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PERFORMANCE OF ALTERNATIVE MATERIAL REBAR

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16. Abstract

The pH of the concrete pore solution is expected to be somewhat lower in concretes using pozzolanic additions than in concrete using unblended cements. Previous research has shown that variations in pH pore solution may be the cause of conflicting reports on the performance of galvanized rebar. To examine that factor, plain and galvanized rebars have been tested for over two years in concrete specimens made with cement type II, with various contents of fly ash and silica fume. Electrochemical impedance measurements and sensitive polarization techniques have been used to measure the rate of metal dissolution in the absence of chloride contamination at two different levels of concrete moisture. The plain steel specimens have shown little tendency for passivation in two of the cement compositions with the highest levels of pozzolanic addition. The galvanized steel passivated in all cases and showed apparent corrosion current densities of less than 0.3 μm/y near the end of the test. Long term tests to assess performance of the material during the corrosion propagation stage where setup and commenced.

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foot	0.3048	meter
square inches	645	square mm
cubic yard	0.765	cubic meter
pound (lb)	4.448	newtons
kip (1000 lb)	4.448	kilo newton (kN)
newton	0.2248	pound
kip/ft	14.59	kN/meter
pound/in^2	0.0069	MPa
kip/in^2	6.895	MPa
MPa	ksi	0.145
ft-kip	kN-m	1.356
in-kip	kN-m	0.113
kN-m	ft-kip	0.7375

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EXECUTIVE SUMMARY

Long term durability goals (75 years and more) have recently become common in construction of reinforced concrete highway structures. This poses new challenges in controlling reinforcement corrosion, which remains one of the most important limiting factors of the service life of concrete. Long-term corrosion control approaches are relying increasingly on extending the length of the initiation period of corrosion (the length of time in which the reinforcement surface is still in the passive condition) since the propagation stage (from the start of active corrosion until damage is externally observed) tends to last relatively few years. Galvanized reinforcing steel bars are being newly considered for long-term durability service in chloride-induced corrosion service. However, exceptional stability of the galvanized layer inside concrete is required if the coating is expected to be effective after an initiation period that may well need to exceed 50 years. Zn and Zn alloys exhibit amphoteric behavior, corroding actively in both acidic and likewise in highly alkaline media. In the absence of carbonation, the pH of concrete pore solutions is usually sufficiently high to prevent acidic corrosion, but excessive corrosion due to a too high pH is a distinct danger.

The main purpose of this investigation was to obtain an indication of whether galvanized reinforcement could meet these low limits during the initiation stage in concretes formulated for high durability service. The behavior of plain steel with surface condition representative of construction site conditions was examined for comparison. A secondary purpose of the work was to set up long term tests with the same concrete formulations and rebar materials to eventually produce information on the comparative performance of the rebar materials in the corrosion propagation stage, once chloride ion contamination had reached the critical threshold level.

The initiation stage tests were conducted with reinforced concrete specimens without chloride ion contamination, kept either under near water saturation or at room humidity ($\approx$65%R.H.). The corrosion condition was monitored by means of electrode potential and polarization resistance measurements. The concrete mix designs tested used plain Type II cement (with water to cement (w/c) ratios of 0.55 and 0.41) and pozzolanic replacement variations including 20% and 30% fly ash replacement, and 20% and 30% fly ash replacement with an additional 8% silica fume replacement. All pozzolanic variations had w/c$\approx$0.4. The propagation stage tests used the same mix designs and specimens standing partially submerged in a synthetic seawater solution. The testing took place over a two year period.

The galvanized steel in the chloride-free concretes with a range of pozzolanic additions reached passive behavior in both wet and dry conditions. Apparent corrosion rates after two years of exposure were very low (<0.3 µm/y), suggesting that a significant portion of the outermost galvanized layer (important for adequate galvanizing performance) could remain in place for a period on the order of 50 years before the arrival of a chloride contamination front.

The pH of the pore solutions (approximate measurement) in the concretes used was below the pH=13.3 value proposed in the literature as the upper limit for stability of the galvanized layer. The measured pH was lowest with the highest pozzolanic content, suggesting that the pozzolanic additions might assist in improving the coating stability. However, galvanized reinforcing steel in one of the high pozzolanic addition mixes with silica fume showed relatively negative potentials and high metal dissolution rates in a fraction of its samples when compared with the rest of the test conditions. Longer-term monitoring is continuing to reveal possible future differences in behavior.

Plain steel controls showed passivation and very low corrosion rates after two years in the dry environment for all concrete mixes, and in the wet conditions for mixes without silica fume. However, the plain steel bars in the wet chloride-free silica fume concretes did not show potentials or apparent corrosion rates indicative of passivity even after two years. The presence of an initial red rust layer on the plain steel specimens, coupled with reduced pore water pH in these concretes was proposed as a possible cause of this behavior.

Experiments to examine the long term behavior of galvanized and plain steel rebars under saltwater contamination were set up and initiated. Because of the high concrete quality of most of the mixes used, most specimens remained in the passive regime after two years of exposure and will be examined in future testing.

Only the specimens in a 0.55 w/c concrete showed activity in the saltwater tests, after a period of about 200 days of exposure. Times to corrosion initiation were somewhat smaller for the galvanized than for the plain steel bars, but the significance of that finding for long-term design cannot be assessed at this time.

Plain steel specimens in silica fume concrete in the saltwater tests had an extended initial period without indications of passivity, but achieved passive conditions by the second year of testing. This behavior may be related to the presence of a large dried concrete portion in the partially submerged saltwater specimens, but no mechanism for the observed behavior has been identified to date.

INTRODUCTION

Long term durability goals (75 years and more) have recently become common in construction of reinforced concrete highway structures. This poses new challenges in controlling reinforcement corrosion, which remains one of the most important limiting factors of the service life of concrete. Long-term corrosion control approaches are relying increasingly on extending the length of the initiation period of corrosion (the length of time in which the reinforcement surface is still in the passive condition) since the propagation stage (from the start of active corrosion until damage is externally observed) tends to last relatively few years.[1]

Galvanized reinforcing steel bars are being newly considered for long-term durability service in chloride-induced corrosion service, specially since adverse experience with epoxy coated rebar in marine substructures[2] has created interest in examining alternative corrosion control methods. There are indications that the chloride concentration threshold for corrosion initiation of galvanized steel is greater than that for plain steel, with consequent extension in the length of the initiation period. However, exceptional stability of the galvanized layer inside concrete is required if the coating is expected to be effective after an initiation period that may well need to exceed 50 years. The chloride concentrations are small during the initiation period, but the galvanized layer is continuously exposed to an alkaline environment. Zn and Zn alloys exhibit amphoteric behavior, corroding actively in both acidic and likewise in highly alkaline media. In the absence of carbonation, the pH of concrete pore solutions is usually sufficiently high to prevent acidic corrosion, but excessive corrosion due to a too high pH is a distinct danger. In an extensive series of experiments Andrade and coworkers have shown that a continuous passivating layer of calcium hydroxyzincate forms on the surface of galvanized steel when the pH is 13.3±0.1 or below.[3,4] Modern concrete formulations for high durability in seawater service include commonly AASHTO Type II cement (for sulfate resistance), a low water to cement ratio, and a high cement factor with pozzolanic replacement. The latter consist of fly ash (for reduced permeability and to reduce temperature rise in mass concrete applications) and, increasingly, microsilica (silica fume) for early strength and reduced permeability. The pozzolanic additions consume $Ca(OH)_2$ and the reaction products may entrap alkali ions that would otherwise be present in the pore water.[5,6] As a result, the pH of the pore water in concretes with silica fume and fly ash additions can be significantly lower than in comparable unblended concretes.[7,8] Thus, there is a possibility that pozzolanic additions actually improve the performance of galvanized steel, at least by extending the initiation stage of corrosion.

The typical thickness of a galvanizing coating is in the order of 100 μm. Therefore, corrosion average rates during a nominal 50-year initiation period should be well below 2 μm/y to ensure that any coating at all remains in place when the chloride ion concentration begins to approach the threshold value. Requirements may be even more demanding since there is evidence that hot-dip galvanizing coatings provide the best corrosion protection when the outer coating layer ("η", nearly pure Zn) is still in place.[3,4,9] After wastage during the initial concrete curing period, the thickness of the η layer may be only 1/5 to 1/10 of the total galvanizing coating thickness. Thus, corrosion rates during the initiation period may need to be as small as a fraction of 1 μm/y for successful coating performance. The main purpose of this investigation was to obtain an indication of whether galvanized reinforcement could meet these low limits during the initiation stage in concretes formulated for high durability service. The behavior of plain steel with surface condition representative of construction site conditions was examined for comparison.

A secondary purpose of the work was to set up long term tests with the same concrete formulations and rebar materials to eventually produce information on the comparative performance of the rebar materials in the corrosion propagation stage, once chloride ion contamination had reached the critical threshold level. Test specimens were prepared to that effect and are being exposed to a simulated marine substructure salt water splash-evaporation regime for future multi-year monitoring.

PROCEDURE

Specimens and Materials, Chloride-Free Concrete Tests.

The concrete specimens were rectangular prisms (75 mm deep, 150 mm wide, and 300 mm high), with two parallel rebars of the same type, protruding 50 mm out of the top end.

The cementitious material used involves cement type II, fly ash class "F", and silica fume. All materials satisfied AASHTO and/or ASTM specification for Florida Department of Transportation (FDOT) construction. The mix design used are shown in Table I. Mix designs B, C, D, and E have a total cementitious content representative of current FDOT concretes for marine substructure applications.

Eight concrete specimens (four with galvanized bars, and four with plain steel bars) were cast for this experiment per mix design and cured for 28 days in a moist chamber. After curing, half of the specimens were allowed to dry in the lab environment (about

60% RH, 22° C). The remaining specimens were kept nearly water-saturated by wrapping them in plastic bags and frequently remoistening with distilled water spray.

