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THE PROTECTIVE EFFICIENCY OF GALVANIZING AGAINST CORROSION OF STEEL IN MORTAR AND IN $Ca(OH)_2$ SATURATED SOLUTIONS CONTAINING CHLORIDES

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ABSTRACT

The behaviour of galvanized steel in $Ca(OH)_2$ saturated solutions containing either no additives, chloride or chloride plus nitrite has been studied. The behaviour of galvanized steel in mortar specimens containing the same types of additives has been simultaneously analysed. The results show that the critical chloride threshold for galvanized steel is higher than that for bare steel before the transition from the passive to the active state takes place. However, protective films formed in the absence of chloride are not able to maintain steel passivity in a $Ca(OH)_2$ saturated solution containing 2% Cl^-. *Copyright © 1996 Elsevier Science Ltd*

Introduction

Ever since the first practical application of hot-dip galvanizing for protecting steel reinforcements was reported in 1931 (1), the procedure has been increasingly used as a preventive measure. Galvanization relies on the assumption that the higher chloride-resistance of zinc relative to steel and the lower volumes occupied by corrosion products from the former can substantially delay deterioration of reinforced concrete (RC) structures in especially aggressive environments. Under milder conditions, the high alkalinity of concrete by itself suffices to preserve the passivity of reinforcements and the durability of RC structures. However, some contradictory results have raised a controversy between advocates of reinforcement galvanization (2–6) and those who are sceptical about this protective efficiency in specially unfavourable situations (7–10). This controversy has originated from the following issues:

(a) Whether the complementary protection given by a zinc coating is adequate in the presence of a high concentration of contaminating chloride ions and in carbonated concrete;
(b) whether zinc is stable in such a highly alkaline medium as concrete;
(c) whether reinforcements are prone to embrittlement by hydrogen released within the first few hours of contact between the zinc layer and concrete; and
(d) whether adhesion of concrete to reinforcements is diminished by galvanizing.

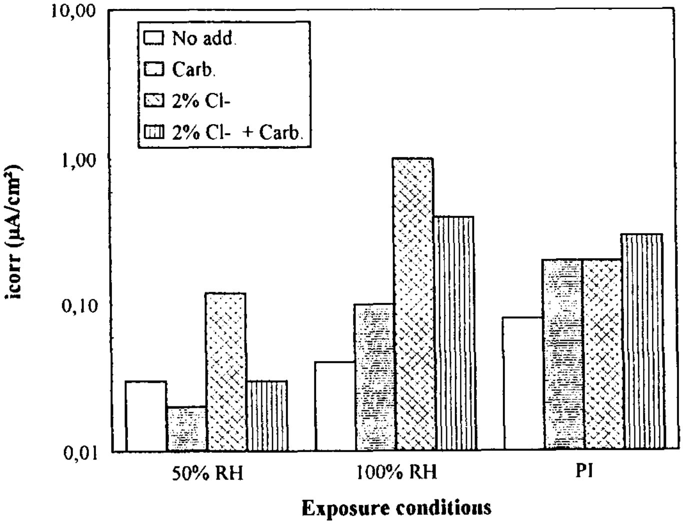

FIG. 1.

Effect of the exposure conditions (concrete carbonation and the presence of chloride ion) on the corrosion rate of galvanized reinforcements. Results obtained after 1 year of exposure under the same conditions.

