Research and Update on Galvanized Reinforcing Steel

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ABSTRACT

Experimental and anecdotal evidence have shown the efficacy of galvanized reinforcing steel in concrete applications. However the mechanism for this performance has not been collectively explored. This paper reviews significant experiences with galvanized rebars, and synthesizes these experiences with a newly reported investigation into a paradigm which is consistent with demonstrated field and laboratory behavior. The superior performance of galvanized bars versus black bars results from a higher threshold for corrosion initiation, reduced corrosion kinetics, and a lowering of stresses induced in the concrete as a result of the mobility of zinc corrosion products.

Keyword: Galvanized Steel, Zinc, Corrosion, Concrete, Zinc Hydroxychloride II

INTRODUCTION

The problem and indeed the general mechanism of the deterioration of concrete structures by reinforcing steel corrosion accelerated by permeation of chloride ions has been well documented. A wide range of engineering techniques have been suggested to ameliorate the problem including specifications for denser concrete and/or deeper steel placement, corrosion inhibitors, physical barriers, admixtures, various rebar materials, and combinations thereof. Among the materials applied to the problem both in wide field exposure as well as scientific study, is galvanized reinforcing steel. This paper reviews and brings current the knowledge base supporting the use of galvanized rebars, and synthesizes a construct for the performance of galvanized rebar, from the growing body of field experience, simulations, and parametric studies.

EARLIER RESEARCH AND REPORTS

The study of the efficacy of any of the technical approaches to solving the concrete reinforcing steel corrosion problem is difficult for at least three reasons:

1) The process causing the ultimate deterioration is exceedingly complex and difficult to model in it's entirety. The rate and mechanism of corrosion of the imbedded bar is governed by an internal environment with multiple and various interrelated equilibria and

gradients which are difficult to characterize, or duplicate in simulation. In essence, much of the kinetics relates to concrete material factors, to rebar material factors, to environmental factors, to elapsed time, and to the interdependencies and relationships among all of those factors, many of which are not easily measured, predicted or simulated with confidence.

- 2) The internal processes are invisible *in situ* so that the "vision" of the underlying corrosion or deterioration processes as they occur has often studied on surrogate measurements such as the growing and compounding arsenal of electrochemical techniques some of which are limited in scope and availability, or "autopsy" examination which carries the risk of destroying the delicate conditions or equilibria of the studied processes.
- 3) Lastly, corrosion-in-concrete specimens, while nominally identical, often behave like "biological" specimens in that there are often a range of small and uncontrolled differences among the specimens which may cause variation in behavior of the seemingly similar units.

A large number of studies, many at full field scale, have been published regarding galvanized reinforcing steel, the majority of which have found that a galvanized coating on reinforcing steel reduces the incidence of, or increases the time to cracking for steel bars imbedded in concrete and subjected to chloride exposure. Numerous "Pilot" through "Bench" scale studies have also been reported ranging from bare zinc to concrete prisms in exposures ranging from natural to solution simulations in beakers.

The complexity of the underlying mechanism has often been studied by partitioning the corrosion phenomena into laboratory simulations where isolated parameters or combinations are studied in the abstract. Notwithstanding the recognized quantitative limitations of these parametric studies in modeling the corrosion induced concrete deterioration mechanism *in toto*, the results of those studies related to galvanized rebar contribute to a reasonably consistent and growing body of evidence which at least qualitatively describes the performance of galvanized reinforcing steel, and in light of the excellent field performance reported, supports its continued use in the future.

Field Studies

Major field studies include the series of performance evaluations^{1, 2, 3, 4} reported by the International Lead Zinc Research Organization (ILZRO), with a follow-up evaluation of one structure in a marine environment. Table 1 lists the years-since-construction for structures studied in the ILZRO series of evaluations as of 1995. Brackets surrounding the age numbers indicate that in the year evaluated, the chloride concentration at the bar level was at or above the critical chloride threshold for bare steel corrosion, taken as 1.1 pounds per cubic yard (0.65 kg/m³) of concrete. Of particular interest is the evaluation completed in 1994 ⁵.

The table (and underlying reports) shows some interesting, and arresting data. For example, the Boca Chica bridge in Florida has been at or above the critical corrosion threshold for bare steel virtually since it was built in that bar level chloride levels were found to be at or above 1.1 pounds per cubic yard (0.65 kg/m³) within three years, and 19 years later, no corrosion distress had been observed for the galvanized bars in place. Cores were extracted from that bridge at 3 and 19 years of service. At 3 years, the average galvanized coating thickness on the extracted cores was reported (Stark 1975) as 5.1 mils (≈ 130 microns) while at 19 years of service, the average values were (Stejskal 1992) 4.3 mils (≈ 110 microns), still in excess of the general Standards for galvanized coating thickness.

Two cores were extracted from the Longbird Bridge in Bermuda in 1995 for examination of the reinforcing steel, chloride analysis and other studies. At the time that these cores were taken, the bridge had been in service for 42 years. The results of these and further analyses of the cores is reported later in this paper.

The results from the series of ILZRO studies are complimented by other examinations including those by Malasheskie⁶ of PennDOT, and Vecchio⁷ in New Jersey, and The European Committee for Concrete (CEB). In a synopsis⁸ of the PennDOT report, the author reported that, for the structures studied, the overall rating for the galvanized rebar-containing decks (0-9 scale with 9 indicating the best performance, in conformance with bridge deck condition rating system for NBIS) was 7.04 average. Individual rebars from cores taken from a number of the galvanized rebar-containing decks were subjectively evaluated as 4.2, (5.0 rating as "new," and 4.0-4.9 indicating excellent condition and no corrosion) after nominally 14 years from installation even though chloride levels were found to be "high" in the surrounding concrete. The condition of the bars taken from cores in the New Jersey evaluation were similar to the PennDOT evaluation after 19 years of service. Comparable results not cited here have also been reported.

The European Committee for Concrete (CEB) has issued a comprehensive report⁹ which deals in part with galvanized reinforcing steel in field studies. Among the data compiled in the report is an inspection report of four structures exposed for several years in the tidal zone and presented below as Table 2. The data lists zinc loss by corrosion for original coating thickness' of 100-200 microns (4-8 mils).