Two types of rebar were used, galvanized and plain steel, both size No.4 (nominal 12.5 mm diameter). The rebar specimens were 300 mm long with a 212 mm unmasked length (surface area of 86 cm^2) directly in contact with concrete. The rebars were cast 75 mm apart in the concrete specimens. An activated titanium rod reference electrode,[10] 3 mm diameter, 50 mm long, was cast centered in each concrete specimen.

The galvanized rebars were hot-dip galvanized, with an average coating thickness of 90μm, as determined by metallographic examination. The thickness of the η layer was typically 25μm. Preparation of the bars followed generally ASTM Specification A 767, but no chromate treatment was used after galvanizing. To simulate construction site conditions, the plain steel bars were cast in the as-received condition, in which an orange rust layer was present. Metallographic examination showed some mill scale still present beneath the rust.

Specimens and Materials, Long Term Tests with Concrete in Saltwater

The concrete specimens for this test had the same general construction and materials as those for the initiation stage experiments, except that the prism thickness was only 50 mm. Six concrete specimens (three with galvanized bars and three with plain steel bars) were cast for each concrete mix design and cured for 28 days in a moist chamber. After curing, the specimens were placed standing in trays containing a synthetic sea water solution so that the lower 10 cm of each prism were immersed in the solution. The synthetic sea water solution was made by dissolving in fresh water a commercially available salt mixture in proportions specified by ASTM D-1141. The synthetic sea water had a resistivity of 20 Ω-cm. The trays with the specimens were exposed to the lab environment. After a few weeks of exposure, light salt accumulation as a result of evaporation ringed the specimens at an elevation of ≈5 cm above the waterline. The salt solution level was made up for evaporation by refilling with fresh water typically once a month. The solution was replaced with newly made solution after the first 21 weeks of exposure.

pH Measurements

The pH of the pore water in blank concrete specimens of each mix design was estimated by an in-situ leaching procedure, described in detail elsewhere.[11] A hole, 6.4 mm in diameter and 25 mm in depth was drilled into a cubic blank sample of each concrete mix, preconditioned by keeping it in a 100% RH chamber for ~ 1 month. Distilled water (0.4 cc) was introduced in the bottom of the orifice, and the pH of the water was periodically determined in-situ with a micro pH electrode calibrated in high pH buffer solutions. The pH measurements were continued over a period of several weeks until a stable terminal pH value was observed. This value was reported as the result of the test (average of two orifices).

Half Cell Potentials

Half cell potentials were taken regularly for each rebar against the internal reference electrode. This internal electrode was periodically calibrated against an external copper-copper sulfate electrode (CSE) placed momentarily against the external concrete surface. In the specimens exposed to salt water, the CSE was placed momentarily in contact with the salt water. For the specimens exposed to the lab environment an additional second calibration was needed after two years of exposure, because of the presence of an external carbonated concrete skin. The procedure was as follows. A hole, 5 mm in diameter and 25 mm in depth, was drilled at the top of each concrete specimen. The potential was measured by placing in the hole a 3 mm diameter, wet wooden rod covered with a plastic pipe to avoid contact with the carbonated layer. The CSE was placed in contact with the top of the wooden rod, with the lower rod tip in contact with the non-carbonated concrete at the bottom of the hole. The small potential difference along the rod was measured independently and corrected. The holes were filled with mortar afterwards to prevent further carbonation.

Electrical Resistance Measurements

Concrete electrical resistance (R) was periodically measured in each specimen between the two rebars. The alternating current measurement was performed using a Model 400 Nilsson soil resistivity meter. Later, R was converted in the chloride-free specimens to an approximate average resistivity value through a geometrical cell constant (Cc) in the following manner:

$$\rho \sim R \cdot Cc$$

The cell constant was determined to be Cc = 11 cm by calibration with rebars in a plastic cell of similar dimensions as the concrete specimens, filled with a liquid of known resistivity.

Polarization Resistance

Polarization resistance of the rebar specimens was determined by both electrochemical impedance spectroscopy(EIS), and a galvanostatic step technique.

EIS tests were conducted in selected specimens at an amplitude typically less than 10 mV, in the frequency interval 0.001 - 200 Hz using custom-made EIS instrumentation.

Galvanostatic step tests were performed simultaneously on groups of up to 16 specimens at the same time. The computer-controlled test technique is described in detail elsewhere.[12] The galvanostatic current was selected to produce a potential deviation characteristically < 20 mV. All conversions to nominal corrosion current densities and corrosion rates were made after compensation for IR drop effects.

RESULTS

Chloride-Free Concrete Tests

Figures 1 and 2 show the evolution of concrete resistance (average of all specimens of each concrete type and for each environmental condition) as a function of exposure time. The specimens at room humidity showed increasing resistance with time, as expected from continuing drying. The moderate long-term trend of increasing resistance of the wet specimens reflects the effect of increased curing. In both environments the highest resistivity was observed for the specimens containing the highest pozzolanic additions, specially types D and E (containing microsilica). The long term curing of the fly-ash specimens is also evident in the increased resistivity trends for the wet environment. The resistivities values ($\rho=R\cdot 11$ cm) in the wet environment are consistent with those reported in the literature for similar concretes.[13]

Figures 3 and 4 show the potentials (averages of quadruplicate bars) as a function of exposure time for the plain steel and galvanized specimens in the room humidity environment. Each material achieved a final potential that was approximately independent of the type of concrete. The potentials reached by each material are comparable to those reported for their respective passive conditions in dry concrete.[14] The early potential history of the plain steel in concrete mixes D and E (both with silica fume) was indicative of slow passivation, specially for mix D.

Figures 5 and 6 show the potential trends in the wet concretes. The galvanized specimens tended to reach final potentials (-400 to -600 mV CSE) similar to those reported elsewhere for the passive condition in wet concrete.[14] However, by day 750 two of the four bars in concrete mix D had reached potentials between -900 and -1000 mV CSE, resulting in a somewhat low average potential of -680 mV CSE. The plain steel specimens in concrete mixes A-C and F reached potentials (~ -100 mV CSE) associated with passive behavior[15] early in the exposure. In contrast, the potentials in silica-fume mixes D and E were highly negative (typ. -700 mV CSE) over the entire exposure period.

Figures 7 and 8 show the nominal corrosion rates (see discussion below), averages of quadruplicate bars for each material in the room humidity concrete tests. The galvanized rebar showed low and continually decreasing rates over the entire test interval, consistent with the potential trends shown in Figure 4. By the end of the test interval, the rates in all concrete mixes were approaching the detection limit (8.6×10^{-3} μm/y). The nominal corrosion rates by the end of the test interval for the plain steel in all corrosion mixes were also very low and approaching the detection limit (7.1×10^{-3} μm/y), in agreement with the final potential values in Figure 3. The nominal rates for mixes D and E were much higher for those periods in which potentials outside the passive regime were recorded.

Figures 9 and 10 show the nominal corrosion rates for the wet concrete tests. The galvanized specimens showed low and continually decreasing rates, generally consistent with those reported elsewhere for passive galvanized steel[16] in wet concrete. The specimens with concrete mix D (8% silica fume, 20% fly ash) showed throughout the test period apparent average rates ~3 times greater than those in the other concrete mixes. The plain steel specimens in mixes A-C and F showed similar, very low nominal rates over the test period, consistent with those expected from well-passivated plain steel in wet concrete.[17] In contrast, the plain steel in silica-fume concrete mixes D and E showed much higher nominal rates throughout the entire test interval, coincident with the observation of very negative potentials shown in Figure 5.

Table 2 shows the results of estimated pH measurements. The concrete mixes D and E showed the lowest pH values, as observed also by other investigators.[7,8]

Long-Term Tests With Concrete in Saltwater.

These specimens are intended for long time monitoring and as a result the corrosion propagation stage had not been reached for the majority of the test specimens within the reporting period of this contract. The results presented here are therefore mostly indicative of the behavior during the initiation period.

Figure 11 shows the resistance (average of triplicate specimens) for each concrete mix as a function of time. The overall trends are similar to those observed for the wet condition in the chloride-free specimens (Figure 2), but with somewhat higher resistivity values since the saltwater test specimens are thinner and only the lower 1/3 of the specimen is submerged.

Figures 12 and 13 show the potential trends (average of six specimens) as function of time for plain steel and galvanized respectively. The plain steel specimens in mixes F, B and C showed during the test period to date essentially the same potential behavior as in the chloride free wet concrete specimens (Figure 5). The plain steel specimens in mixes D and E showed, as in the case of the chloride free wet concrete specimens, an initial period of very negative potentials, but after about one year both potentials become similar to those in mixes F,B and C. After initially achieving values typical of passive behavior, the potential of plain steel in mix A started a downward trend at day 200. By the end of the test period, the potential of the steel in mix A was near -500 mV CSE. The galvanized steel specimens showed potential trends not very different from those in the wet, chloride free concrete counterparts, with the exception of the bars in mix A. As in the case of plain steel, the galvanized bars showed a distinct negative potential transition starting around day 200.

Figures 14 and 15 show the nominal corrosion rates (see discussion below) as a function of time, averages of six bars for each material. The trends are generally similar to those observed in the chloride-free wet concrete specimens, with exceptions already noted in the potential results for the plain steel bars in mixes D,E and A, and for the galvanized bars in mix A.

