

# Corrosion of Reinforcement in Concrete Construction

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## THE INFLUENCE OF STEEL GALVANIZATION ON REBARS BEHAVIOUR IN CONCRETE.

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### 1 INTRODUCTION

Concrete is commonly considered to be an easily produceable and readily available material. However, this presumption has meant that the application of this material is often not supported by an adequate understanding of its properties and of the effective limits to its use in relation to durability problems not only in particularly aggressive environments.

When correctly applied, the present level of knowledge relating to concrete technology, makes it possible to predict the average life of a reinforced concrete structure, the major limitation to durability being the corrosion of the steel reinforcement.

Due to the rising costs of restoration, there is increasing interest in the prevention of corrosion in reinforced concrete structures exposed to aggressive environments. For concrete structures exposed to chlorides or carbonation induced corrosion risk, the most effective approach to producing durable structures is to manufacture a low porosity, high quality concrete (corresponding to a water/cement of less than 0.50 according to ENV 206)<sup>1</sup> with an adequate cover thickness (at least 40-50 mm as recommended by Eurocode 2).<sup>2</sup>

However, even when the concrete is correctly designed, defects may still occur due to lack of control, poor workmanship or accidental causes. Therefore, in aggressive environments, where the risk of corrosion is greatest, the durability of the structure can only be guaranteed by providing additional protection to the steel reinforcement, and at the same time manufacturing a concrete of high quality, which is sufficiently impermeable to the penetration of aggressive agents.

Among the possible methods for improving the corrosion resistance of reinforcement in concrete, new consideration has recently been given to the use of galvanized rebars, in view of their relatively low cost when compared to other protection systems. However, the benefits of using galvanized steel in reinforced concrete structures, is still uncertain due to contradictory data on their effectiveness. Indeed, although successful practical results have been reported in the literature,<sup>3,4</sup> laboratory test results remain fairly controversial.<sup>3-11</sup> Swamy<sup>12</sup> recently stated that the results of laboratory tests must be viewed with caution due to the fact that the simulated environment does not fully match the actual conditions. In general, however, it is recognized that, in comparison to the severe attacks observed on uncoated steel, zinc coatings are effective in delaying corrosion initiation of reinforcing steel.

For structures without macrodefects, Yeomans<sup>13</sup> has clearly illustrated the generally accepted conceptual model to describe the mechanism of corrosion of galvanized steel reinforcement in concrete. This model shows that steel galvanization prolongs the average service life in comparison to bare steel reinforcement, thus increasing the durability of reinforced concrete structures.

An additional hazard arises when cracks appear in concrete structures as a consequence of plastic settlement, shrinkage, creep, thermal stresses, dynamic loads, etc. In such cases carbon dioxide and/or chloride ions can penetrate through the cracks and corrosion can occur even with a low porosity cementitious matrix and thick concrete covers.<sup>14-18</sup>

The effect of cracks or damage to the concrete on corrosion of the reinforcement has not been seriously considered until recently. Beeby<sup>19</sup> has addressed this issue and pointed out that the results obtained by simulating corrosion in atmospheric conditions cannot be extended to corrosion processes occurring underwater. In fact, in immersed structures a large area of embedded steel may act as a cathode, with the very small area of exposed steel at the bottom of the crack acting as the anode. Beeby also claims that there is no basis for assuming a direct relationship exists between corrosion and crack width, even if larger cracks might initiate corrosion in a shorter time.

The role played by cracks is one of the most controversial subjects concerning the corrosion of reinforcement in concrete structures exposed to aggressive environments. The effectiveness of zinc coating in protecting steel rebars in the presence of cracks is also subject to some controversy, and contradictory results<sup>12,20-23</sup> have been presented by different researchers. Galvanization has however been consistently observed to delay the onset of steel corrosion, with this delay being considerable in the case of uncracked concrete.