Pilot Scale Research

A number of studies have reported on less than "Field" scale, but greater than "Bench" scale evaluations of galvanized rebars, just four of which are discussed here. Such smaller scale studies are often considered as "comparative" in nature as the scale-up factor between specimen size and configuration together with natural or accelerated test conditions, and full scale natural exposures is generally not determined. It is reasonable to expect that the such factors as water/cement ratio (as it affects chloride diffusion coefficients), which are often

chosen to be higher than normal to compress the test duration may be a particularly important factor in projecting performance measured in smaller scale test, to full scale application.

Burke¹⁰ tested various protective agents, including galvanizing, with 6 inch (15.24 cm) diam, 24 inches (63.5 cm) long cylinders containing four #4 rebars each at depths of cover ranging from 0.5 inches (1.27 cm) to 2 inches (5.08 cm) in natural sea-water intertidal zone for 76 months at Key West, FL. Data for the 1 inch (2.54 cm) and 2 inch (5.08 cm) cover specimens (the only ones for which chloride levels were reported) follow in Table 3. The author reports that the plain rebar specimens were rust stained and cracked at the end of the 76 month period, while those with galvanized rebar exhibited no external rust staining or cracking.

Swamy¹¹ has published data on experiments using both natural (tidal zone exposure) and accelerated conditions, reporting on the chloride penetration and the frequency of rust on pilot scale specimens containing uncoated or galvanized rebars. Tables 4 through 6 below indicate that galvanized bars have a very high tolerance limit for chlorides vs. uncoated steel, resisting corrosion in natural exposure at chloride level of 4,000 ppm which is equivalent to 25 pounds per cubic yard (14.8 kg/m³) of concrete.

The data in total clearly infer either a higher chloride threshold before corrosion is initiated, and / or a lower corrosion rate for galvanized vs. uncoated rebar.

A seven year pilot scale program has been reported by Rasheeduzzafar, et al¹² wherein 120 mm (4.72 inches) square by 350 mm (13.78 inches) concrete prisms were cast around two 0.5 inch (12.7 mm) diameter deformed rebars of various types at the corners of the square cross section with 1 inch (2.54 cm) cover. Chloride at levels of 4, 8, and 32 pounds per cubic yard (0.6, 1.2, and 4.8 % weight of cement respectively) (2.37 kg/m³, 4.75 kg/m³, 18.98 kg/m³) was added to the mix to accelerate corrosion, and to represent the condition of concrete mixed with salt-contaminated water. The prisms were exposed for seven years to the coastal environment of Eastern Saudi Arabia, and monitored for cracking. While the results of the experiment are far too comprehensive to adequately discuss here, the results of the seven year exposure, restricted to just bare and galvanized steel are shown in Figure 1

It can be seen from Figure 1, for example, that after seven years exposure, 58% of the 4 pounds per cubic yard (2.37 kg/m³) galvanized specimens were uncracked while only 13 % of the uncoated steel specimen were uncracked. Continuing, for the 32 pounds per cubic yard (18.98 kg/m³) specimens, 87% of the galvanized specimens were below condition 5 (Heavy Cracking), none were at Condition 6 (Spalling), while 100% of the uncoated steel specimens are at condition 6 (Heavy Cracking). Qualitatively similar results in a seawater study using zinc, nickel, and steel rods in concrete were reported by Baker et al. ¹³ Further comparisons can be made from these and other reported data.

Among the information resulting from the test, the authors report that time for first crack to appear after casting-in 32 pounds of chloride per cubic yard (18.98 kg/m³) of concrete was 172 days for galvanized steel but 65 only days for uncoated steel. Similarly, metal loss to corrosion of uncoated steel was almost twice that for galvanized steel. Generally similar and confirming results, not further described here, has been reported by Treadaway et al, ¹⁴ as well as others.

It is important to note that the test conditions represent the case where chlorides do not have to permeate to the rebar surface, they are cast in as internal chlorides from the start of the test. Thus, the differential behavior of galvanized vs. uncoated steel must be the result of either a lower corrosion rate for zinc at nominally similar chloride levels and / or a lower volumetric expansion for the zinc reaction products.

Pfeifer, Langren and Zoob¹⁵ conducted an FHWA-sponsored study of 11 corrosion protection systems. A total of 124 small reinforced concrete slabs were subjected to a 48 week, cyclic wet and dry saltwater exposure, using various water/cement ratios, and bar clear cover depths. Figures 12 and 13 respectively show the corrosion current and half-cell potential measured over the test period on the two replicate slabs for w/c = 0.5 and 1 inch (2.54 cm) cover for bare steel (System 1) and galvanized steel (System 4). In each case, both top and bottom mats are the same. System 5 used a galvanized top mat and a black steel bottom mat.

The chloride content at time of corrosion start (rapid potential shift midway through the first 10 week period) was 0.023 % by weight of concrete, corresponding well with previous work. At the end of the test period, the chloride content was 0.443-0.407 % by weight of concrete for the black bars. The ending chloride content for the galvanized bars in System 4 was not reported by the authors, however the mean value for all w/c=0.5 and 1 inch (2.54 cm) cover, the class of which System 4 was a member, was 0.451 % by weight of concrete.

The time-to-corrosion (two replicates) for the black bars was 5-8 weeks, while the time-to—corrosion for the galvanized bars was 9-11 weeks. At the end of the test period, the authors reported that there was no rust on the galvanized bars but 73% rust on the black bars with severe corrosion on and near rebar deformations. The mat-to-mat resistance for the two System 1 black bar replicates rose from 185-190 ohms to 450-660 ohms during the test period. The authors did not report the resistance values for System 4, but for System 5, where the larger uncoated cathode area of the bare bottom mat would be expected to drive the corrosion of the zinc coating, the mat-to-mat resistance rose from 200-190 ohms to 1900-2400 ohms during the test period.