Metallographic Examination

Two specimens of the chloride-free concrete tests were cut open after two years of exposure to examine the condition of the reinforcing steel bars. The specimens were one of the plain steel specimens in wet concrete Mix D, and one of the galvanized specimens in wet concrete Mix E. Metallographic examination of the galvanized bar specimen was initiated by slicing the concrete perpendicular to the bar surface, and allowing epoxide metallographic mount compound to bath the surface of the concrete slice containing the rebar segment. The slice was then treated as a metallographic specimen and ground to a 600 grit finish with grinding paper lubricated with kerosene. The surface was then polished to a 1 μm diamond finish in a polishing wheel surface lubricated with oil. For the plain steel specimen, the concrete was split to expose the entire rebar surface. Portions of concrete were still adhered to the rebar at places. The bar was sliced with a dry saw and the fragments were mounted in epoxide compound (preserving adhered concrete whenever possible) and ground and polished as indicated above.

The plain steel bar had experienced the highly negative potentials and high nominal corrosion rates indicated in Figure 5 and 9. Examination of the bar surface after extraction showed a gray-to-rust color surface except where air voids were entrapped at the steel surface. In those spots the surface still retained the initial orange-rust appearance. The metallographic examination of the scale in contact with the concrete revealed a mill scale quite similar in thickness (about 30 μm) as in the initial condition, together with some red rust.

The galvanized layer in the exposed condition (Figures 16 and 17) did not differ significantly in appearance and dimensions from that present in the initial material. Figure 16 shows the typical etched microstructure, revealing a significant amount of η layer still present in this specimen, which was in a group that showed comparatively high rates of nominal corrosion rate. Figure 17 shows microhardness indentations in a section of the same specimen confirming the expected behavior of the different layers. The microhardness values were (in the Knoop scale) 70-72 for the η layer, 175-185 for the ζ layer and 240-300 for the δ layer, in agreement with the expected range [9].

DISCUSSION

Chloride-Free Concrete Tests

Galvanized Steel

The accuracy of the nominal corrosion rate calculated from polarization resistance measurements is contingent upon the accuracy of the R_p measurements themselves and upon the reliability of the conversion from R_p to corrosion rate. The R_p calculations from experimental data are based on a simplified model of the interface that agrees generally with the result of more detailed electrochemical impedance tests.[12] Because of the large apparent interfacial capacitances of these systems, values of R_p can only be interpreted by extrapolation and thus should be considered as apparent values. The conversion from apparent polarization resistance to nominal corrosion current density was made in the passive regime by means of a Stearn-Geary constant B=52 mV, from which metal dissolution rates were obtained assuming double ionization of Zn. The 52 mV constant was determined empirically by Andrade et al from gravimetric measurements of passive galvanized steel using polarization resistances obtained by comparable methods.[18] Those investigators reported accurate corrosion rate determinations within a factor of 2. It is therefore expected that the present nominal corrosion rates of passive galvanized steel have a comparable level of error.

The above evaluation of corrosion rate does not invoke any specific mechanism for dissolution of zinc in the passive state. However, some theoretical justification for the conversion approach used may be derived by assuming that metal loss occurs by dissolution of the passive layer at the layer-pore water interface, and growth of the layer by zinc ions resulting from oxidation of the bulk metal at the layer-metal interface. If the rate of passive metal dissolution follows the potential-independent trend of an ideal passive polarization curve,[19,20] the electrochemical admittance of the overall anodic reaction is zero, and the overall admittance at the polarization resistance limit is that of the cathodic reaction. Assuming it to be simple oxygen reduction, not limited by diffusion since the reaction rate is low, the polarization resistance would be given by $R_p = \beta/2.3\ i_{corr}$, where β is the Tafel slope of the cathodic reaction. Therefore the Stearn-Geary constant is $B = \beta/2.3$, which for $B = 52$ mV yields $\beta = 0.12$ V, a value which is consistent with the independently observed typical kinetic parameters for oxygen reduction in concrete.[21]

The potential and nominal corrosion rate results suggest that the galvanized steel has developed stable passivity after two years in all concrete mixes in the room humidity concrete, and in mixes A-C and E-F in wet concrete. The potential of two of the galvanized specimens in wet mix D concrete fell outside the range normally associated with passivity, but the nominal corrosion rates for those specimens were found to be similar to those of the other specimens in the same group which retained potentials in the normal passive regime. The average nominal corrosion rates for all the galvanized specimens show a tendency to decrease with time in both environments.

Galvanized reinforcement is being evaluated in this investigation primarily for its expected resistance to higher levels (compared with plain steel) of chloride ion contamination before initiation of the active corrosion. An increased contamination threshold means that longer time would be required for diffusion or other transport processes to build up the necessary critical chloride concentration at the rebar level, thus increasing durability with respect to plain rebar construction. Therefore, the ability of the galvanizing coating to be present to the end of a long initiation period is essential.

Keeping the limitations of the test techniques in mind, the results in Figure 10 show nominal rates of metal wastage after two years in the galvanized specimens in mix D wet concrete of less than 0.3 µm/y. The nominal corrosion rates after two years were less than about 0.12 µm/y for mixes A, F, C, and E. The limited metallographic evidence available to date is consistent with the electrochemical results in that wastage of the galvanized layer appeared to be minimal. Considering the observed trend for increasingly smaller nominal corrosion rates with time, the results suggest that a usable fraction of even the small η layer thickness could remain in place after 50 years of initiation service. Penetration through the remaining galvanized layers[22,23] would be expected to involve longer time periods. The performance in concrete exposed to room humidity appears to be significantly better than in wet concrete, with consequent increase in the chances of survival after a long initiation period.

The results to date suggest that the pozzolanic additions tested do not create an environment aggressive to galvanized steel. From the pH estimates in Table 2, the pozzolans may actually assist in keeping the pore solution away from the aggressive pH limit of 13.3 suggested by Andrade et al.[3] There is no clear indication that too much of a reduction in pH from the pozzolanic reaction may be taking place, but the behavior of galvanized steel in concrete mix D (low potentials in some specimens) must be monitored with attention in the future.

The scope of the above discussion is limited to the survival of the galvanizing coating during the initiation stage of corrosion, when chloride ion levels are small for a large portion of the time and assuming that the concrete does not contain cast-in chloride contamination. The effect of rapidly increasing levels of contamination near the end of the initiation stage has not been yet considered as it is expected to involve a relatively small fraction of the total initiation time. Cases of initial contamination and the effect of very small chloride levels during buildup should be examined in the future. The performance of galvanized steel in the propagation stage of corrosion is being investigated in related experiments to be reported elsewhere.

Plain steel

The behavior of the plain steel bars was as expected in the case of mixes A,F and B,C, yielding very low nominal corrosion rates for both wet and room humidity concretes. The estimation of nominal corrosion rates is based on empirical "B" constants (52 mV for passive steel and 26 mV for active steel) reported in the literature,[24] and it is expected that reasonable estimates were obtained for specimens in the passive condition. In silica-fume mixtures D and E, in wet concrete, conditions normally associated with passivity were never reached. In dry concrete those conditions developed only after relatively long periods. These anomalous behaviors are puzzling.

The nominal corrosion rates reported for the anomalous behavior in mixes D and E cannot be substantiated at this time and must be considered only as apparent magnitudes. Several causes of uncertainty exist. EIS tests of specimens in the anomalous conditions suggest the presence of a very low apparent polarization resistance, but because of the comparatively high electrolyte resistance not enough resolution could be obtained to provide an accurate estimate of R_p (additional testing is in progress to determine the EIS response with greater precision). Similar inaccuracy affects the anomalous condition R_p values from the galvanostatic tests, which can only be considered as order-of-magnitude estimates. A more important uncertainty concerns the cause of the low apparent polarization resistance. It may be due to only high corrosion rate of the steel, which would not have yet experienced passivation in the lower pH environment of the mixtures with highest and most reactive pozzolanic addition. However, even the lowest pH values observed (12.6, mix E, Table 2) could be expected to cause passivity after a relatively short time. Moreover, sustained corrosion rates on the order of 25 μm/y may cause visible cracking of the concrete cover after two years in the specimen configuration used,[25] but no cracking was observed.

An alternative interpretation can be proposed based on the initial, red rust condition of the plain steel specimens. If this surface layer is rich in Fe^{+++} ions, reduction to Fe^{++} may be expected as a possible cathodic reaction in concrete.[26] This cathodic reaction could be matched by conversion to a higher oxidation state of oxides in the mill scale, and/or the base metal, until an equilibrium is reached followed by formation of the usual passive condition. The lower pH expected (and observed) of the high pozzolanic concrete mixes would have retarded passivation in the normal manner, allowing for the development of processes such as the one proposed. The standard Fe^{+++}/Fe^{++} equilibrium in aqueous solution at pH 12-13 takes place at potentials approaching -900 mV CSE,[27] which would be consistent with the observed potential values. A red rust layer 30 μm thick (as revealed by the metallographic examinations) could provide ample material to support electrochemical reaction rates on the order of those observed for times comparable to the duration of the test. Strain relief (and consequent lack of cracks) is conceivable given the friable and porous nature of the rust layer and the combinations of possible volume changes involved in oxide transformations. In the wet specimens oxygen availability is limited by slow diffusion through the concrete, and the low potential regime would be expected to last longer than in the drier specimens, as observed. Because of the increasing use of silica fume for long term durability applications, resolution of the behavior of these specimens is important. Careful monitoring for longer times and demolition of selected specimens is planned to elucidate these possibilities.

Long-Term Tests With Concrete in Saltwater.

The results for this set of specimens represent the first stage of a test that will continue over a longer time period. Despite the thin concrete rebar cover used, the quality of the concretes investigated caused the time for corrosion initiation in most mixes to extend beyond the reporting period for this contract. As a result, in most instances the results paralleled those observed in the chloride-free, wet concrete specimens. The similitudes become more evident when considering that only about one third of the height of the specimens in saltwater was submerged. Thus, in those cases showing behavior comparable to the wet chloride-free tests the concrete resistance values observed were higher. The apparent corrosion rates were somewhat smaller than in the wet chloride free counterparts, suggesting (as it was expected) that most of the electrochemical activity was concentrated in the moist portion of the specimens. In addition, the excitation current for the polarization resistance measurements was expected to reach preferentially the region of the rebar with the lowest electrolyte resistance,[28] thus giving polarization admittances representative of that zone only. Since the nominal corrosion rates presented are obtaining by dividing by the entire bar area, the final result is correspondingly smaller.