Another controversial issue is that of the bond strength between galvanized rebars and the concrete. Indeed, conflicting results and opinions are reported in the literature<sup>24-26</sup> regarding the loss of adherence between galvanized rebars and concrete. This loss of adhesion is considered to be due to hydrogen evolution on the rebar surface resulting from the attack of the zinc coating by the hydroxyl ions released into the concrete pore solution during cement hydration.

Passivation of the zinc surface by chromate ions is a valid preventive method of inhibiting hydrogen evolution. It should be pointed out that chromates, which are the most effective passivating agents for zinc, are hazardous to human health and may cause a contact allergy (chromium eczema). As a consequence, a serious effort is being made to find alternative and equally effective passivating agents which could replace chromates. Unfortunately, these efforts have been unsuccessful so far. For health and environmental reasons the addition of chromates to the concrete mix must also be considered unacceptable. In fact, the European Community is currently working on a directive that will impose a reduction in the content of hexavalent chromium ions in concrete to very low levels (< 2 ppm).

The aim of the present work is to investigate the corrosion mechanism and the electrochemical performance of galvanized steel reinforcement embedded in cracked concrete which is immersed in seawater. A secondary aim is to investigate the adhesion of galvanized steel to concrete and the interaction of the two materials. For this purpose, the experimental program presented here included pull-out tests on bare, galvanized and chromated galvanized smooth steel bars.

## 2 EXPERIMENTAL

Ninety prismatic reinforced specimens (100 x 100 x 400 mm, Figure 1) were produced using CE IV/A 42.5 cement with a water/cement equal to 0.50.

Some of the specimens (type A in Figure 1) were reinforced with a single steel plate (340 x 40 x 1 mm), either bare, hot dip galvanized (80  $\mu$ m thick zinc coating) or hot dip galvanized and chromated. The plate was embedded 30 mm from the specimen side containing a preformed notch (10 mm deep). The choice of steel plates as reinforcement was justified by the need to enhance the macrocell effect, and to control the crack width induced in the specimens by a flexural stress.

The remaining specimens (type B in Figure 1) were reinforced with two steel plates, which were not in contact with each other; one (80 x 40 x 1 mm) was placed as described above, centered with respect to the notch; the second (340 x 40 x 1 mm) was embedded 40 mm deeper, in order to obtain the same concrete cover on both plates. Various combinations of bare steel, galvanized, and chromated galvanized plates in the upper and lower positions were employed.

A few galvanized plates were scratched to bare steel in order to investigate the corrosion behaviour of galvanized reinforcement damaged during placement.

Before casting, insulated cables were attached to each steel plate for electrical connection to the measuring apparatus.

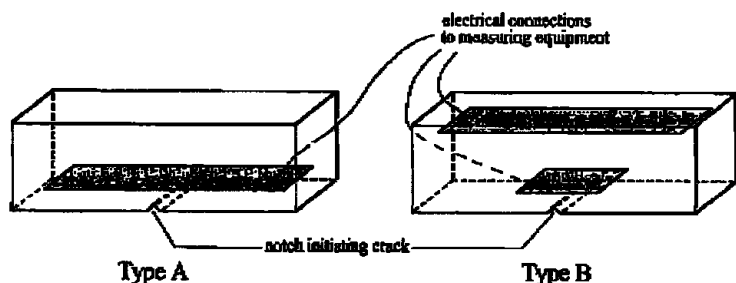


Figure 1 Prismatic concrete specimens reinforced by one (Type A) or two (Type B) steel plates

After about one month of air curing, some sound specimens of both types A and B were directly exposed to an aggressive environment to provide reference results for uncracked concrete. All the other specimens were stressed by bending, by loading the surface opposite to the notch, to initiate the development of a crack. Crack widths equal to 1.0 mm were obtained with sufficient accuracy by slowly varying the applied load.