Three observations are notable from comparison of Figures 12 and 13. First, the half-cell potentials for the black steel bars rises rapidly after a short period, and continues to rise over the test period. This potential shift coincides with a dramatic rise in corrosion current and is

most likely indicative of the arrival of the chloride permeation front. Second, roughly midway through the first 10 week period, the galvanized steel bars show a potential shift, however after reaching a peak over the next 20 week period, the potential reversed towards the original levels. The measured corrosion current went through a similar (but shallower) rise and fall during the period of the potential shift and reversal, returning to essentially the value at the start of the test. Third, at the later stages of the test period, the corrosion currents for the black steel bars varied either side of $160-250~\mu A$ midpoint, while the corrosion current for the galvanized bars in similar conditions were negligible in a chloride environment which is corrosive to black steel. The rise of current at the arrival of the chloride permeation front, followed by a return to low corrosion current levels suggests a value to an "active" coating which responds to the chloride corrosion stimulus in an almost "biological" way.

At the end of the test period, after the "biological response" to the arrival of the chloride permeation front, the galvanized bars had negligible corrosion current in a chloride environment over 18 times larger than that which had initiated, accelerated, and maintained corrosion currents in black rebars.

Parametric or Bench Scale Studies

A number of studies of isolated effects or parameters have been reported which contribute to the synthesis following. While such studies are clearly not the basis for which quantitative estimates can be directly made for full scale application, they serve uniquely to illuminate or suggest particular factors or mechanisms which are part of the overall kinetics, and as such can be confirmatory or supporting in nature. Among those are the chloride threshold for corrosion of the zinc surface in the concrete environment, chloride diffusion kinetics in concrete, and the presence of and parameters related to a passivation effect for the zinc surface at high pH.

The critical chloride threshold for zinc corrosion in a concrete-like environment has been studied by Ishikawa, Cornet and Bresler¹⁶. Duval and Arliguie¹⁷ studied similar phenomena and also the formation of calcium hydroxy-zincate on zinc surfaces in high pH solution. Ishikawa et al. found a markedly higher chloride concentration necessary for corrosion of the zinc surface relative to steel in saturated Ca(OH)₂ solutions, the ratio measured to be about 0.45 / 0.08, a ratio of 5.6:1. Given the slow permeation of external chlorides from the concrete surface to the rebar surface, the higher threshold for corrosion activation suggests a significantly longer time period before galvanized steel becomes active vs. bare steel, the time extension dependent on the diffusion rate of the chloride ions, which in turn depends on concrete parameters.

Duval and Arliguie (1974) studied the anodic polarization behavior of zinc surfaces in saturated Ca(OH)₂ solutions to determine the resistance of the passivating layers of calcium

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hydroxy-zincate to corrosion of zinc by chloride penetration. Zinc electrodes with and without a zincate surface layer were immersed in solutions with variable Cl⁻ ion concentrations to determine the potential (and Cl concentration) at which rupture of passivity occurs. With zinc electrodes which had been immersed in saturated Ca(OH)₂ solutions for 15 days prior to testing to allow the formation of a zincate layer, the minimum concentration of chloride ion necessary for zinc corrosion was about 0.2N vs. 0.04N for the untreated zinc electrodes. The solution concentration ratio is 5:1. The pure zinc electrode data confirms the previous findings of Ishikawa (1972). Anodic polarization curves similar to that of Duval and Arliguie (1974) have been published by Cheng et al¹⁸, and Sergi et al (1985),

The subject of the calcium hydroxy-zincate protective layer Ca(Zn(OH)₃)₂·2H₂O has been studied by a number of researchers. An earlier paper by Rehm and Laemmke¹⁹ describes the formation of the passivating layer on zinc in Ca(OH)₂ solutions which extinguished further reaction. Subsequent experiments showed the compound formation in reaction with cement pastes. Both the formation of, and the protective nature of the calcium hydroxy-zincate has been studied and reported by other researchers.

Macias and Andrade²⁰ have shown a threshold of pH 13.35 (\pm 0.10) below which, immersion of a zinc surface will become passivated with the corrosion current reduced to <10⁻¹ μ A/cm². At higher pH, the passivation is inhibited, and it has been shown that the inhibition of passivation is related to the reduction in the availability of Ca⁺⁺ ions due to decreased dissociation of Ca(OH)₂ because of the K_{sp} effect at high pH. Fratesi (1997), in work cited later in this paper, worked with European cements of "high alkaline contents" and observed that using the method proposed by Andrade, the pH values of the aqueous solutions obtained after various dwell times and agitation of the cements in water did not exceed 13 which is well below that which is generally considered as the lower edge of a critical threshold for the corrosion of zinc (pH=13.3).

In further experiments, Blanco et al.²¹ showed that once the calcium hydroxy-zincate passivating layer is formed, subsequent exposure to solutions higher than the critical pH of 13.3 does not destroy the passivating nature of the calcium hydroxy-zincate surface layer. Additionally, Cornet and Bresler²², citing the work of Duval and Arliguie, have shown that once formed, the passivation layer raises the critical concentration for chloride attack on zinc by just under one order of magnitude.

The kinetics of formation of the passive layer on zinc has been shown by Andrade and Macias²³ to occur over a period of up to 30 days in solutions, after which corrosion rates dropped to far lower values than initially seen. E_{corr} and i_{corr} of the zinc surfaces diminished substantially after 2 days in saturated $Ca(OH)_2$ solutions. In a partial immersion test using galvanized rebars in mortar samples made from various cements, Andrade and Macias²⁴ showed that the corrosion currents after one year were one order of magnitude less than the one day values. The corrosion currents at the one year point were generally below $0.1\mu\text{A/cm}^2$

where the pH of the cement suspensions ranged from 12.0-12.8. Other research²⁵ has shown similar behavior in that the initial corrosion response of zinc at high pH or in concrete environments decays to dormant values over a reasonably short period.

Duval and Arliguie (1974) have published a diagram showing schematically the calcium hydroxy-zincate and other phases formed on a zinc surface in concrete, reproduced here as Figure 2. The formation over time is consistent with the dormancy period of the zinc surface in concrete and concrete solution simulations.

The question as to whether chloride ions inhibit the formation of the passivating layer is not fully answered. Andrade and Macias (1988) have shown that in saturated $Ca(OH)_2$ solutions, chloride additions in the range of 0.3 - 0.9M NaCl does not alter the passivation formation, and resulting corrosion currents (i_{corr}). Sergi, Short and Page²⁶ suggest that at low Cl concentrations there is little or no effect, but at higher concentrations the effect of chlorides on passivation is evident even though the presence of chloride-containing deposits could not be confirmed in all cases. The authors did not report the threshold.