Only the specimens in concrete mix A showed signs of corrosion activity from chloride ion contamination during the test period reported. This observation agrees with the high water to cement ratio (0.55) used in this mix, much greater than in the other mixes. From the potential and nominal corrosion rate trends, both the plain steel and galvanized bars reached active behavior in mix A after ≈200 days of exposure. As indicated in the previous section, the nominal rates of corrosion to date provide only a nominal indication of corrosion severity. Since the apparent corrosion rates for both plain steel and the galvanized bars were of the same order (Figures 14 and 15), evaluation of the relative performance of these materials will be postponed until specimen autopsies to be conducted at a later date. The times for first observation of corrosion initiation (based on the potential and polarization resistance data) were somewhat smaller for the galvanized rebars than for the plain steel specimens. This appears to indicate that the threshold for corrosion initiation of the galvanized rebars was about the same or even smaller than plain steel in this relatively early age concrete with the open pore structure expected from the high w/c mix used. The significance of this finding to long term design applications cannot be ascertained until corrosion initiation trends develop for the specimens with the other, denser mix properties.

The plain steel behavior in mixes D and E exposed to salt water resembled in its early stages that of the steel in both the wet and dry chloride-free concrete. However, after about one year of exposure the steel in both mixes D and E in seawater showed only passive characteristics, showing a transition generally similar to that of the steel in the dry, chloride free concrete specimens. In the saltwater specimens most of the steel is in the upper part, in which the concrete has dried in laboratory air. The similarity in behavior is therefore not completely unexpected. However, a mechanism by which the submerged portion of the steel would have passivated as a result of coupling with the upper portion needs to be identified to explain the observed behavior. The information available to date is not enough to single out a process. Direct examination of the steel surface (as indicated in the previous section) in future tests will be necessary to elucidate this matter.

Monitoring of these specimens will continue followed by post-demolition analyses in the future.

Implications on Design for Long Durability

The results of this investigation have revealed initial trends that justify the continuing consideration of galvanized rebar (GR) as a possible altemative rebar material for corrosion control in Florida marine substructure service.

The potential gains resulting from using GR compared with plain steel rebar (PR) can be evaluated in the context of the initiation-propagation model [1] to envision the effect of corrosion-related damage. Under chloride-induced corrosion conditions, the length of the initiation period is determined by the amount of time required to build the corrosion concentration in the concrete at the rebar up to the critical threshold for corrosion initiation. The length of the propagation period is determined by the rate at which corrosion-related damage accumulates and by the maximum amount of damage that is deemed tolerable.

The length of the initiation period t_i may be estimated by assuming on first approximation that chloride ion transport through the concrete obeys a simple diffusional mechanism with diffusion coefficient D, and that the chloride concentration at the concrete surface is constant at a value C_S. If the critical chloride concentration threshold for corrosion initiation is C_T, it can be shown [2] that for conditions typical of marine substructure service ($C_T/C_S \approx 0.1$) with a concrete cover thickness d the time for corrosion initiation is approximately proportional to the following:

$$t_i \propto (C_T / C_S)^{1/2} D^{-1} d^2 \tag{1}$$

Because of the approximate square root dependence of t_i on C_T an increment of the concentration threshold by a factor of two to three [2], when using galvanized instead of plain steel rebar, would increase t_i by approximately ≈40% to ≈70% . This improvement would be in addition to the effect of possible reductions in the rate of corrosion of galvanized rebar in chloride-contaminated concrete compared to that of plain steel rebar. Using the conservative approach of equating the corrosion-free service life to that of the initiation period only, the above estimate suggests that substantial (≈40% to ≈70%) DSL extension could be derived from the successful application of galvanized rebar.

To realize the potential long-term DSL extension indicated above several necessary conditions must be satisfied. A critical necessary condition is that the galvanized coating (especially the external η layer) must survive the lengthy initiation period before chloride contamination reaches values close to the corrosion initiation threshold. The results from the present investigation indicate that the apparent corrosion rates of the galvanized coating in chloride-free concrete were small enough to expect survival of the coating under chloride-free conditions. Sufficiently small rates were observed in several concrete classes that are presently used, or are candidates for future use, in FDOT marine substructure design. The results suggested that the pore water in those concretes was not excessively aggressive by itself to the galvanized coating. Specification of cements and pozzolanic admixtures for concretes using galvanized reinforcement should carefully limit the alkali content to not exceed present acceptable levels.

Future directions.

Other necessary conditions to be satisfied, not addressed in this study, include demonstrating the ability of the coating to resist simultaneously the alkaline environment and low levels of chloride contamination during the latter stages of the initiation period, when $0.01<C_T/C_S<0.1$. Tests with chloride contents in this range should be conducted in the future. It is necessary also to ensure that in the low permeability concretes specified for long durability in FDOT design the length of the corrosion propagation period is not unduly shortened by the formation of zinc corrosion products when compared with those of plain steel. Continuation of the experiments in saltwater is expected to provide valuable information on this issue.

As part of a cooperative investigation with International Lead-Zinc Research Organization (ILZRO), FDOT is conducting long term field tests of galvanized reinforcement at the FDOT Matanzas Inlet test site. The test columns feature 50 mm concrete cover over the rebar and high performance concrete formulations (Type II cement, with 20% fly ash or 20% fly ash plus 8% microsilica replacement, with total cementitious content of 444 Kg/m^3). The reinforcement corrosion performance is monitored regularly by means of half cell potential and polarization resistance measurements. The test columns have been placed starting in 1993. The long term field performance data will be used together with the results of this and future investigations to develop decisions on the applicability of galvanized rebar for marine substructure service in Florida. Pending on the results of these programs, experimental feature installations of galvanized rebar in actual service structures could be taking place over the next decade.

CONCLUSIONS

1. Galvanized steel in chloride-free concretes with a range of pozzolanic additions reached passive behavior in both wet and dry conditions. Apparent corrosion rates after two years of exposure were very low (<0.3 μm/y) , and metallographic examination showed also minimal wastage, suggesting that a significant portion of the η layer could remain in place for a period on the order of 50 years before the arrival of a chloride contamination front.

2. The estimated pH of the pore solutions in the concretes used was below the 13.3 limit suggested for lack of stability of the galvanized layer. The estimated pH was lowest with the highest pozzolanic content, suggesting that the pozzolanic additions might assist in improving the coating stability. However, galvanized reinforcing steel in one of the high pozzolanic mixes with silica fume showed the highest passive corrosion rate and low potentials (but still passive corrosion rates) in a fraction of its samples. Longer-term monitoring is continuing.

3. Plain steel controls showed passivation and very low corrosion rates after two years in the dry environment for all concrete mixes, and in the wet conditions for mixes without silica fume. However, the plain steel bars in the wet chloride-free silica fume concretes did not show potentials or apparent corrosion rates indicative of passivity even after two years. The presence of an initial red rust layer on the plain steel specimens, coupled with reduced pore water pH in these concretes was proposed as a possible cause of this behavior.

4. Experiments to examine the long term behavior of galvanized and plain steel rebars under saltwater contamination were set up and initiated. Because of the high concrete quality of most of the mixes used, most specimens remained in the passive regime after two years of exposure and will be examined in future testing.

5. Only the specimens in a 0.55 w/c concrete showed activity in the saltwater tests, after a period of about 200 days of exposure. Times to corrosion initiation were somewhat smaller for the galvanized than for the plain steel bars, but the significance of that finding for long-term design cannot be assessed at this time.

6. Plain steel specimens in silica fume concrete in the saltwater tests had an extended initial period without indications of passivity, but achieved passive conditions by the second year of testing. This behavior may be related to the presence of a large dried concrete portion in the partially submerged saltwater specimens, but no mechanism for the observed behavior has been identified to date.

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STATEMENT OF BENEFITS

The FDOT needs to identify realistic alternatives to the recently discontinued use of epoxy-coated rebar as one of the main forms to protect against corrosion of reinforcement of marine bridge substructures. In addition to concrete-oriented measures (denser concrete, thicker concrete cover and related approaches) the use of alternative corrosion resistant reinforcement materials would provide additional protection. Because of the long history of availability of galvanized rebar, this material was a natural item for consideration. This investigation examined the minimum requirement that galvanized reinforcement should satisfy to be considered for long term design: the ability to retain its coating integrity after multiple decades of service, before the chloride ion contamination at the rebar depth would reach a critical corrosion initiation level. The research has provided a positive indication that, during the long initiation stage of corrosion, galvanized coatings may withstand the highly alkaline concrete environment. The answer has been obtained for a variety of concrete formulations of immediate importance for long-term design service life of Florida marine bridges. In particular, the investigation has revealed that concretes with additions of pozzolanic materials (fly ash, silica fume), currently used to increase strength and reduce chloride penetration in FDOT design, did not cause during the test period corrosion rates severe enough to project significant damage of the galvanized layer during an extended service life of the structures.