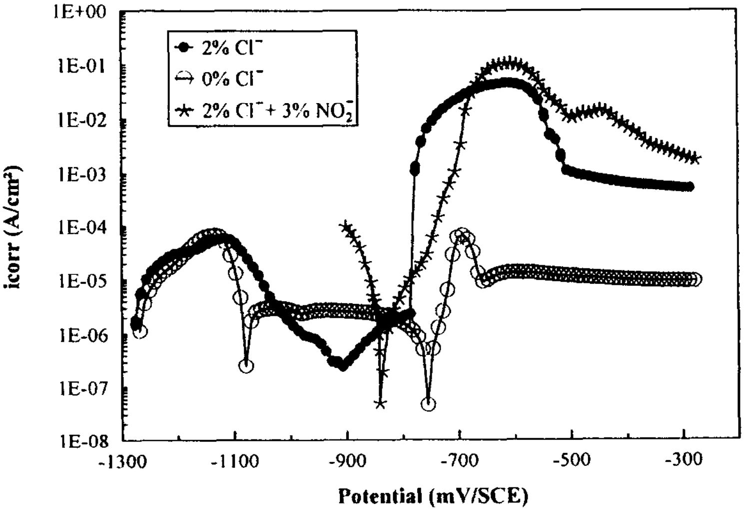

FIG. 2.

Polarization curves for galvanized steel in $Ca(OH)_2$ saturated solutions containing no additive, 2% Cl^- and 2% Cl^- + 3% NO_2^-.

Concrete carbonation is known not to significantly augment corrosion of galvanized reinforcements–occasionally, as shown in Fig. 1, derived from previously reported results (12,13), it even decreases corrosion to a significant extent.

On the other hand, whether galvanization is effective against corrosion in highly chlorinated media remains uncertain. This paper throws new light on this subject, which is the most important among the above-mentioned controversial issues–because if the protective efficiency of reinforcement galvanization were inadequate, use in RC structures would be unwarranted and questions *b–d* above pointless. This paper also analyses the ability of nitrite ion, the most

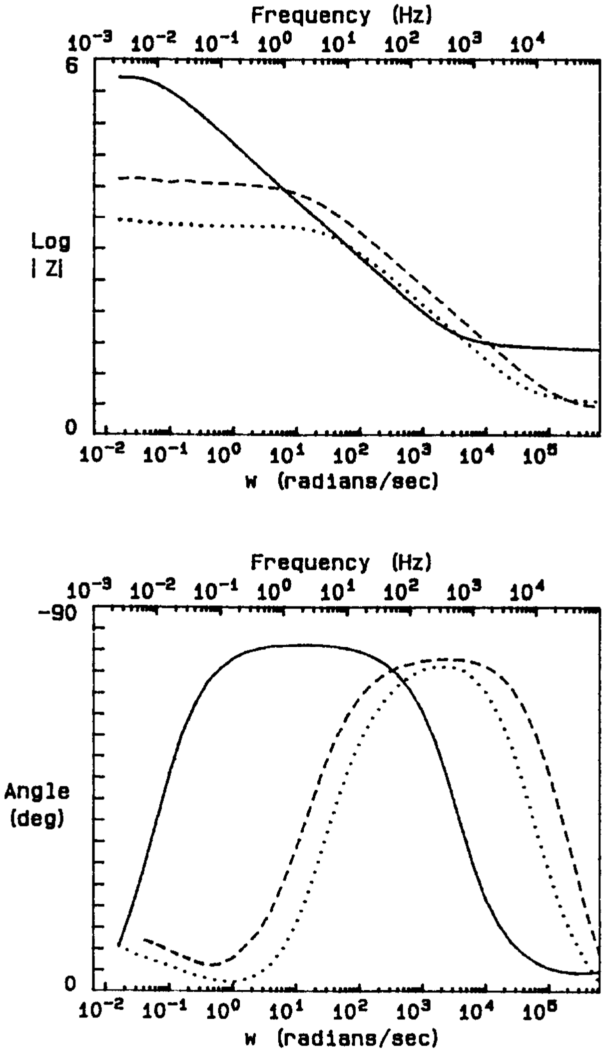

FIG. 3.

Impedance diagrams for galvanized steel in $Ca(OH)_2$ saturated solutions: (—) no additive, at 6 days; (...) 2% Cl^-, at 15 min; (---) 2% Cl^- + 3% NO_2^-, at 24 h.

widely used corrosion inhibitor for RC structures (14), to diminish or completely suppress the corrosion of zinc-coated steel embedded in concrete.