Exposure in an aggressive environment was simulated by continuous full immersion of the specimens in natural seawater at a marine site in the Ancona harbour. Monitoring of the potential with respect to a calomel electrode was carried out on all the specimens; in addition, short circuit currents were measured for the specimens reinforced with two steel plates using a null resistance ammeter. After completion of these measurements, some specimens of each type were split and the steel plates were disbonded at fixed times to allow visual observation and to evaluate the extent of corrosive attack.

Pull-out tests were carried out according to CEB Recommendations RC 6<sup>27</sup> to investigate the extent of adherence between rebars and concrete. About one hundred concrete specimens were made employing CE IV/A 42.5 cement and bare or galvanized or chromated galvanized smooth steel reinforcing bars. After two months air curing, half of the specimens were partially immersed (about 6 cm deep) in tap water, while the other half were placed in a 3% aqueous solution of sodium chloride. Pull-out tests were performed at predetermined times, by recording the tensile force as a function of the relative displacement and transforming the tension forces into bond stresses.

## 3 RESULTS AND DISCUSSION

### 3.1 Reinforcing Steel Protection by Galvanization

The free corrosion potential of bare and galvanized steel reinforcement was monitored from the time of concrete casting. Bare steel reinforcement in fresh concrete showed potential values of -350 mV (SCE), which rose to about -130 mV (SCE) after 30 days air curing. At the same time, galvanized and chromated galvanized steel reinforcements showed average potential changes from -1200 mV (SCE) to -500 mV (SCE) for galvanized steel and from -850 mV (SCE) to -580 mV (SCE) for chromated galvanized steel. It should be pointed out that for the galvanized steel, a potential variation of 600 mV occurred within the first five days of curing, causing the potential to change from an active state of corrosion to a passive one. This phenomenon can be explained by the precipitation of calcium hydroxide on the zinc surface which then becomes passivated. The results of tests carried out on zinc electrodes immersed in an aerated saturated  $\text{Ca}(\text{OH})_2$  solution support this hypothesis. In these tests it was possible to observe the formation of a continuous coating of calcium hydroxide crystals on the zinc surface along with a sharp variation in potential, similar in magnitude and duration to the one described for the reinforced concrete specimens.

The potential values of bare, galvanized, and chromated galvanized steel plates are shown as a function of the immersion time in seawater in Figures 2a and 2b. Figure 2a shows the results for the plates embedded in sound concrete, while the data in Figure 2b refers to the plates embedded in cracked concrete. In the presence of cracks, which allow the immediate exposure of the reinforcement to seawater, a rapid decrease in the potential of the steel plates is produced which is independent of the surface conditions, and thus causes each reinforcement type to reach an active state of corrosion. When the concrete is sound, this change of state is delayed and no trace of corrosion is detectable after one year of immersion in seawater, regardless of the type of reinforcement used. In spite of the apparently more rapid activation of the galvanized steel plate with respect to the bare one, a tendency of zinc to increase its potential value with time is observed (Figure 2a).

In cracked concrete, the potential value of the galvanized steel plates was not influenced by chromation or by scratching of the galvanization (Figure 2b). In fact, during the first immersion, all the potential values settled in the -1200 to -1000 mV (SCE) range and no variation from this range was observed during the entire testing period. In spite of this, the zinc corrosion rate at the crack apex remained low and there was no evidence of penetration of the corrosive attack, in contrast to the results obtained under the same experimental conditions for the bare steel plates. In particular, observation by optical

microscopy of the cross sections of the galvanized plates corresponding to the crack apex, indicated a progressive reduction (sometimes baring the underlying steel after one year or more of immersion) of the zinc coating in this area. No iron corrosion products were observed for either the chromated or the non-chromated galvanized steel plates. Furthermore, no traces of steel corrosion were detected on the scratched galvanized areas, thus supporting the idea that the zinc can act cathodically to protect these bare steel zones. In all cases a thick, white, compact deposit was observed wherever zinc dissolution had occurred. This deposit, which appeared well adherent to the steel plate and sealed the corroded area, was identified by X-ray diffraction as calcium hydroxylzincate.