As a result of this investigation, the use of galvanized rebar can be considered further as a candidate supplemental corrosion protection method for the materials and conditions used for FDOT marine substructure applications. The findings of this investigation indicate that a necessary condition for further consideration has been satisfied, and open the way for the next stage of testing of this material. Some of that next stage is already in progress as a result of a preparatory task in this study, in which specimens of galvanized rebar in concretes using FDOT formulations are being exposed to saltwater environments. This work has thus developed over two years of advance in the further evaluation of galvanized rebar in the laboratory. Together with ongoing FDOT exposures at the Matanzas inlet field test site, future testing will permit establishing the strengths and weaknesses of galvanized rebar as an additional element in extending the service life of the substructure of marine bridges. If appropriate use of galvanized rebar results in even a fractional extension of the service life of future FDOT structures (for example by 10%), the maintenance and cost savings applied to the future inventory of FDOT bridges would create a multimillion dollar benefit. A comparable benefit could have been derived if this investigation would have revealed fundamental shortcomings in this material, thus avoiding the need for future maintenance costs to repeal a foreseeable problem.

TABLE 1
Concrete Mix and Properties

Mixes	Cementitious Material	Cementitious content (Kg/m^3)	Water to Cementitious Ratio	Measured Strengh 28 day (MPa)
A	100%PC	333	0.55	37
F	100%PC	360	0.41	34 *
B	80%PC+20%FA	444	0.41	46
C	70%PC+30%FA	444	0.43	42
D	72%PC+20%FA+8%MS	444	0.39	58
E	62%PC+30%FA+8%MS	444	0.39	56

PC= Portland Cement Type II; FA= Fly Ash Class "F"; MS= Micro Silica.
* Design, measured not available.

TABLE 2
Concrete pH Pore Solution

Mixes	Estimated pH
A	13.02
F	13.04
B	13.00
C	13.02
D	12.92
E	12.66

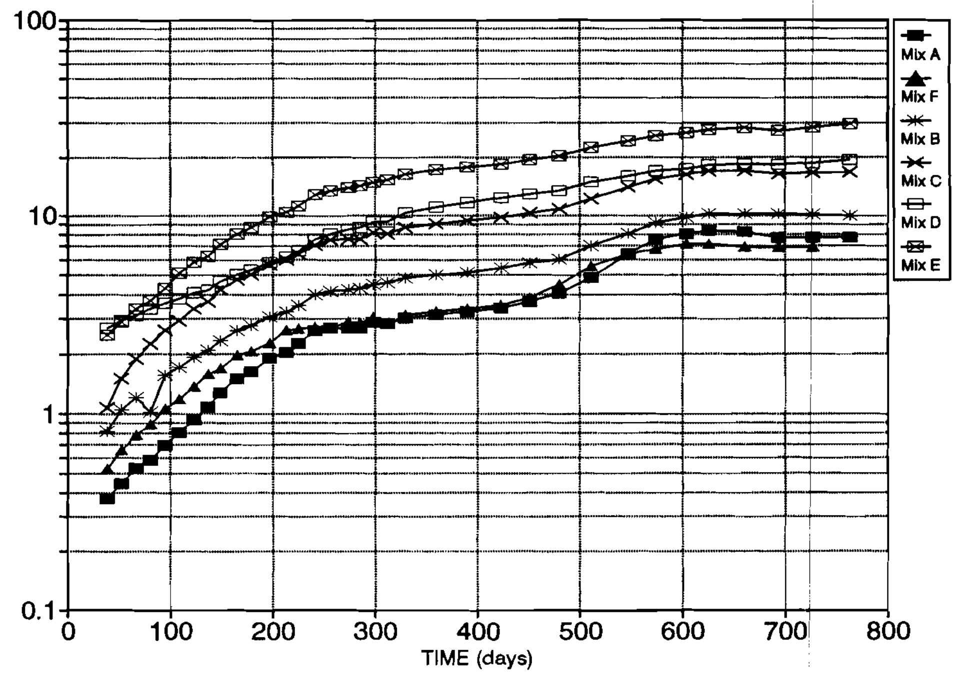

Figure 1. Evolution of concrete resistance in the laboratory air environment, as a function of exposure time (Resistivity ρ ~ R x 11 cm).

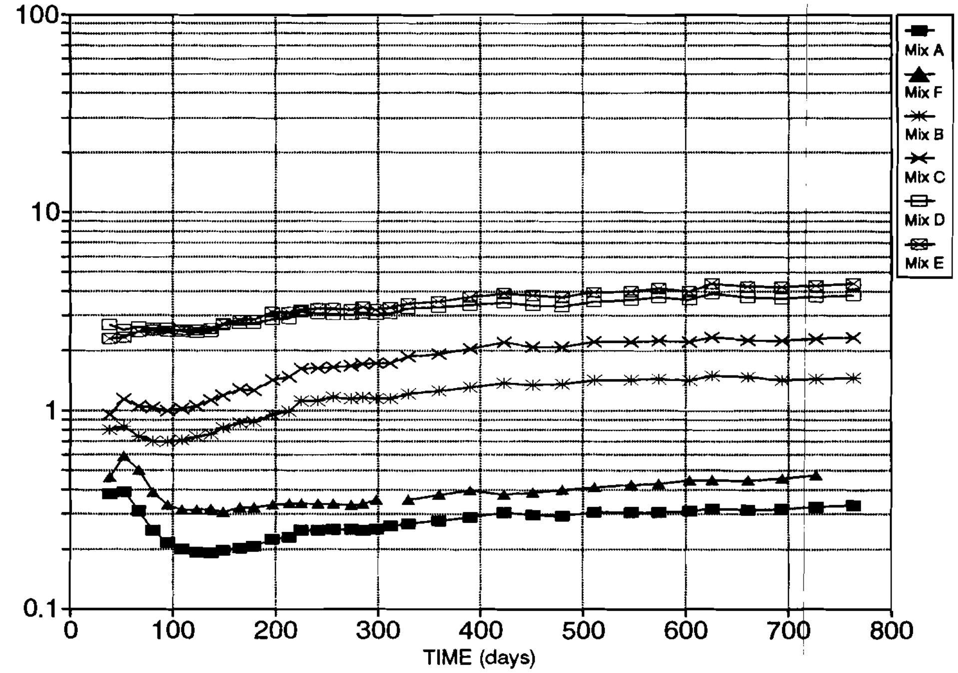

Figure 2. Evolution of concrete resistance in the wet specimens, as a function of exposure time (Resistivity ρ ~ R x 11 cm).

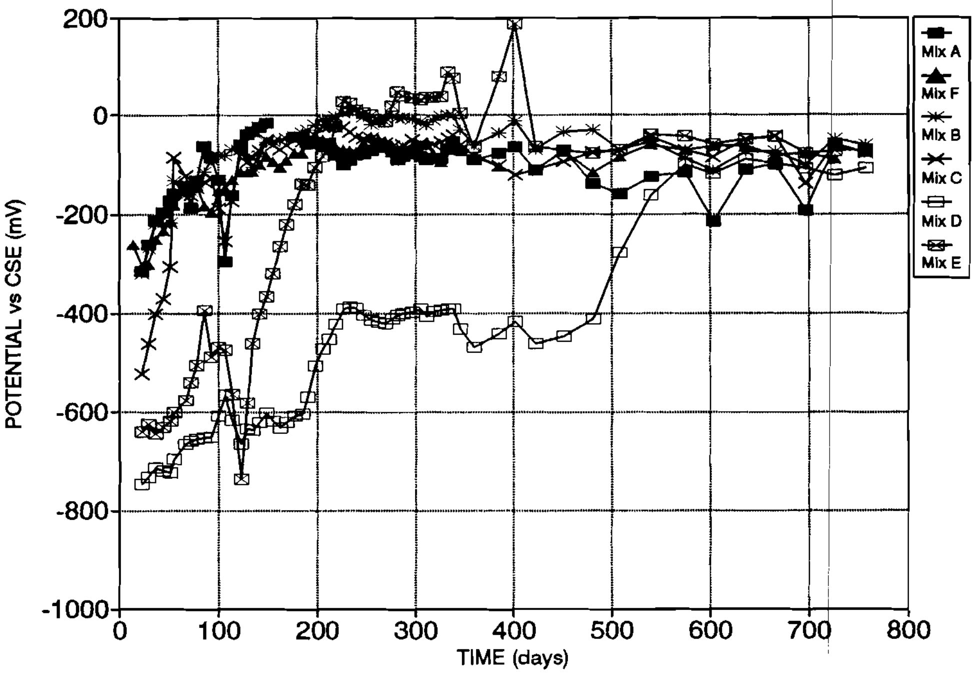

Figure 3. Potentials as a function of exposure time for the plain steel in the laboratory air concrete specimens.

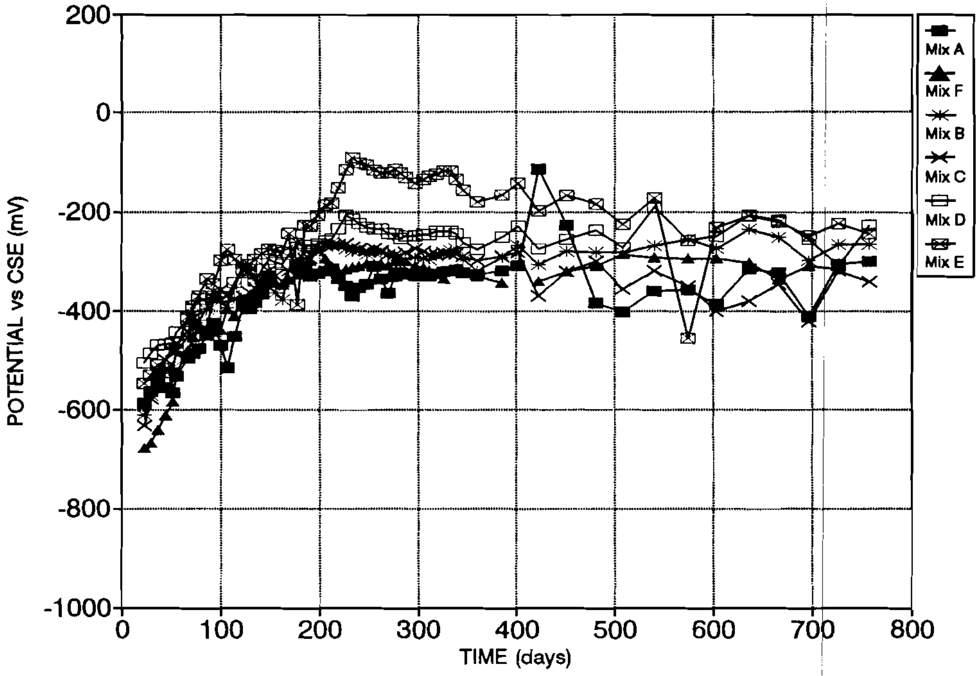

Figure 4. Potentials as a function of exposure time for the galvanized steel in the laboratory air concrete specimens.