Many of the "bench" scale or solution tests have shown i_{corr} values for zinc or galvanized coatings after passivation (within a few days in sat. calcium hydroxide) and stabilization in the range of $10^{-1} \,\mu\text{A/cm}^2$. These corrosion currents for zinc are equivalent to a metal loss rate of about 1.5 $\mu\text{m/yr}^{27}$. An ASTM 767 Class I galvanized coating in practice has a thickness of $\geq 150 \,\mu\text{m}$ ($\geq 6 \,\text{mils}$).

It is critical to note that the use of NaOH or/and KOH to simulate the electrochemical environment and behavior of zinc in concrete without sufficient calcium ions can lead to inaccurate, even implausible results, particularly when such "bench scale" results are extrapolated to predictions of field behavior. For example, McDonald²⁸ et al performed screening tests including polarization resistance measurements in 0.3N KOH+0.05N NaOH+Various amounts of NaCl solutions on galvanized bars as well as others. A general "rule of thumb" for calculating approximate pH of solutions of strong bases²⁹ is pH = 14.00+log[base]. The log of the combined concentration of the two strong bases [log(0.3+0.05)]= -0.456, thus the approximate pH of the test solutions would be 14.00+(-0.456)=13.54. The pH of Saturated Ca(OH)₂ is in the range of 12.6, or potentially almost one order of magnitude less than that calculated above. Additionally, the calculated pH is well above that where Macias and Andrade (1983) showed that zinc either slowly, or will not polarize. Given that the pH of the test solutions was most probably above the critical pH reported in 1983, as well as the absence of calcium ions which are necessary for the formation on the hydroxyzincate "normal" protective layer, it is no surprise that McDonald et al found low polarization resistance (R_p) values in their tests.

Using the Stern-Geary relationship, with assumed Tafel slopes, the authors calculated relatively high corrosion currents (i_{corr}) which when applying the method of Rodriguez et al³⁰

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(related to corrosion of iron) determined that galvanized bars had a time-to-cracking of about one year, similar to their determination for black bars. This similarity is striking in that the galvanized bars in the subject tests had R_p relative to black bar of only 0.07. The authors note in their paper that the test conditions are much more severe than typical field conditions, and that the absence of calcium (available or otherwise) in the test solutions made the performance of zinc-coated bars limited and non-representative. From these solution tests, the one year time-to-cracking for zinc-coated bars determined by the authors is totally inconsistent with field performance results spanning over 40+ years.

In the absence of chlorides during the early period of a concrete structure, the formation of a zinc passivation layer has been generally confirmed. It is further suggested that there is some level of permeating chlorides below which the passivation is retained, and above which, the zinc surface will again become active and react at some rate which could eventually lead to it's consumption. Therefore, the time for sufficient chlorides to diffuse to the passivated zinc surface is an important element in the service life of galvanized rebars. The diffusion kinetics have been investigated by a number of researchers, and mathematical treatments for those kinetics are now available. Sagüés³¹ is among those who have investigated both experimentally and mathematically to develop diffusion coefficients for chloride ions in typical bridge decks, and has published interesting curves of computed time for the appearance of a spall as a function of chloride diffusivity, critical chloride threshold for metal depassivation, and rebar cover. For bare steel, the time until spalling after depassivation by the advancing chlorides is taken as 3.5 years, and is added to the computed diffusion value. For galvanized steel, the appropriate value may be much higher. In essence, for bare steel bars, the time-to-cracking is effectively the time-to-depassivation plus a few years, therefore the diffusion coefficient for chlorides through concrete and therefore the time-todepassivation is the factor which governs the service life of bare steel reinforcing bars.

RECENT RESEARCH AND REPORTS

As noted earlier, two cores were taken from the Longbird Bridge in 1995 in a small project organized by this author with support from ILZRO, the Bermuda Ministry of Public Works, the U.S. Navy, and Zinc Corporation of America. The cores had no cracking associated with underlying steel corrosion, either on the outer flat surface of the core exposed to the environment, or internally on the cylindrical surface of the core.

Figure 3 shows an "as-received" section of core #1 which contained a relatively smaller rebar, and Figure 4 show an "as-received" section of core #2 containing a relatively larger rebar segment. Note that the small amount of iron corrosion product on the "face" of the rebar in core #1 is the result of sea water being used as the core drill coolant. Virtually no iron corrosion products were found at the bar-concrete interface, and no cracks or other distress was seen as a result of whatever zinc corrosion had occurred. Figures 5 and 6 show the extracted small rebar from core #1, Figure 5 is the side of the bar "away" from the advancing

chloride front, and Figure 6 is the surface "toward" the outer flat surface of the core. Figure 7 shows the extracted bar from core #2.

The thickness of the remaining galvanized coating, after 42+ years of exposure to the tropical marine environment, was found in each case to average well in excess of that required by the Standards for new galvanized reinforcing steel³². Figure 8 shows the typical remaining coating in core #1. Almost all of the coating in core #2 was similar to that shown in Figure 8 for core #1. However, in a few small areas, the galvanized coating had been consumed/converted to corrosion products. As can be seen in Figure 9, the remaining galvanized coating is providing cathodic protection to the exposed steel in the few pinpoint where the coating has been consumed in core #2. Other photomicrographs confirm the observations of Yeomans³³ and others, that the corrosion of the *eta* layer of the galvanized coating proceeds in favor of the slower kinetics of the zinc-iron intermetallic layers, and that when the coating kinetics results in the uncovering of the underlying iron surface, the cathodic mechanism of the zinc-iron cell protects the steel for an extended period of time. Earlier work³⁴ had shown that the distance over which such cathodic performance could be expected is about 8 mm.

The remaining galvanized coating on the two bars examined using direct optical reading of the coating cross-section (average of ten circumferential readings) is shown in Table 7.