Materials and Methods

Materials. An experimental series was carried out in $Ca(OH)_2$ saturated solutions containing no additive, 2% Cl^- or 2% Cl^- + 3% NO_2^-. The same experiments were conducted on mortar

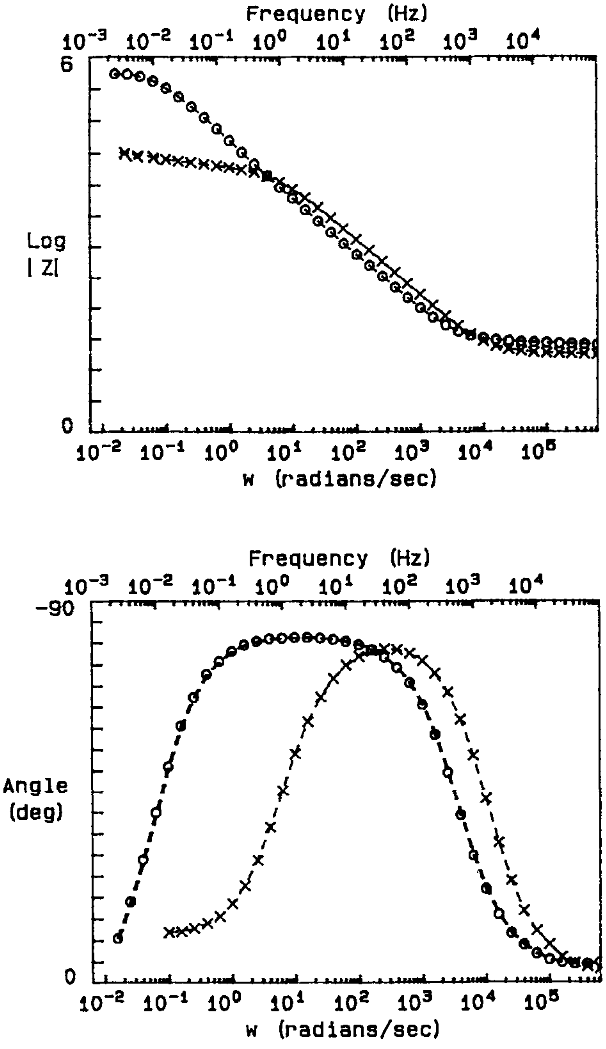

FIG. 4.

Impedance diagrams for galvanized steel in a $Ca(OH)_2$ saturated solution containing no additive: (o) at 6 days; (×) at 4 h.

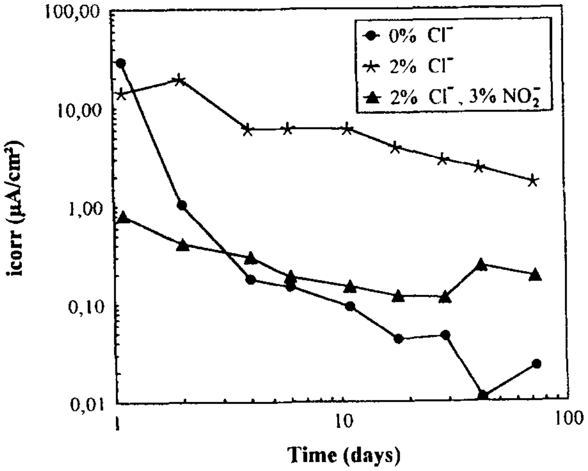

FIG. 5.

Temporal changes in i_{corr} for galvanized steel embedded in mortar containing no additive, 2% Cl^- and 2% Cl^- + 3% NO_2^-, exposed to a high relative humidity.