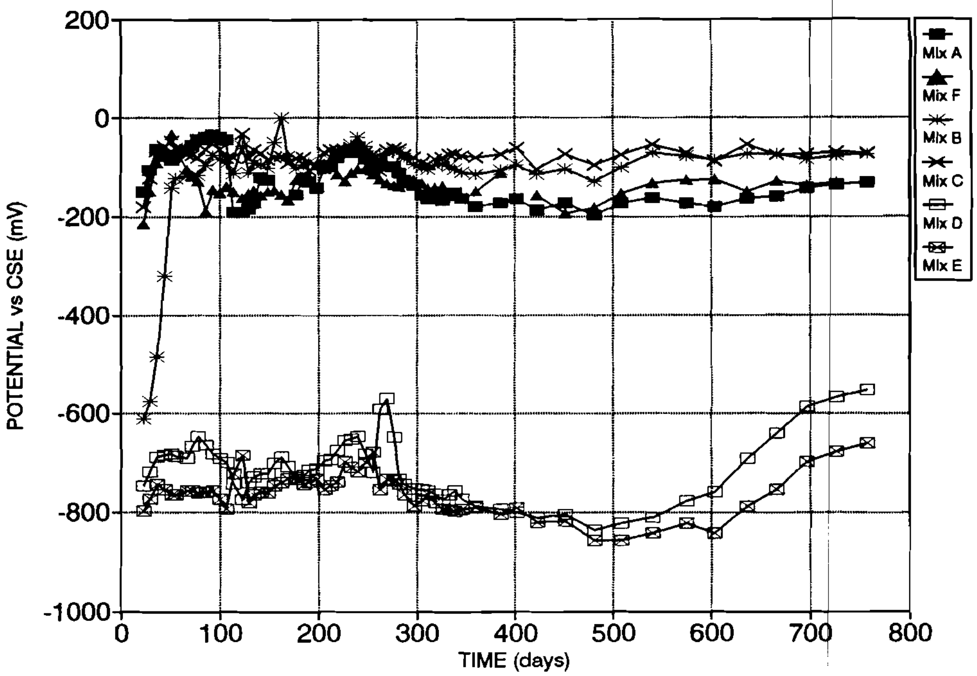

Figure 5. Potentials as a function of exposure time for the plain steel in the wet concrete specimens.

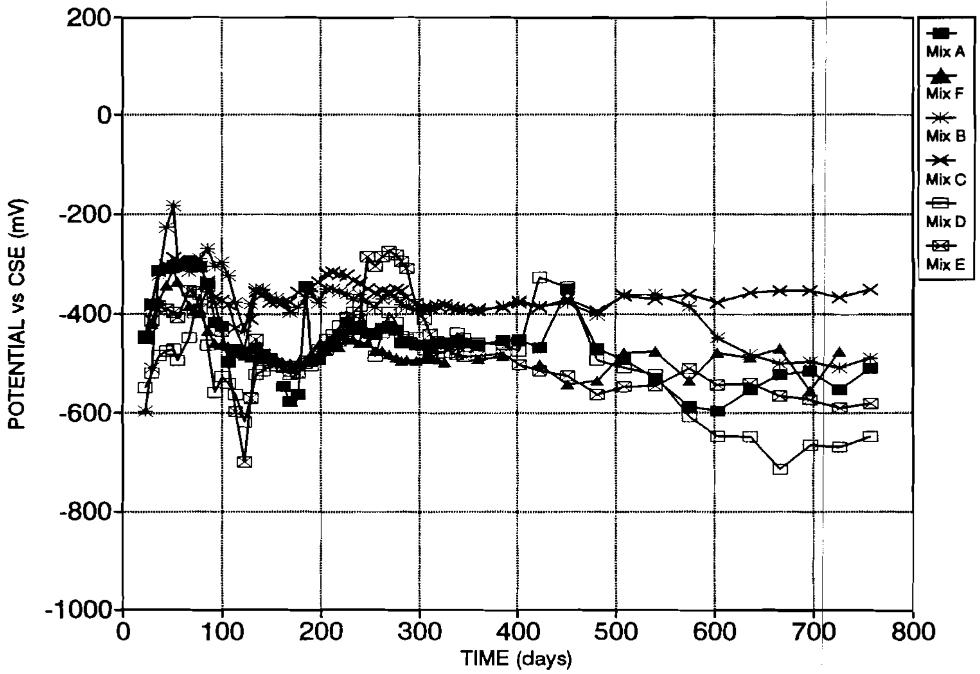

Figure 6. Potentials as a function of exposure time for the galvanized steel in the wet concrete specimens.

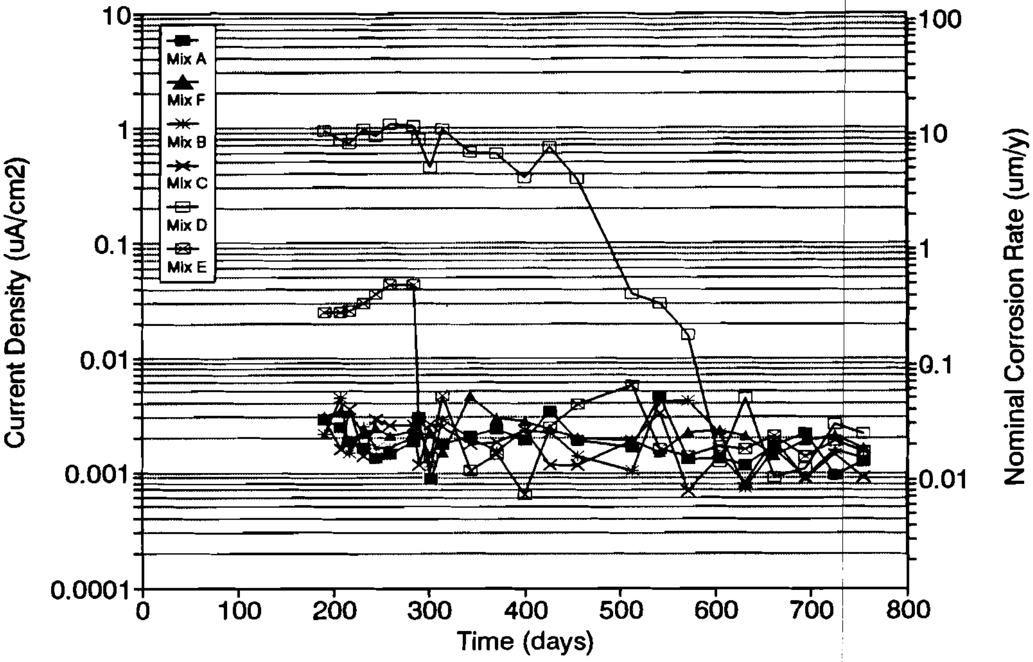

Figure 7. Evolution of the current densities and nominal corrosion rates as a function of exposure time for the plain steel in the laboratory air concrete specimens. See text for interpretation of the high apparent rates for mixes D and E.

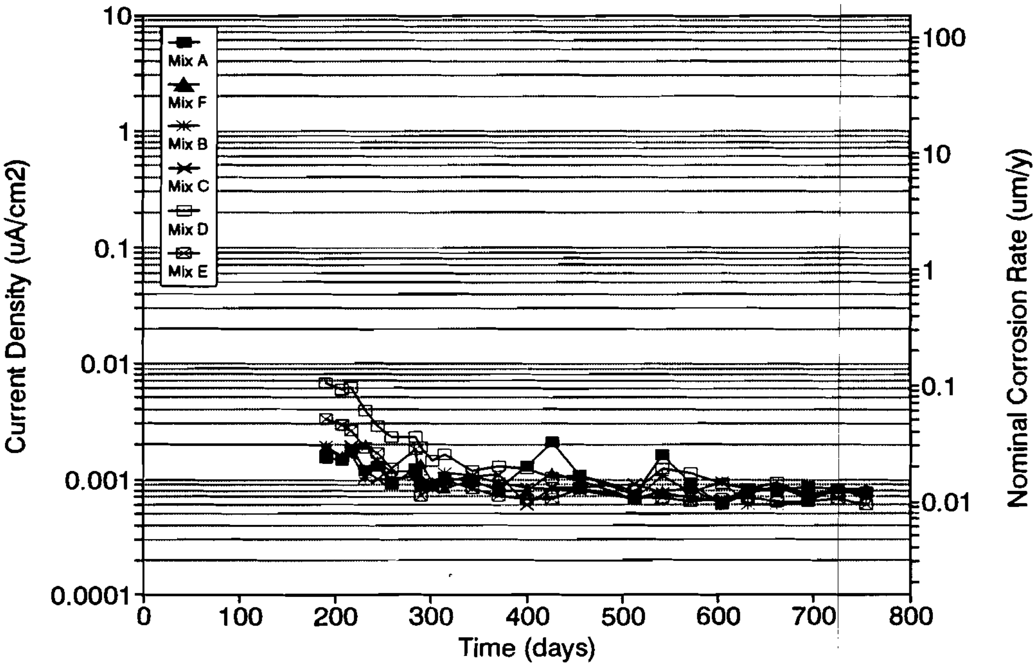

Figure 8. Evolution of the current densities and nominal corrosion rates as a function of exposure time for the galvanized steel in the laboratory air concrete specimens.