The acid-soluble chloride content at the bar levels were 3.24 and 8.81 pounds per cubic yard (1.92 kg/m³ and 5.23 kg/m³) respectively, well in excess of the generally accepted threshold for bare steel corrosion. As shown in Table 1, the subject structure was above the critical threshold, at bar level at examined sites, when first studied in 1977, when the structure was nominally 23 years old, and continue at many times the threshold level through the recent examination at structure age 42 years. Other structures in Bermuda were also qualitatively examined in 1994, supporting and confirming the findings of Allan³5 reported in 1991. Similar findings have be reported by others.

The corrosion products were found to be "loose and powdery" similar to the observations of others when examining aged galvanized rebars in the field. The corrosion products were collected from the large bar of core #2, and subjected to semiquantitative analysis using SEM-EDX techniques. The result (for elements Sodium and higher), when normalized to 100% and reported as stoichiometric oxides, is shown in Table 8.

The same sample as above was used for X-ray diffraction analysis with the compounds identified as either major, minor, or trace amounts in Table 9. Absent from the corrosion products was the compound zinc hydroxychloride II (Zn₅[OH]₈Cl₂·H₂O), which was reported by Hime and Machen³⁶ to be the single corrosion product³⁷ of zinc in the chloride-laden mortar they had studied. The relevance and background of this work to "natural" chloride infiltration in concrete will be examined further in this paper.

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A section of core #1 was taken to examine the steel bar/coating/concrete interfaces by SEM, and to study the distribution of elements along that continuum. Figure 10 shows the interfacial area – the light gray zone at the far left of the photo is the underlying steel, the off-white area is the galvanized coating, and the dark area which occupies most of the photo is the concrete. This, as well as all other photos of the interfacial area showed no cracking of the concrete regardless of the amount of corrosion which might have taken place. Figure 11 is the elemental map (zinc, iron, calcium, and silicon) of the area shown in Figure 10. For clarity, silicon was not included in the composite on the right of Figure 11.

The composite picture in Figure 11 clearly shows the migration of zinc-containing compounds into the adjacent concrete matrix, extending 15-20 mils beyond the surface of the coating. This elemental map composite supports the theory that zinc corrosion products will migrate into the surrounding concrete rather than accumulate at the surface of the galvanized coated bar. The migration prevents build-up of internal pressure which would eventually lead to concrete cracking and spalling. (Dugan, 1995)

The observations of the migration of zinc corrosion products above is supported by independent work by Yeomans³⁸ reported in 1998, and previously cited. He found by SEM study of the interfacial zone that zinc corrosion products migrated away from the zone and filled micro-cracks and small voids (and lined larger pores) in the concrete matrix at some distance from the bar/coating surface. This work showed a noticeable densification of the matrix adjacent to the bar interface, with small regions of zinc corrosion products at remote pore sites at a greater distance from the bar/coating region. X-ray diffraction identified the corrosion product filling these smaller pores and capillary spaces as the oxide mineral zincite (ZnO) with no evidence of the presence of complex zinc oxychloride type minerals such as reported by Hime and Machen. As in the work by Dugan (1995), metallographic and SEM/spectral/diffraction results were compatible and confirming, and there was no evidence to suggest that the zinc corrosion products caused any distress in the bar/matrix interfacial region, nor in the bulk matrix itself.

The two examples cited above are further supported by anecdotes coming from the work of Covino et al³⁹ in experiments dealing with the use of metallized zinc on concrete surfaces as a anode. The zinc corrosion products were found to migrate away from the interfacial zone. Additionally, these observations are consistent with the work of Duval and Arliguie (1974) as shown in Figure 2, where the migration of zinc corrosion products is schematically diagrammed (from experimental results). In a program investigating adhesion and bond strength of galvanized rebars in concrete, Fratesi⁴⁰ reported a similar "bridging" and migration at the galvanized bar/concrete matrix interface, with an increase in bond strength in the within months of casting. This increase in bond strength over time has been reported by others, and is consistent with an infiltration of products resulting of the concrete and zinc interactions.

As to the expectation of the formation of zinc hydroxychloride II (Zn₅[OH]₈Cl₂·H₂O) in concrete, in the 1993 paper, Hime and Machen state in the "Introduction" paragraph that "The present work reviewed the failure of the masonry facade at a bank in Cleveland, OH, where cracking of the mortar and brick over galvanized rebars embedded in mortar-filled cores of the brick was observed. The bars had corroded significantly. Although corrosion products of the underlying steel were present on some bars, others were coated only with a thick, white Zn corrosion product." No further identification of the corrosion phenomenon studied was made, nor was the source of the chloride ions other than to state that the mortar was made with a Cl containing admixture. No other "abnormality" was described, however in the context of "natural" infiltration of concrete by external chlorides, the phenomenon reported is clearly special, even anomalous in the context of "general" studies of the performance of galvanized rebars.

During the late 1960's to the mid-80's an inordinate number of masonry failures⁴¹ were reported which had as a common thread, the use of a new admixture product ⁴², a polymer of vinylidene chloride - the failures being evidenced by "expansion" of the mortar with corrosion distress to the underlying reinforcement, and ultimately failure of the brick facade or other affected structure. There was much litigation relating to liability for the restoration of the affected structures. In some of this litigation, Erlin, Hime Associates was a participant as an expert witness for the plaintiffs and the study reported in the 1993 paper is derived from that work. In these proceedings, it was shown that the "additive" product would, under exposure to the high alkaline environment of concrete paste and pore water, decompose releasing large quantities of chloride ions which led to corrosion of the reinforcement and/or other embedded steel. It has been reported that there were many out-of-court settlements by the additive producer, many under court seal, but a number of claims went to trial virtually all of which were lost by additive manufacturer⁴³. Because of the litigation, there were some early published reports^{44,45}, but perhaps not complete disclosure or trade-press coverage until about 1989. A thorough description of the case can be found in Kaminetzky.