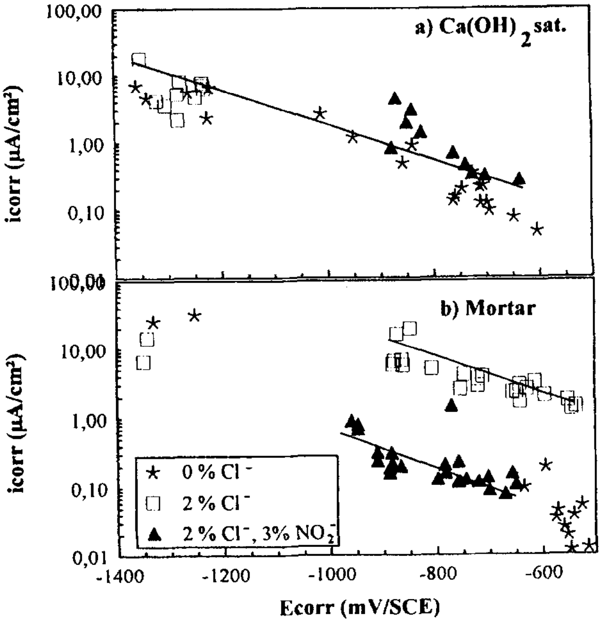

FIG. 6.

Relationship between i_{corr} and E_{corr} for (*a*) galvanized steel exposed to a $Ca(OH)_2$ saturated solution containing no additive, 2% Cl^- and 2% Cl^- + 3% NO_2^-, and (*b*) galvanized steel embedded in mortar containing the same additives.

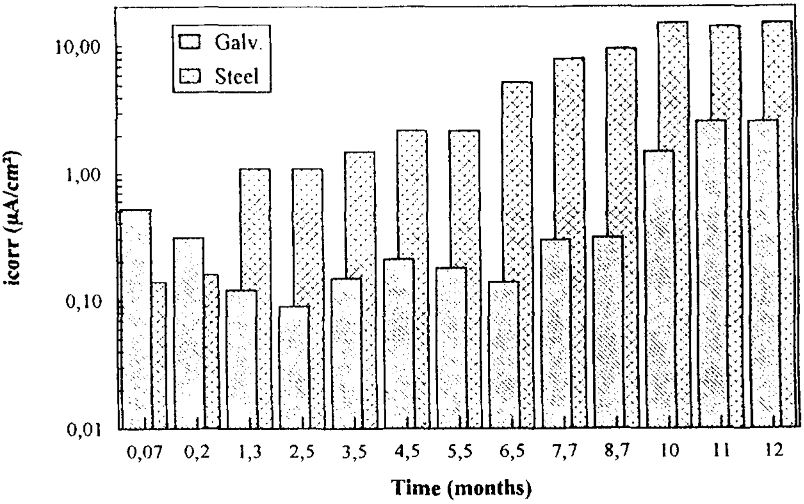

FIG. 7.
Variation of the corrosion rate for bare and galvanized steel reinforcements embedded in mortar specimens containing no chloride immersed in artificial sea water over a 12-month period.

specimens (2 × 5.5 × 8 cm) that were identical to those employed in previous work specimens (2 × 5.5 × 8 cm) that were identical to those employed in previous work (12,13,15,16) Mortar was made in a 1:3:0.5 cement/sand/water proportion and contained no additive or the same Cl^- or $Cl^- + NO_2^-$ concentrations used in the $Ca(OH)_2$ saturated solution. Chloride and nitrite ions were added as $CaCl_2$ and $NaNO_2$, respectively, relative to cement weight.

The working electrode (WE) used in the solution tests was a 1.5-mm thick carbon steel sheet that was coated with a 60-µm film of zinc by hot-dip galvanization at 450°C. The active surface

FIG. 8.
Typical scanning electron micrograph for galvanized steel immersed in a $Ca(OH)_2$ saturated solution containing no additive.

was always confined to 1 cm^2 and bounded by means of adhesive tape into which a hole of 12 mm diameter was drilled. Reinforcing corrugate steel bars of 8 mm nominal diameter and 8 cm length galvanized under the same conditions were embedded in the mortar specimens. The WE area exposed to the medium was 10 cm^2.

Measurement Methods. Corrosion was monitored by potentiodynamic recording of polarization curves at a scan rate of 1.0 mV/s, from polarization resistance measurements, and from impedance diagrams for the WE.

