured inside each specimen (3–3.5 cm below the surface) as a function of the concrete cement/sand and water/cement ratios after 12 months of exposure. As can clearly be seen, the recommended Cl^- level for conventional reinforced concrete (1) was exceeded except in specimens containing abundant cement and little

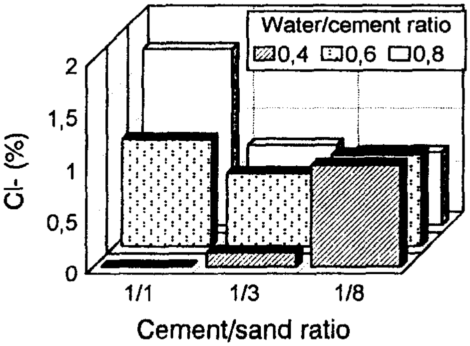

FIG. 5.

Percent weight of Cl^- relative to cement in concrete specimens of variable cement/sand/water ratios after partial immersion in artificial sea water for 1 year.

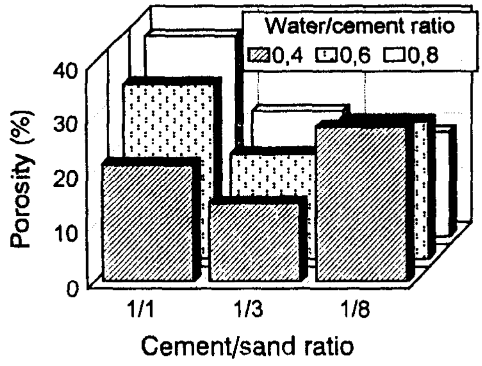

FIG. 6.
Variation of the overall porosity of concrete as a function of mortar composition.

water/cement ratio. As can be inferred by comparing Figs 5 and 6, the chloride penetration resistance of concrete is determined by its porosity. However, the parameters plotted in both graphs are not strictly linearly related since the amount of Cl^- that can penetrate the concrete depends not only on its total porosity, but also on its pore size distribution. The higher the cement content of a concrete mixture is at a given degree of porosity, the more favourable are interactions with some cement component. In summary, a high cement content decreases the amount of free Cl^- ions within concrete but can increase that of bound chloride; this accounts for the fact that the highest Cl^- proportion was obtained for the specimen containing the higher cement/sand and the lowest water/cement ratios.

Discussion

We should bear in mind that galvanizing steel reinforcements is only justified in very aggressive enviroments where corrosion is highly probable. In no chloride or not carbonated concrete the passivity of bare steel is the best guarantee of durability. In fact, as can be seen in Fig. 2, the lowest i_{corr} values were obtained from bare steel from the beginning of exposure (when no chloride ion had yet reached reinforcement surfaces).

However, galvanized steel in chloride-contaminated concrete corrodes at a lower rate than does bare steel, so galvanizing reinforcements always increases the time needed to reinforcements depassivation and the service life of concrete structures in media with low or moderate chloride concentrations.

As can be deduced from Fig. 2, corrosion products form a protective film on galvanized steel during the first few months of exposure; while the film cannot fully passivate reinforcements, it does diminish their corrosion rate. However, as can also been seen in Fig. 2, galvanized material in a marine environment reaches a point where the corrosion rate starts to increase. At that time, chloride ions which have reached reinforcements through the concrete pores are at such a high concentration on their surface that their attack cannot be countered by the inhibitory effect of hydroxyl ions; as a result, corrosion increases. While this chloride concentration threshold is higher for galvanized steel than for bare steel, once it is surpassed —which, for structures

TABLE 1

Time Taken by Galvanized Steel Reinforcements to Reach a Corrosion Rate Above 1 $\mu A/cm^2$

	water/cement ratio		
cement/sand ratio	**0.4**	**0.6**	**0.8**
1/1	> 12 months	9-10 months	8-12 months
1/3	2-7 months	10-12 months	8->12 months
1/8	< 2 days	7 days- 6 months	< 2 days

exposed to sea water is only a matter of time— the Zn protective coating is depleted within a few years.

The higher chloride threshold of galvanized steel relative to bare steel and the delayed corrosion onset at identical concrete compositions are consistent with previous results of Yeomans in accelerated tests (14).

A comparison of Fig. 5 with Figs 1 and 2 reveals that the time chloride ions take to reach their threshold concentration and hence the corrosion protection of concrete to be overcome are directly dependent on the cement content of the concrete. Thus, concrete with a high cement/sand ratio contains few porosity (particularly macropores) and is therefore optimal for protecting structures exposed in coastal areas. Table 1 gives the time taken by galvanized steel reinforcements to reach a corrosion rate above 1 $\mu A/cm^2$ (equivalent to a penetration of 15μm/year for Zn, at which a conventional galvanized coating thickness would take 4–6 years to strip). These calculated figures probably underestimate the risk of corrosion as they assume that the metal is attacked uniformly when, in practice, pitting is frequently observed. As a result, when galvanized steel undergoes corrosion at such a high rate, the additional service life galvanizing can provide is very short in any case.