The conditions necessary for the stability of zinc hydroxychloride II has been known for many years. Feitknecht⁴⁹ has shown that at pH values >7 with low chloride levels, ZnO and βZn(OH)₂ are the stable forms of zinc corrosion products. Figure 12 (pCl⁻ - pH)⁵⁰ shows stability domains of various zinc compounds as a function of the pH and chloride concentration. In the field to the left of line ABCD, no solid compound is formed. The field ABF, is the stability domain of zinc hydroxychloride II, also denoted as ZnCl₂·4Zn(OH)₂. The field FBCG is the domain of zinc hydroxychloride III, and below line CG, there is a metastable equilibrium among zinc oxide and various zinc hydroxides, but no chloro-hydroxo complexes or compounds. Thus at the conditions expected for galvanized steel embedded in initially chloride-free concrete sufficiently dense to retard chloride diffusion according to modern practices, the chloride levels and pH (lower right-hand corner of Figure 12), would be such that zinc hydroxychloride II would not be formed at the bar surface. Indeed, the inverse could be said that the formation of zinc hydroxychloride II denotes an unusual chemical

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condition at the bar interface, which is consistent with the clearly punishing chemical attack resulting from the degradation of the admixture material which is the subject of the Hime and Machen study. It can be generally said that at a pH >8, zinc hydroxychloride is implausible.

The assay of the corrosion products formed in the Bermuda study (Tables 8 and 9) in that zinc hydroxychloride II was not found, and no cracking was evident in the cores or the structures themselves, is consistent with the stability domain for zinc hydroxychloride II outlined above and shown in Figure 12. $ZnCl_2\cdot 4Zn(OH)_2$ was reported by Pfeifer et al (1987) together with ZnO as the corrosion products on the top half of the System 4 bars, but the ratio of occurrence of the two was not given, nor was any cracking noted.

Hoke, Pickering, and Rosengarth⁵¹ have published experiments where lower stress generation for corroding zinc-coated bars versus corroding uncoated bars was found. Rosengarth⁵² in a limited experiment, concentrically cast galvanized and bare rebars respectively in mortar cylinders within a Titanium sleeve which were instrumented with strain gauges to monitor the "hoop" stresses created by chloride induced, and accelerated corrosion. The experiments showed that under similar induced-corrosion conditions, galvanized rebars produced less measured stresses than bare steel bars. In that less stress would be equated with less concrete damage, or longer time for damage to occur, the results are qualitatively, completely consistent with other field and experimental observations cited above. Rosengarth (1981) reported a thin inner layer of ZnCl₂·4Zn(OH)₂ among the corrosion products found with chlorides "built-in" rather than transported by natural diffusion, and impressed current to accelerate corrosion of the zinc surface.

DISCUSSION AND SYNTHESIS

The integration of the field performance galvanized rebars and smaller scale studies can be best understood within the paradigm often ascribed by numerous authors to Tuutti⁵³, as adapted in Figures 15 and 16, and also the work of Barton⁵⁴ on atmospheric corrosion of zinc, to which there are some parallels.

Figure 15 shows that the corrosion of metals imbedded in concrete is often preceded by a dormant period as a result of the passivating effect of the concrete internal environment on the metal, which has often been called the "initiation" period labeled in Figure 15 as time period "A." The term "initiation" also refers to the time during which external corrosion stimulators are diffusing or permeating into the concrete matrix to ultimately "initiate" a corrosion response. It is in fact the period prior to "initiation" of active corrosion. At some point in time, if the local metal/concrete interface changes due to permeation of activating species from the concrete surface, the previously dormant surface may "depassivate" and enter a corroding state often termed the "propagation" period, the rate of which depends on the interrelated equilibria and kinetics at the interface.

Figure 16 depicts various degrees of corrosion "propagation", as time period "B", with "a" being a higher, and "c" a lower corrosion rate. The result of these corrosion intensities may be (but is not always) the deposition of solid corrosion products, the volume of which (to the extent that they are not mobile) exerts a "wedging" action⁵⁵ or "hoop" stress at the interface which, if accumulates to higher than the inherent strength of the matrix, cracks and ultimately spalls the concrete - the point at which the extent of physical damage exceeds some acceptable limit.

While Figures 15 and 16 indicate some relationship between corrosion, damage, and time span in that at some time the degree of corrosion occurred could result in stresses exceeding some acceptable limit of damage, not all metallic materials have the same corrosion/damage/stress/time response relationship. It is important, therefore, to explore:

- 1) the <u>corrosion rate</u> intrinsic to the interface of a metal and local environment over the period of exposure,
- 2) the volumetric expansion of the products associated with that unit corrosion, and
- 3) the <u>mobility</u> or the degree to which the concrete matrix accommodates the formation of those corrosion products. All three of these factors influence the development of destructive forces.

The depassivation point in time (the break between the "initiation" and the "propagation" periods) in Figures 15 and 16, is a function of the rate of diffusion and the critical chloride level to activate the metal surface. Therefore, if one metal surface has a higher critical chloride threshold than another, all other things being equal, the metal with the higher critical threshold will have a longer "initiation". period. The work by Ishikawa and others, previously cited, has clearly shown that zinc has a higher critical chloride threshold than steel, often estimated at 4 times or greater. The corrosion current data from Pfeifer et al (1987) suggests that the chloride threshold for zinc is perhaps many times higher than that previously thought. Thus the activation point for zinc on the "Tuutti" diagram will be to the right (perhaps considerably so) of that for uncoated steel.

Both the Field Studies and the Pilot Scale Research cited above are completely consistent with a higher critical chloride threshold and / or a lower corrosion rate for zinc vs. uncoated steel. Further, the stress generated by constrained corrosion product production related to metal consumption appears favorable for zinc vs. uncoated steel.

The "Tuutti" paradigm has been modified for galvanized steel by Yeomans⁵⁶ to reflect both the increased time for depassivation vs. uncoated steel, and the lesser development of stresses

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with time related to lower corrosion rate and / or decreased unit stress development for zinc vs. uncoated steel (for example line "c" in Figure 16). An adaptation of the Yeomans diagram follows as Figure 17. The time period "B" represents the added dormant time for zinc vs. uncoated steel as a function of the higher critical chloride threshold, or depassivation point for zinc vs. uncoated steel. Insight as to the magnitude of the time effect of the higher threshold can be received by application of the published curves of Sagüés to the modified "Yeomans" diagram. Figure 19 shows the computed time to appearance of a concrete spall for a rebar cover of 4 inches (10.16 cm), a chloride concrete surface concentration of 20 pounds per cubic yard (11.87 kg/m³), and three levels of critical chloride concentration, (1.2 pounds per cubic yard (0.71 kg/m³) often cited for bare steel, and 2.4, 3.6 pounds per cubic yard (1.42 kg/m³, 2.13 kg/m³) respectively) as a function of chloride diffusivity.