The corrosion current was estimated from the Stern–Geary equation (17),

$$i_{corr} = B/R_p \ (\textit{or} \ i_{corr} = B/R_T)$$

where R_p is the polarization resistance and R_T is the transfer resistance, which were measured with a potentiostat and by electrochemical impedance spectroscopy (EIS), respectively. An intermediate value of 26 mV for constant B was used in every case.

The appearance of corrosion products was examined by scanning electron microscopy (SEM) and their composition determined by energy-dispersive x-ray diffraction (EDXD) spectroscopy.

Results

Figure 2 shows typical polarization curves for galvanized steel run from -1300 to -300 mV *vs* SCE in $Ca(OH)_2$ saturated solutions containing no chloride, 2% Cl^- and 2% Cl^- + 3% NO_2^-. The solution containing no additive exhibited an open-circuit potential or corrosion potential (E_{corr}) of *ca.* -750 mV *vs* SCE and a passivation range at more positive potentials at 10 μA/cm^2. The small passivation peak may have been produced by the formation of passivating compounds in small areas that remained unprotected. Polarizing in the cathodic direction, a new anodic branch between -1080 and -1300 mVis found. This branch has a maximum about -1120 mV, that is associated with the oxidation of zinc to a new corrosion product, probably zinc oxide.

Adding a $Ca(OH)_2$ saturated solution containing 2% Cl^- over a passivating film previously formed in a similar solution containing no chloride resulted in a potential shift by about 500 mV in the negative direction and an increase in i_{corr} by a factor of 10–100 within a few hours. The polarization curve obtained in the presence of chloride exhibited a first passivation peak at *ca.* -1100 mV that decreased the current density to below 1μA/cm^2. However, such an effective passivation was scarcely stable; in fact, a well-defined breakdown potential (E_b) was observed at -800 mV beyond which the passivating layer was broken and the current increased sharply. At higher anodic polarization potentials, a new critical passivation potential similar to that for the solutions containing no chloride was rapidly reached, which suggests that the surface compound formed was the same. However, the protective efficiency of this compound was much lower in the presence of chloride, so much so that the current density rose to *ca.* 400 μA/cm^2 (nearly two orders of magnitude higher than in the absence of Cl^-).

Addition of nitrite to the chloride-containing solution shifted E_{corr} from -1300 to *ca.* -830 mV (between the two passivation peaks). The galvanized coating behaved passively, yet the passivating compound was highly prone to local breakdown, with an E_b value that was very similar to E_{corr}. Also, a new passivation peak appeared at the same potential as in the solution containing Cl^- as the sole additive; however, as in this solution, the passivation was scarcely efficient since it resulted in current densities in Cl^- + NO_2^- solution as a high as or even higher than in Cl^- alone.

FIG. 9.
Typical scanning electron micrograph for galvanized steel immersed in a $Ca(OH)_2$ saturated solution containing chloride.

Electrochemical impedance spectra showed two well-defined plateaux in the Bode diagram obtained by plotting, in logarithmic form, impedance against frequency (log Z *vs* log f) at values corresponding to the ohmic resistance of the solution (R_s) and $R_s + R_T$ (Fig. 3). The two resistance-controlled zones were separated by another, capacitance–controlled zone that allowed estimation of an electrolytic double layer capacitance (C_{dl}) of *ca.* 10 μF/cm^2. The estimated i_{corr} values ranged from 0.01 and 0.1 μA/cm^2 in the passive state and between 1 and 10 μA/cm^2 in the active state. The corrosion currents obtained in the solutions containing chloride and nitrite were somewhat higher than those measured in the solutions containing no additive, but quite similar and typical for a passive state in any case.

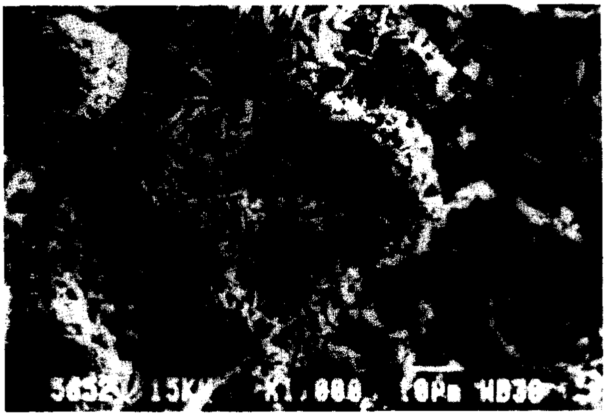

FIG. 10.
Acicular crystallites observed on the surface of the galvanized coating on exposure to a $Ca(OH)_2$ saturated solution containing chloride.