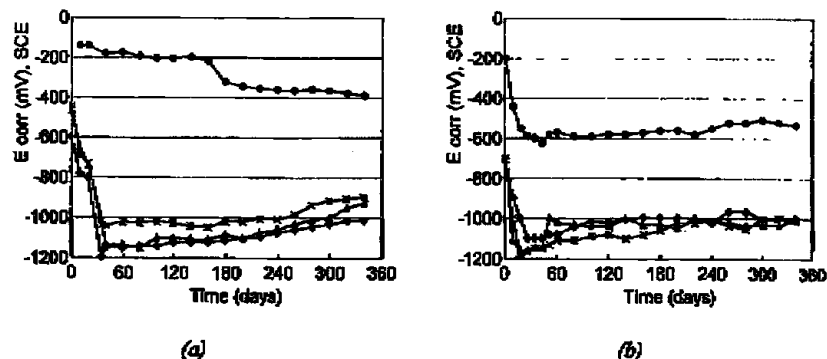


Figure 2 Average values of free corrosion potential for continuous full immersion in seawater of uncracked (a) and cracked (b) type A specimens:

● bare steel, ▲ galvanized steel, \* scratched galvanization, ◆ chromated galvanization

Generalized corrosion was also observed on galvanized steel plate surfaces, and was considered to be due to the chemical reaction between zinc and the hydrolysis lime produced by cement hydration. However, after one year's immersion in seawater, no steel corrosion products were detected on any of the specimens. Chromated galvanized steel plates showed a similar behaviour, but exhibited lower generalized corrosion on the surfaces.

Measurements of the short circuit potential and current were carried out by electrically coupling the two steel plates embedded in type B specimens, with the smaller plate acting as the anode, and the larger plates acting as the cathode. The experimental program considered the following combinations of plates respectively: (anode (a) and cathode (c)): bare steel (a) - bare steel (c), galvanized steel (a) - galvanized steel (c), galvanized steel (a) - bare steel (c) and chromated galvanized steel (a) - bare steel (c). The short circuit potential of the plates was about -600 mV (SCE) in the double bare steel coupling, and about -1000 mV (SCE) in all the other cases. These results indicate that the smaller steel plate reached by the crack is able to polarize the other plate which is embedded in sound concrete when the two are electrically connected. In fact, the circuit opening resulted in potential changes in all the steel plates which were acting as cathodes and embedded in sound concrete, except for the case of the double galvanized steel

coupling; in this case the potential remained constant at -1000 mV (SCE) even after the plates were electrically disconnected.

The short circuit currents measured in the cracked concrete specimens reinforced by two steel plates are shown in Figure 3 as a function of time. The measured values and the flow of current indicate the formation of a macrocell for the cases of bare steel (a) - bare steel (c), galvanized steel (a) - bare steel (c) and chromated galvanized steel (a) - bare steel (c), where the steel plates reached by cracks act as anodes. Zero or insignificant currents were observed when the coupled steel plates were both galvanized. However, in all the cases considered, the higher currents were observed within the first few weeks of immersion and tended to decrease with time, reaching very low values after one year of immersion.