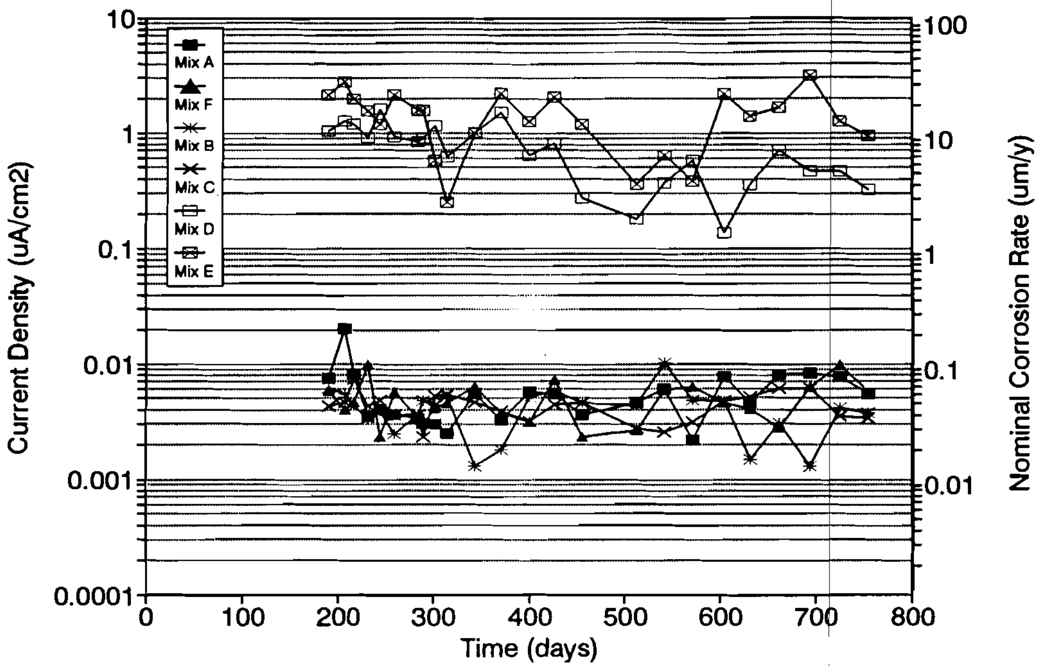

Figure 9. Evolution of the current densities and nominal corrosion rates as a function of exposure time for the plain steel in the wet concrete specimens.

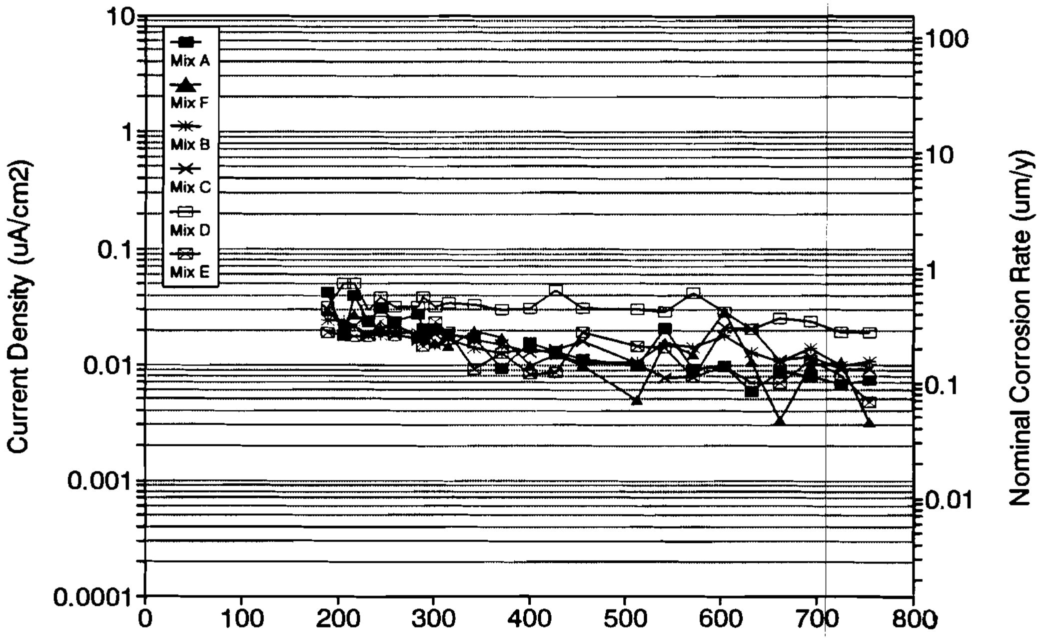

Figure 10. Evolution of the current densities and nominal corrosion rates as a function of exposure time for the galvanized steel in the wet concrete specimens.

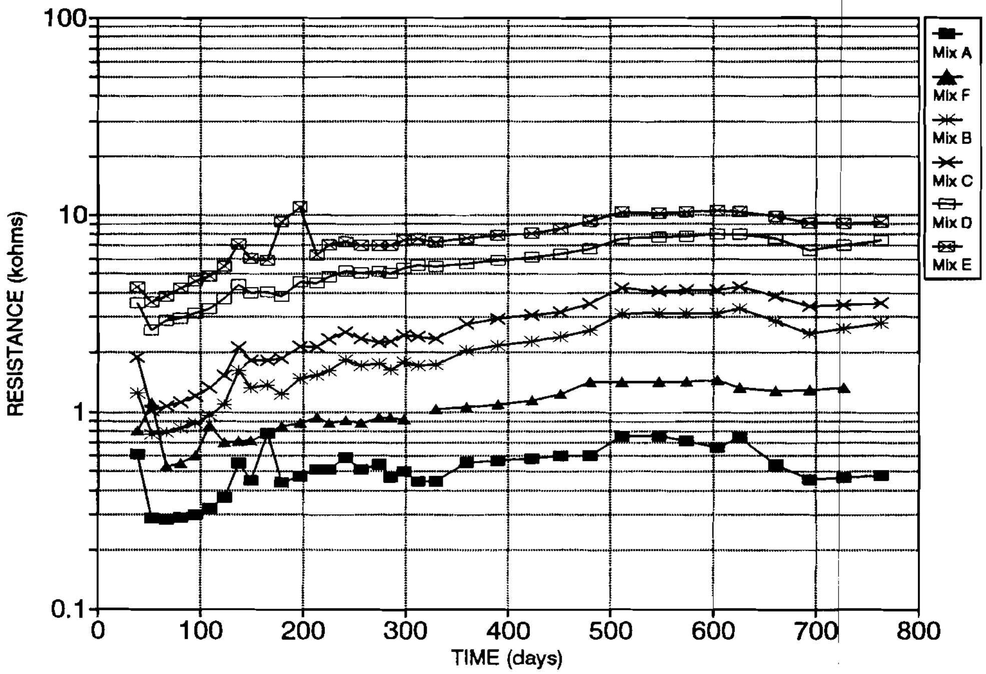

Figure 11. Evolution of concrete resistance in the saltwater environment, as a function of exposure time (Resistivity ρ ~ R x 11 cm).

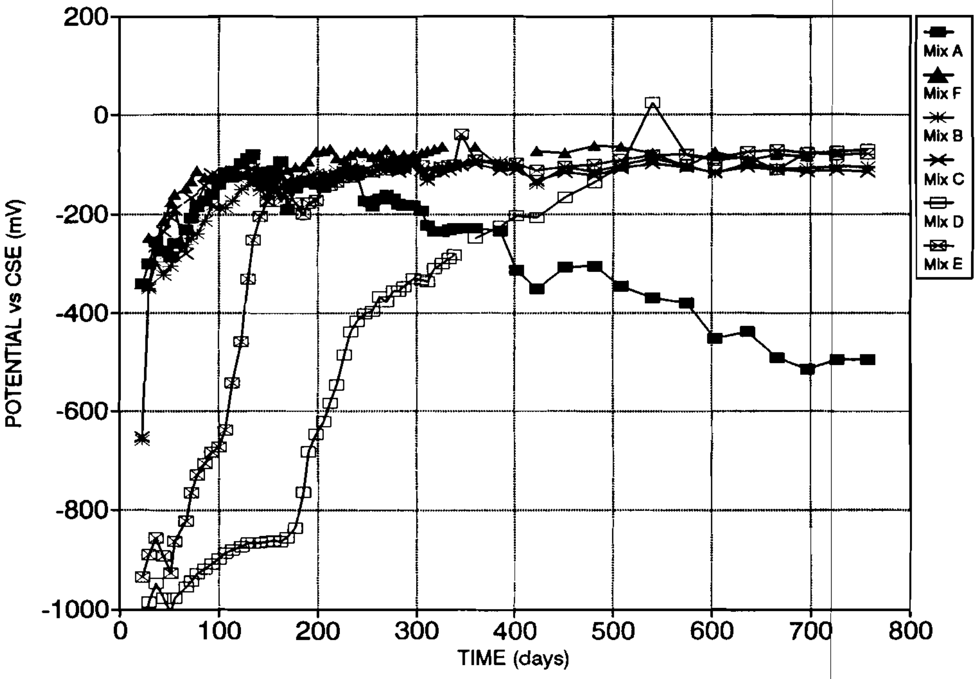

Figure 12. Potentials as a function of exposure time for the plain steel in the saltwater concrete specimens.