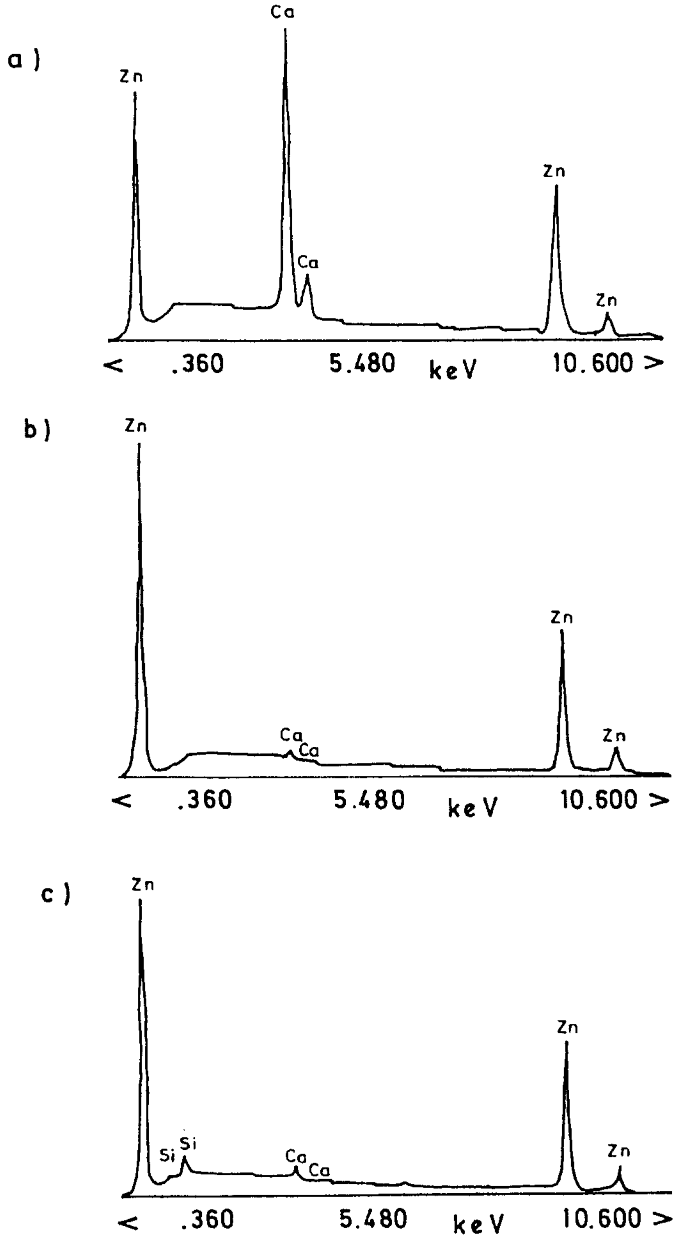

FIG. 11.

X-ray diffractograms for the corrosion products on galvanized coating. (*a*) In the middle of one of the polygonal plates shown in Fig. 8. (*b*) Among the polygonal plates of Fig. 9. (*c*) In the acicular conglomerates of Fig. 10.

Galvanized steel initially behaved as an active electrode on immersion in the solution containing no chloride (Fig. 4). After a few hours, R_T rose sharply coinciding with the transition from the active to the pasive state. The transition also reflected in a change in E_{corr} by 400 mV or more in the positive direction. The R_p values obtained by using direct current and polarizing the WE at ± 10mV were quite consistent with R_T values estimated from impedance diagrams such as those of Figs. 3 and 4.