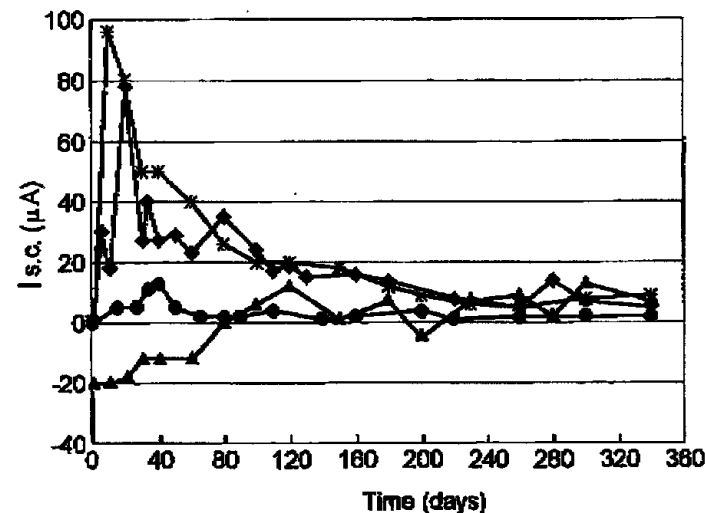


Figure 3 Average values of short circuit current measured between the steel plates embedded in continuously and fully immersed type B cracked specimens:

● Fe(a) - Fe(c), ▲ Zn(a) - Zn(c), \* Zn(a) - Fe(c), ◆ Zn-Cr(a) - Fe(c)

The highest short circuit current values were measured in the cracked specimens when bare steel plates were used as cathodes, and galvanized or chromated galvanized steel plates as anodes. These currents initially reached values of 80 to 100  $\mu A$ , but decreased to less than 10  $\mu A$  after one year of immersion. A similar trend was observed for the double bare steel coupling, even though the short circuit current values were lower than those obtained for the galvanized steel (a) - bare steel (c) coupling, due to the lower electromotive force in the macrocell. However, the corrosive attack on the bare steel anodes was shown to be penetrating and localized in the very narrow crack area. Conversely, as observed in the type A specimens, the galvanized anodes showed a generalized corrosion over a much larger area in the crack zone, leading to the higher

values of current measured. Finally, if the higher values measured at the beginning of the monitoring phase are neglected, the magnitudes of the short circuit current over the surface area of the steel plates are in good agreement with the data relating to oxygen flow through saturated concrete reported in the literature.<sup>28-30</sup>

Due to the presence of calcium hydroxide and the generalized attack on the zinc surface, caused by the interaction between zinc and the cement paste, it was not possible to determine the weight loss of zinc at the apex of the crack area. The weight loss could only be determined on bare steel plates, where after splitting of type A and B specimens the zones reached by the cracks showed localized, more or less intensely corroded areas covered with black corrosion products which were easily removed by acid pickling. Immediately after steel plate disbonding and before the removal of corrosion products, the pH was measured at the center of the corroded area. These measurements indicated acidic values (usually about 5) sometimes falling down to 3-4. The weight losses were then determined and the related currents were calculated using the Faraday relationship to produce average values of around 15  $\mu\text{A}$ . The short circuit current measured by the null resistance ammeter was found to be much lower (about 3  $\mu\text{A}$ , Figure 3) than the one calculated from the weight loss. Since the macrocell current is due only to oxygen reduction and its value was lower than that calculated from the effective weight loss, another cathodic reaction must occur, which contributes to the overall corrosion process. Such a reaction might involve the reduction of hydrogen ions originating at the crack apex as a result of iron chloride acid hydrolysis. This mechanism, already suggested in the literature,<sup>30-32</sup> seems to be supported by the acidic pH values measured just inside the corroded areas after splitting of the specimens.

By referring to the Pourbaix diagram, for the potential values between -500 and -600 mV (SCE) exhibited by the steel reinforcement in the presence of concrete cracks, it can be seen that the system representation falls below the hydrogen reduction line, and therefore there is no thermodynamic barrier preventing the cathodic reduction of hydrogen.

### 3.2 Adhesional Behaviour of Galvanized Rebars

Figure 4 shows the tensile force as a function of the relative displacement during pull-out tests on bare, galvanized and chromated galvanized steel reinforcing bars before exposure to the testing environments. The values of the ultimate bond stress are reported in Figures 5a and 5b as a function of the time of exposure to the different experimental conditions.