All of the current thinking in bridge deck protection has as a central theme, the control and decrease of chloride ion diffusion by concrete mix and additives such as pozzolans or silica. Target diffusion coefficients in the range of 0.05 in² / yr. and lower are currently being considered practical and desirable. To the extent that the values in Figure 19 from Sagüés are reasonably correct, time to first spall for embedded metal with a critical chloride threshold of 1.2 (such as is commonly accepted for uncoated steel), with a concrete mix having a chloride diffusion coefficient of 0.05, would be about 50 years. However, with an embedded metal with a higher critical chloride threshold, the time to first spall would be considerably higher.

It should be noted by Fratesi (1997) and others^{57,58} that the addition of pozzolans, slags or silica will lower the bulk alkalinity of the concrete, which may well have the effect of lowering the pH of the pore space solution to 13 or below. At these lower pH values, the pH tolerance of zinc versus bare steel may well have an added benefit.

The calculations underlying the diagram in Figure 19 assume a "Propagation" period of 3.5 years (as line "a" in Figure 16). Thus, for all practical purposes, the years-to-spall on the ordinate are effectively years-to-depassivation, at least for long time periods. Given the demonstrated higher critical chloride threshold, it would not be unreasonable to use 3.6 pounds per cubic yard (2.13 kg/m³) for zinc, and at the same chloride diffusion coefficient (0.05 since it is a function of the concrete and not the rebar material) the years-to-depassivation would be just below 100, or just over twice that for uncoated steel.

The assumed propagation period of 3.5 years is unarguably far too low for galvanized steel in that field experience and experimental observations such as outlined previously indicates much lower stress development as measured by concrete cracking. For example, the Longbird Bridge in Bermuda (as well as others documented by the ILZRO series) has been above the chloride corrosion threshold for uncoated steel for virtually all of it's life. Yet no concrete distress can be found, and the remaining galvanized coating is the most part plentiful and well intact. Those areas were the galvanized coating has been consumed seem to be cathodically protected by the remnant zinc in the adjacent coating. This incontrovertibly suggests a low corrosion rate for galvanized steel in the subject exposure. Thus the lower slope of the line

representing the corrosion of zinc on the "Yeomans" diagram (Period "D" in Figure 17) is quite reasonable.

The absence of concrete distress for the studied galvanized bar structures and experiments is clearly the result of other positive factors. As a general observation, authors who have characterized the reaction products on extracted galvanized bars have often indicated the "loose" and "powdery" nature of the deposits as well as its mobility. The mobility for the zinc reaction product which is accommodated by the pores and interstices of the concrete matrix has been clearly demonstrated. In essence, an unconstrained and mobile reaction product of zinc will generates less stress on the concrete matrix than iron which expands "in place."

Barton (1970) contrasted the (atmospheric) corrosion of iron and zinc as being uniquely different. In response to his question of "Why is zinc which is far less noble than iron thermodynamically, so resistant to corrosion?" He showed that the reaction surface which determines the corrosion rate of iron is at the iron/rust boundary, while with zinc, the corrosion rate governing processes takes place not at the metal/corrosion product phase boundary, but at the outer corrosion product/atmosphere boundary. Thus, the slower reactions at the zinc corrosion product outer boundary control the overall system response to the atmosphere, shielding the zinc surface from rapid attack. The advantageous behavior of zinc in the atmosphere is related thus principally due to the formation of corrosion product films, their properties, and their rate of destruction. The purpose of the underlying zinc is to act as a reservoir to replenish the outer reaction product protection layer in contact with the environment. Zinc acts in a qualitative way similar to that of an organism responding to an invading pathogen.

On the other hand, the lesser nobility of zinc relative to iron allows zinc to give cathodic protection to iron in cases in the presence of adequately conductive electrolytes, and with depletion of the naturally protective reaction product layers. Thus, borrowing from the work of Barton, there are three periods in the "life" of a galvanized product when exposed to atmospheric attack (and by extension, to the environment in concrete):

- I. A short initial period in which the protective layers are formed. This period (days-to-months) is relatively short, and results in the "dormancy" for which zinc coatings are noted.
- II. The longer period (years-to-decades) of actual corrosion of the compact layer of zinc reaction products, with replenishment as needed from the underlying zinc. Thus the duration of this period is directly related to the thickness of the zinc reservoir layer, and inversely related to the aggressivity of the environment. The beginning of this period is often marked by a "biological" response at the surface of the Period I protective layer.

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III. The last period in which the consumption of a major portion of the zinc has occurred, but in which (given conductive electrolyte) zinc provide electrochemical protection to the adjacent exposed iron.

Figure 18 shows the three reaction periods according to Barton on the modified Yeomans (Tuutti) diagram with the (schematic) level of chloride from diffusion superimposed. The Barton period I, the formation of the protective layer (which would be the "patina" in atmospheric corrosion) is essentially an *In-situ Protective Response* (IPR). The formation of the IPR layer in concrete is supported by the various collective works of Andrade, Macias and Blanco, by the works of Duval and Arliguie, Rehm and Laemmke, Pfeifer et al, Fratesi, Yeomans, Covino et al, Cheng et al, Serge et al, and others. The delay or dormancy period between the end of period I and the beginning of period II in spite of the increasing chloride content is supported by the works of Ishikawa, Burke, Swamy, Yeomans, and others. The short line in Figure 18 between the end of period I and the beginning of period II is the critical threshold for propagation of corrosion of bare steel indicated at a point of chloride content which is perhaps one fifth that of zinc: that ratio supported by the work of Ishikawa et al, and Duval and Arliguie. The time to reach that critical chloride threshold (start of period II) is a function of chloride diffusion coefficient. If the diffusion coefficient were reduced further than current target ranges, the beginning of period II for zinc could be delayed perhaps beyond the life of the bridge. In that case, the corrosion kinetics of zinc in periods II and III becomes moot, however bare, or bare spots in otherwise-passive coating bars would most likely into their relevant Period II, and therefore subject to not only corrosion, but resulting concrete damage.