Figure 5 compares temporal changes in the i_{corr} values estimated from R_p measurements for galvanized reinforcements embedded in mortar containing no additive, chloride and chloride plus nitrite. As can be seen in Fig. 6, which shows the variation of i_{corr} with E_{corr}, the corrosion rates obtained were comparable to those for the $Ca(OH)_2$ saturated solutions containing the same additives.

Figure 7 illustrates a different situation, *viz.* that where chloride was not added to the mortar composition, but penetrated concrete by diffusion (18). It shows the i_{corr} values obtained for 4 bare steel and 4 galvanized steel reinforcements embedded in mortar containing no chloride that was immersed in artificial sea water for 1 year. Initially, the galvanized material was more severely attacked than bare steel; however, while i_{corr} for the former decreased in the process, that for the latter increased considerably and surpassed that of galvanized steel within a few days. After a few months, i_{corr} for galvanized steel also increased, but never to the levels of bare steel.

Inspection under the SEM of corrosion products for the galvanized material revealed the surface immersed in the $Ca(OH)_2$ saturated solution containing no chloride to be almost completely covered with polygonal plates (Fig. 8). There were also some isolated zones where two morphologically rather different products coexisted (Fig. 9). The area not covered with polygonal plates (unprotected area) was much larger for the material immersed in the solution containing chloride; in addition, conglomerates of small lamellar or acicular crystallites were observed (Fig. 10).

EDXD analyses showed the plates to contain a substantial proportion of calcium (Fig. 11*a*); this indicates the presence of calcium hydroxyzincate crystals (19,20). However, calcium was excluded from the composition of the corrosion products observed between the plates (Fig. 11*b*) and from acicular conglomerates (Fig. 11*c*), so both were probably zinc oxide.

Discussion

Based on Fig. 1, galvanized materials are scarcely prone to carbonation-induced corrosion. Therefore, galvanized rebars may be effective for application to low-quality concrete, easy to carbonate, in order to substantially delay the appearance of rust stains and corrosion of steel in the active state.

On the other hand, chloride (at high enough concentrations) fosters corrosion in the active state. Passivation in the presence of chloride can be accomplished by anodic polarization, which, however, is much less efficient than in its absence. As can be seen in Fig. 2, the difference between the corrosion potential, E_{corr}, and breakdown potential, E_b, is very small, and consequently the passive state stability is small as well. The corrosion rate in the active state is much higher than in the passive state, and i_{corr} usually exceeds 1 $\mu A/cm^2$ (Figs. 3, 5–7). At such an i_{corr} value, the typical thickness of galvanized coatings would be stripped in a relatively short time (4–6 years) since 1 $\mu A/cm^2$ results in a penetration of *ca.* 15 μm/year for zinc.

One may think that an existing passivating film previously formed in a solution containing no chloride might withstand the subsequent attack of chlorides. Unfortunately, the results are far from being cause for optimism. In fact:

(a) Passivating films cannot maintain passivity on immersion in a $Ca(OH)_2$ saturated solution containing 2% Cl^-.

(b) When chloride was supplied by diffusion from artificial sea water to the surface of galvanized reinforcements in mortar containing no chloride, the reinforcements abandoned their passive state and reached corrosion rates above 1 $\mu A/cm^2$ within a few months (Fig. 7). It should be noted, however, that the Cl^- concentration threshold that cancels passivity is much higher for galvanized steel relative to bare steel since i_{corr} starts to increase sharply much sooner in the later (Fig. 7).

On the other hand, the addition of nitrite counters the action of chloride; it maintains the passive state as reported by other authors (10). Unfortunately, while quite efficient (Figs. 3, 5 and 6), the effect is rather unstable, as reflected in the similarity between E_b and E_{corr} for $Ca(OH)_2$ solutions containing 2% Cl^- + 3% NO_2^- (Fig. 2). In any case, using two complementary protection methods seems unjustified when nitrite ions by themselves offer better protection than in combination with galvanizing (21).