The highest initial resistance to pull-out (measured after two months air curing before partial immersion) was observed for the galvanized rebars, and the lowest resistance was noted for the chromated galvanized rebars, whereas intermediate values were recorded for the bare steel rebars. During the first year of partial immersion in a 3% sodium chloride aqueous solution (Figure 5a), an increase in the bond stress was observed for all the reinforcement types. Both the total increase in bond stress and its development over time, vary according to the type of reinforcement. The results obtained for the galvanized reinforcement were encouraging, since its resistance to pull-out, and therefore its adherence to the concrete, were always high, particularly after exposure to an aggressive environment. As a general observation, the galvanized rebars usually showed concrete fragments attached to the surface after disbonding, while the surfaces of the chromated galvanized rebars generally appeared bright and perfectly clean, provided that the chromate film had not dissolved.

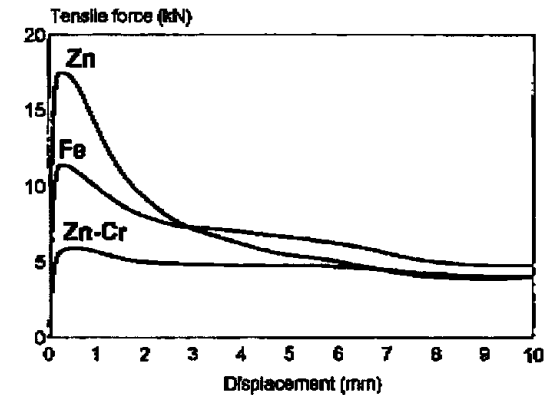


Figure 4 Tensile load as a function of the relative displacement for bare, galvanized and chromated galvanized rebars

The results of the bond tests on specimens exposed to tap water are much more ambiguous than those for the sodium chloride solution, due to the much higher scatter observed in the values of the ultimate bond stress measured after longer exposure times (Figure 5b).

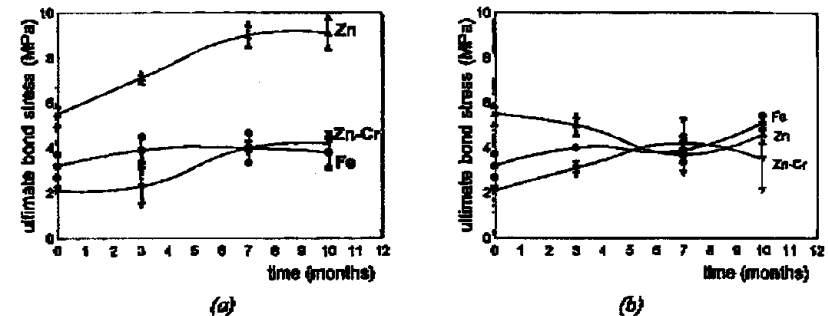


Figure 5 Ultimate bond stress versus exposure time in sodium chloride solution (a) and in tap water (b)

The significant increase in ultimate bond stress between galvanized rebars and concrete immersed in sodium chloride aqueous solution (Figure 4) could be explained by densification of the transition zone between the zinc coating and the cement paste, as a result of the penetration of the non-expansive zinc corrosion products into the concrete pores near the interface. This process would contribute to sealing the pores and microvoids in the interfacial zone, causing the formation of bridges between the metal and the concrete, as already suggested by some models reported in the literature.<sup>34,33</sup> This

phenomenon could be enhanced by the presence of chloride ions, since they are able to facilitate the zinc dissolution. This interpretation is supported by the increase in the ultimate bond stress observed for the chromated galvanized rebars. Initially the value of the ultimate bond stress is at its lowest (Figure 4) due to the presence of chromates which inhibit the corrosion of zinc. The bond stress starts to increase only after dissolution of the chromate film is complete, when, due to the appearance of zinc on the rebar surface, the mechanism described above is initiated.

### 3.3 Microscopic Observation of the Rebar/Concrete Transition Zone

Cross sections of some specimens were examined after their disbonding in order to observe the rebar/concrete interface with optical and scanning electron microscopes.