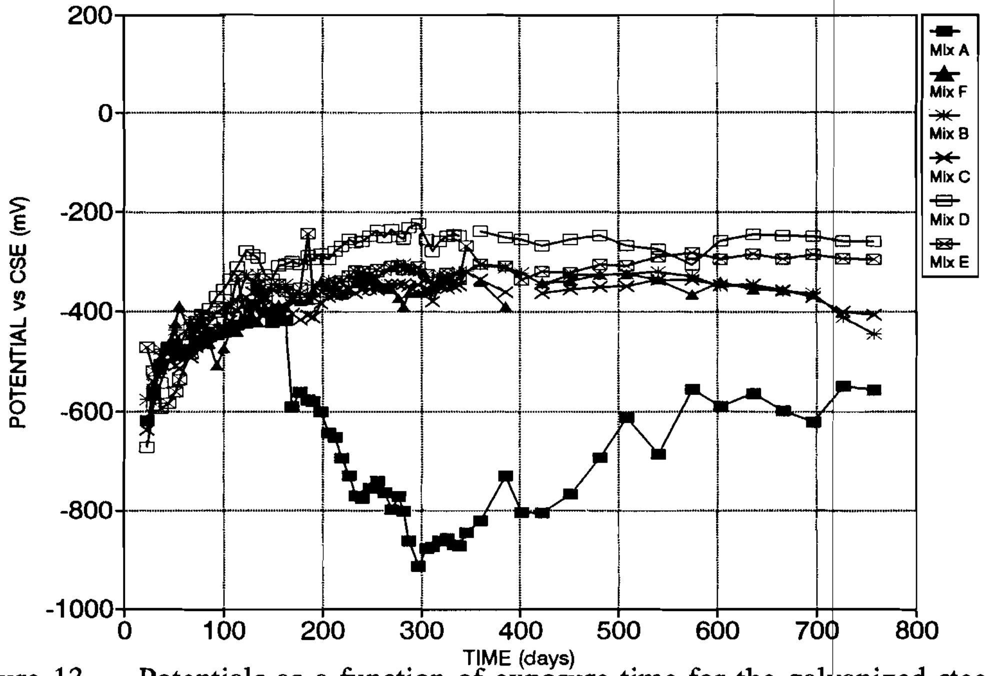

Figure 13. Potentials as a function of exposure time for the galvanized steel in the saltwater concrete specimens.

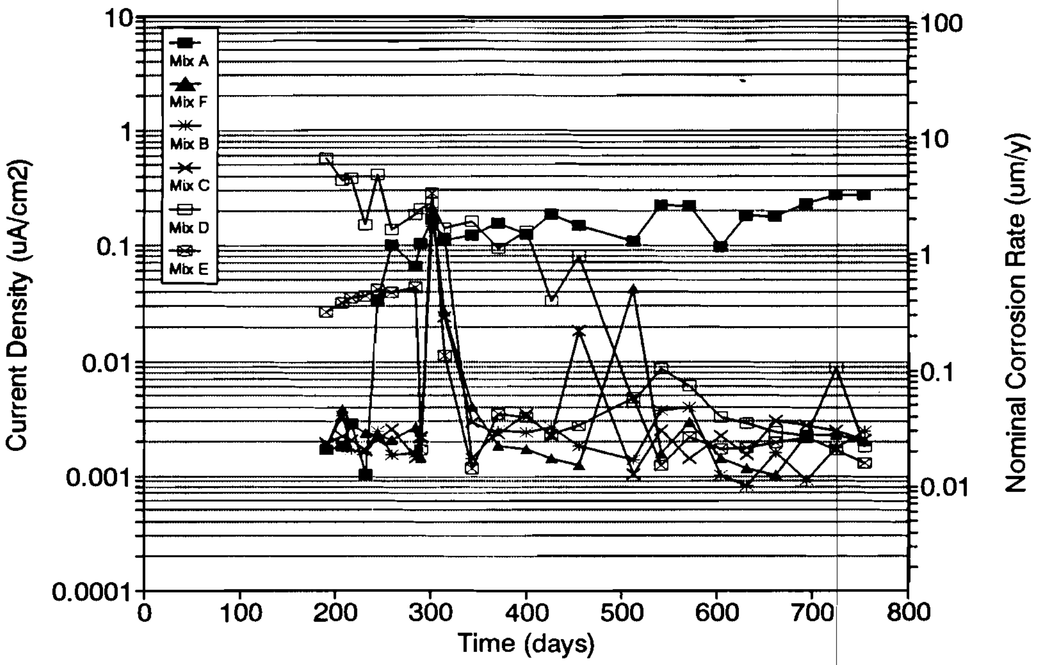

Figure 14. Evolution of the current densities and nominal corrosion rates as a function of exposure time for the plain steel in the saltwater concrete specimens.

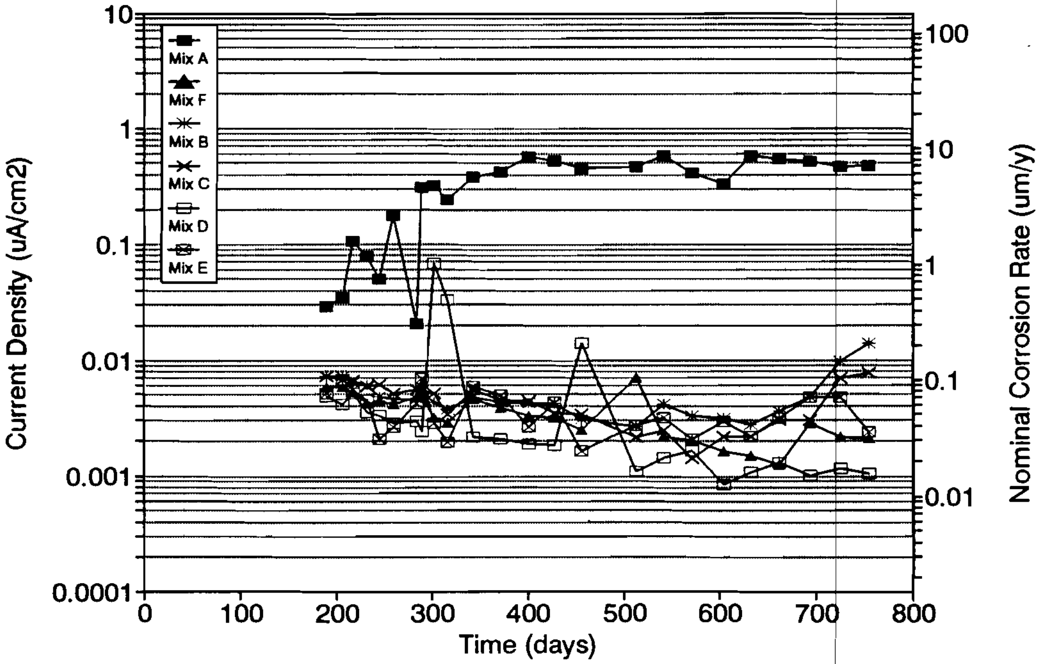

Figure 15. Evolution of the current densities and nominal corrosion rates as a function of exposure time for the galvanized steel in seawater concrete specimens

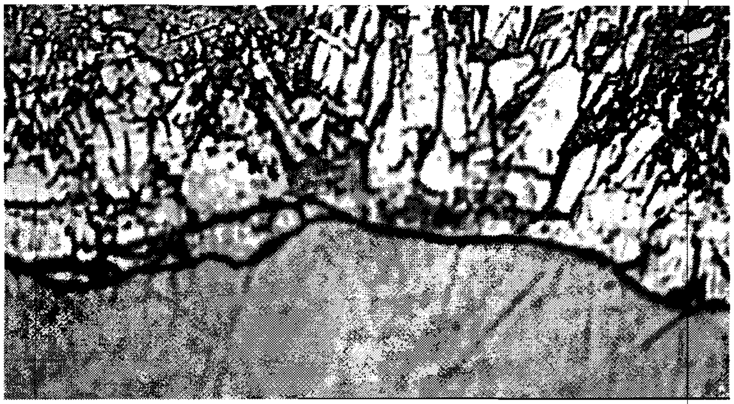

Figure 16. Metallographic cross section of the galvanized layer on a reinforcing steel bar exposed for 2 years in wet chloride-free concrete Mix E. The picture field is 175 μm high.

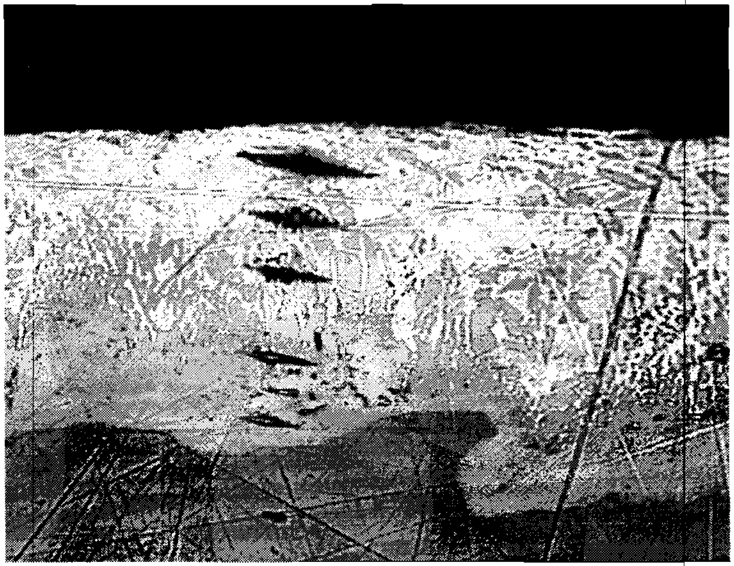

Figure 17. Metallographic cross section (unetched) of another location of the galvanized layer on the same specimen as in Figure 16, showing the Knoop microhardness indentations (see text). Same magnification as in Figure 16.