Based on our analytical results (Fig. 11) and previously reported data (11,19,20), the large polygonal plates shown in Fig. 8 consist of calcium hydroxyzincate, whereas the interplates areas shown in Fig. 9 and the acicular conglomerates of Fig. 10 are composed of zinc oxide. Because nearly the whole surface is covered with hydroxyzincate plates in the absence of chloride ions, the plates might be associated with the passivation of the galvanized coating. Even if the formation of the hydroxyzincate were mandatory for the passive state to be reached, our results suggest that this also requires the chloride concentration not to exceed a critical threshold. Such a threshold is higher than that for bare steel (Fig. 7) but lower than the 2% Cl^- concentration tested.

Conclusions

The results obtained in this work allow us to draw the following conclusions:

(a) Galvanized steel has a higher critical chloride threshold than bare steel before the transition from the passive to the active state takes place.

(b) After that, galvanized steel is less markedly corroded than bare steel under the same exposure conditions; however, the former reaches i_{corr} values above 1 $\mu A/cm^2$, so the usual galvanized coating thickness can be stripped in about 5 years.

(c) The presence of discontinuities in the hydroxyzincate layer does not hinder preservation of the passive state in a $Ca(OH)_2$ saturated solution containing no chloride.

(d) Passivating films associated with hydroxyzincate plates cannot maintain passivity on immersion in a $Ca(OH)_2$ saturated solution containing 2% Cl^-.

(e) Nitrite effectively counters the action of chloride, thereby maintaining the passive state in both $Ca(OH)_2$ saturated solutions and mortar. However, the protective effect is unstable owing to the small difference between the breakdown and corrosion potentials.

References

1. F.C. Porter, Concrete, 8, 29 (1976).
2. A.R. Cook and S.F. Radke, Chloride corrosion of steel in concrete, ASTM-STP 629, p. 51, American Society for Testing Materials, Philadelphia (1977).
3. D. Stark, Measurement techniques and evaluation of galvanized reinforcing steel in concrete structures, ASTM-STP 713, p. 132, American Society for Testing Materials, Philadelphia, (1980).
4. I. Cornet and B. Bresler, Mater. Prot., 5 N° 4, 69 (1966).
5. T. Ishikawa, I. Cornet and B. Bresler, Proc. 4th Int. Cong. Met. Corros., p. 556, Amsterdam, Sept. 1969.
6. R. Duval and G. Airliguie, Mém. Scient. Rev. Métallur., 11, 5 (1974).
7. C. E. Mange, Mater. Perf., 16 N° 7, 34 (1977).
8. H. Arup, Newsletter (Korrosion Centralen, Denmark), N° 1, 1 (1978).
9. H. Hildbrand and W. Schwenk, Werk. Korros., 37, 163 (1986).
10. N.S. Berke, D.F. Shen and K.M. Sundberg, Corrosion rates of steel in concrete, p. 38, ASTM-STP 1065, American Society for Testing Materials, Philadelphia, 1990.
11. C. Andrade and A. Macías, Surface Coating-2, p. 137, A.D. Wilson, J.W. Nicholson and H.J. Prosser Eds., London, 1988.
12. C. Andrade and J.A. González, Rev. Iberoam. Corros. Prot., 15 (4) , 35 (1984).
13. J.A. González and C. Andrade, Brit. Corros. J., 17, 21 (1982).
14. N.S. Berke, Mater. Perf., 28 N° 10., 41 (1989).
15. W. López and J.A. González, Cem. Concr. Res., 23, 328 (1993).
16. W. López and J.A. González, Cem. Concr. Res., 23, 1130 (1993).
17. M. Stern and A.L. Geary, J. Electrochem. Soc., 104, 56 (1957).
18. A. Bautista and J.A. González, Cem. Concr. Res, 26, 215 (1996).
19. A. Macías and C. Andrade, Brit. Corr. J., 22, 119 (1987).
20. A. Macías and C. Andrade, Brit. Corr. J., 22, 162 (1987).
21. E. Ramírez, Doctoral Thesis, Universidad Complutense de Madrid, Fac. CC. Químicas, Madrid, 1994.