SEM observations of concrete fragments attached to the surface of the galvanized rebars showed a continuously dense transition zone (Figure 6a, where A and B indicate the zinc coating, and C and D the interfacial zone), while the EDXA analysis carried out during the microscopic observations confirmed that the cement paste (E in Figure 6a) surrounding the galvanized rebars had been widely penetrated by zinc corrosion products.

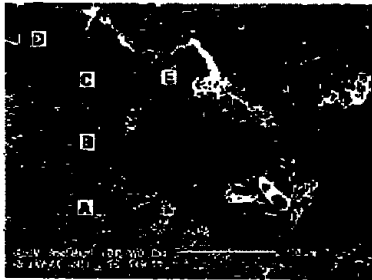


Figure 6a SEM analysis of galvanized rebar/concrete interface



Figure 6b SEM analysis of bare steel rebar/concrete interface

Magnification of the galvanized rebar/concrete transition zone where the zinc coating was slightly corroded revealed the formation of calcium hydroxyzincate crystals perpendicular to the rebar surface (Figure 7). These crystals act as bridges between the metal and the concrete, providing further confirmation of the mechanism hypothesized to explain the increased adherence of the galvanized rebars.

Where formed, iron corrosion products may also diffuse into the cement paste, but in this case, because of their expansive nature, they contribute to the formation of a disjointed layer of corrosion products between the reinforcement and the concrete (A in Figure 6b).

After about one year of exposure to an aqueous solution of sodium chloride, the surface of the zinc coating on the disbonded bars appeared dark grey on the non-chromated rebars; but on the chromated rebars, the surface was still bright even when it had been reached by the chloride ions. Dark zones were observed only on portions of the chromated surface, indicating the disappearance of the  $\eta$  phase layer. This indicates that when the chromate film breaks down in presence of chloride ions, the formation of calcium hydroxyzincate is inhibited.

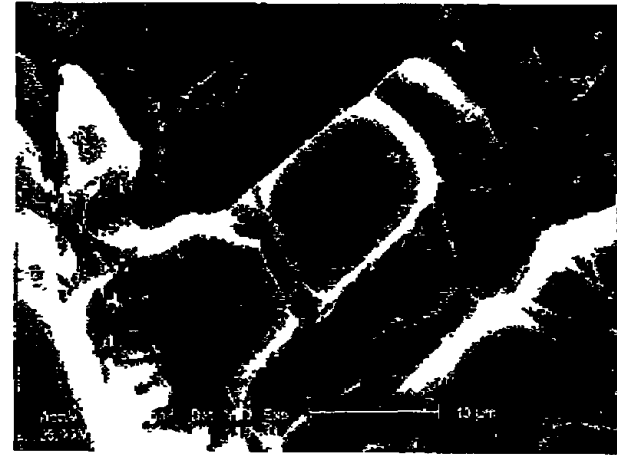


Figure 7 Calcium hydroxyzincate crystals formed at the galvanized rebar/concrete interface

## 4 CONCLUSIONS

In cracked reinforced concrete immersed in seawater, localized corrosion around the cracked area occurred when a bare steel reinforcement was used. There was experimental evidence for a process of hydrogen reduction contributing to the corrosion mechanism occurring under these conditions.

Using galvanized rebars to prevent corrosion, appeared to be an effective solution for cracked concrete, after at least one year of exposure to an aggressive environment. The zinc coating appeared to be able to cathodically protect the rebars when the steel reinforcement was locally uncovered. The galvanized steel embedded in cracked concrete gave the worst results when it was electrically coupled with bare steel embedded in sound concrete.

Regarding the adhesional behaviour of the galvanized rebars, the excellent results obtained do not always agree with the data reported in the literature by other researchers, and thus require further confirmation. For instance, it is suggested that the pull-out tests should be repeated using different cements and employing a wider range of aggressive environments. Above all, much more effort should be put into trying to replace chromates as passivating agents, due to their toxic nature. Finally, some full scale applications should be encouraged in buildings to verify the experimental results.

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