As can be seen from Fig. 4, galvanized steel invariably has a more negative potential than bare steel; however, on identical potentials, carbon steel exhibits a higher corrosion current than galvanized steel. Such a difference between the corrosion potentials for Zn and Fe has been used to identify complete stripping of the galvanizing film and the onset of steel corrosion (14).

The fact the corrosion products of Zn are as harmful as those of Fe can be ascribed to the formation of $Zn_5(OH)_8Cl_2 \cdot H_2O$ from zinc embedded in concrete (15). The specific volume of this compound is 2.6 times higher than that of pure zinc, so it clearly offsets the volume increase due to the formation of ZnO (*ca.* 50%) or even that resulting in corrosion of bare steel.

While the corrosion products of Fe (reddish) are less aesthetic than those of zinc (whitish), contrary to the widespread belief, the latter can produce stresses that are as hazardous as or even more so than those one can expect from attacks on Fe.

Concrete to be used in coastal areas should therefore be prepared in such a way as to restrict diffusion of aggressive chloride ions to embedded reinforcements. This can be accomplished in two complementary ways, namely: (*a*) by using thicker concrete layers; and (*b*) by reducing concrete porosity using a high cement/sand ratio or even with additives which reduce porosity.

As reflected in our results, the protective effect of galvanizing lasts only a few years in media containing high chloride concentrations. In such highly aggressive media, adding inhibitors at the concrete manufacturing stage (16) or introducing cathodic protection after corrosion has started (17) appear to be the two most efficient choices for guaranteeing the projected service life of reinforced concrete structures.

Conclusions

- Bare and galvanized steels exhibit a critical threshold level for chloride ion, not determined here, above which their corrosion current rises sharply (Fig. 2).
- It is clear that the critical chloride threshold of galvanized steel is higher than that of bare steel, because the galvanized steel delays for a longer time the appearance of high corrosion rates (Fig. 2).
- After transition from passive to active state has taken place, galvanized steel employed here had lower corrosion rates than bare steel under the same exposure conditions (Fig. 1).
- However, the galvanized steel reaches i_{corr} values in the active state above $1 \mu A/cm^2$, so usual galvanized coating thickness can be corroded in about only 5 years.
- The durability required for a given structure can be attained using thick covers with low permeability (high c/s and low w/c ratio) and higher chloride thresholds (galvanized rebars), at least in media with low or moderate chloride concentrations.

Acknowledgements

This work was supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of the Ministry of Education and Science of Spain. We acknowlege the financial support provided by the Ministerio de Educación y Ciencia de España for one of the authors (A.B.).

References

1. ACI Standard 201, 2R-77, "Guide to Durable Concrete", ACI Manual of Concrete Practice (Part 1), American Concrete Institute, Detroit (1992).
2. A. Macías and C. Andrade, Brit. Corros. J. 22, 162 (1987).
3. A. Macías and C. Andrade, Brit. Corros. J. 22, 113 (1987).
4. A. Macías and C. Andrade, Brit. Corros. J. 22, 119 (1987).
5. C. Andrade and A. Macías, Surface Coatings-Vol.2, p. 137, A. D. Wilson, J. W. Nicholson and H. J. Prosser eds., London, 1988.
6. C. Andrade and J. A. González, Rev. Iber. Corros. y Prot. 15, 35 (1984).
7. E. Maahn and B. Sorensen, Corrosion (NACE) 42, 187 (1986).

8. T. P. Cheng, J. T. Lee, K. L. Lin and W. T. Tsai, Corrosion (NACE) 47, 436 (1991).
9. G. Sergi, N. R. Short and C. L. Page, Corrosion (NACE) 41, 618 (1985).
10. J. A. González, A. J. Vázquez and C. Andrade, Materiaux et Constructions 15, 271 (1982).
11. J. A. González and C. Andrade, Brit. Corros. J. 17, 21 (1982).
12. ASTM D 1141-75, Annual Book 1978, part 31, 909.
13. J. A. González, Control de la Corrosión: estudio y medida por técnicas electroquímicas, Chapter V, p. 101, CSIC eds., Madrid, 1989.
14. S. R. Yeomans, Corrosion (NACE) 50, 72 (1994).
15. W. G. Hine and M. Machin, Corrosion (NACE) 49, 858 (1993).
16. E. Ramírez, Doctoral Thesis, Universidad Complutense de Madrid, Fac. CC. Químicas, Madrid, 1994.