The beginning period II is the chloride temporal point at which the zinc IPR enters the consumption-replenishment cycle, an indication of which, as a second phase IPR, can be seen in the work of Pfeifer et al. The low rate of corrosion and the low rates of stress generation (shallow slope of the corrosion line) during period II is supported by the works of Pfeifer et al, Rasheeduzzafar, Swamy, Dugan, Hoke, Rosengarth, Baker et al, Duval and Arliguie, Burke, Malasheskie, Cornet and Bresler, Allen, the collected works of the ILZRO series, the collected works of Yeomans, and others.

Period III is the time in which partial depletion of the IPR layer allows for zinc to provide cathodic protection to the adjacent steel. The increased slope of the deterioration curve in period III of Figure 18 is debatable but the qualitative nature of the effect can be easily seen in the Bermuda work reported by this author and Dugan, where no concrete distress or cracking, and no iron corrosion product was found (Figure 9) in the zinc-depleted area. In that there is no concrete distress in the area where there has been complete zinc consumption, the end of period III shown in Figure 18 as <u>below</u> the upper bound for acceptable corrosion limit is fully supported, and that for rebar corrosion to ultimately damage concrete, iron corrosion will ultimately have to take place indicated by the higher slope corrosion line beyond the end of period III in Figures 17 and 18. This is anecdotally supported by comments of Kaminetzky⁵⁹ related to the Cleveland National Bank mortar occurrence notwithstanding the contradictory

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description by Hime and Machen. The cathodic protection mechanism is further supported by the work of Yeomans. Note that bare steel bars or bare spots in otherwise-passive coating bars would not have the electrochemical possibility for period III protection.

The conclusion of McDonald, that galvanized rebar corrosion will crack concrete in one year of exposure, and/or with one mil (25 µm) of zinc consumed is clearly in opposition to the mass of material cited here, specifically the work of Dugan, and others. It has been shown by Yeomans, Covino et al, that a migration of zinc into the concrete matrix occurs as a result of the IPR, but Duval and Arliquie schematically diagrammed that penetration as 10µm (0.4 mils) or so. Dugan shows (reproduced as Figures 10 and 11) that after 42+ years of marine exposure and superficial corrosion, that the zinc is indicated by X-ray mapping of the bar/zinc-coating/concrete interface as much as 20 times that distance. It can be seen in Figure 10 that the dark area between the coating surface, and the concrete is an area in which a small amount of zinc has been consumed, yet no zinc corrosion product is shown, as well as no concrete damage. The elemental map of Figure 11 clearly shows the transport of zinc into the concrete matrix away from the zinc corrosion zone seen in Figure 10. The transport of zinc away from the corrosion zone is persuasively demonstrated, and an implicit result would be a slow, or no build-up of concrete cracking stress, a fact supported by the absence of any concrete cracks at the bar surface even though in a small area (Figure 9), all of the zinc was consumed. The absence of zinc hydroxychloride II in field examples not subject to crushing chemical attack by degrading admixtures, built-in chlorides before period I reactions, or other anomalous conditions/materials is supported by Feitknecht.

Thus it has been demonstrated that the higher chloride threshold of zinc for corrosion initiation, the lower corrosion rate and stress generation related to the mobility of zinc corrosion products, and the cathodic mechanism of remnant zinc coatings confirms the efficacy and value of galvanized reinforcing steel in concrete applications. Known field performance of galvanized rebar and experiments cited here are unified in the Barton/Yeomans/Tuutti construct.

Acknowledgement

Assistance in the study of the Bermuda cores by Barry Dugan of Zinc Corporation of America is gratefully acknowledged.

Table 1 - Data Compiled in 1995 from ILZRO Field Evaluations of Galvanized Rebars

Bridge or Structure	Location	Constr. Yr. Project #	1975 ZE 206	1977 ZE 247	1982 ZE 320	1992 ZE 389	1994 ZC 1	Years-to- Date Above
Name		•						Cl ⁻ Corrosion
				Years sin	ce Constru	ction		Threshold
					-			
PCA Slabs	IL	63/68	[6]					
Boca Chica	FL	72	[3]			[19]		[21]
Seven Mile	FL	72	[3]					[19]
Longbird	BDA	52		[23]			[42]	[42]
Flatts	BDA	66	8				[28]	[28]
Ames	ĺΑ	67	7		14	[24]		[26]
Montpelier	VT	71	3		[10]			[21]
Manicouagan	QUE	66	8					
Penno's Wharf	BDA	64/66/69		[11*]		[28*]	[28*]
Hamilton Dock	BDA	66		[11]			[28]	[28]
RBYC Pier	BDA	68		[10]			[26]	[26]
Athens	PA	73		[8]	[8]	[18]		[20]
Betsy Ross	PA	73			8			
Coraopolis	PA	72			9	[19]		[21]
Hershey	PA	75			[6]	[16]		
Orangeville	PA	74			7			
Tioga	PA	74			7	19		

[X] = At or above 1.1#Ci/cu. yd. Black Steel Corrosion Threshold* = Typical

Table 2 - Data from CEB Bulletin D'Information No. 211. Pg. 26

Str	ucture	Age, Years	Cover, cm	% Chloride By Weight of Cement	Loss of zinc, µm
	1	7	13.2	1.4	2
	1	10	6.2	2.2	5
	1	12	8.0	2.7	13
	2	8	7.4	1.6	<2
	3	10	5.4	0.8	5
	3	10	6.8	1.4	4
	4	23	10.5	1.9	5

Table 3 - Rebar Corrosion and chloride Determination (Burke, 1994)

Specimen Type	Depth of Cover	Percent of Surface Area affected by Rust	Soluble Chloride in Pounds / yd³
Plain Rebar	1 inch	19	16.5
Galvanized Rebar	1 inch	0.5	15.9
Plain Rebar	2 inch	1 <i>4</i>	10.1
Galvanized Rebar	2 inch	0.5	10.3

Table 4 - Chloride Ion Penetration into Concrete (Swamy 1991)

Distance from Surface in mm	Chloride Concentration ppm at cover in mm			
	20	40	70	
Tidal Zone Exposure				
10	8,500	7,500	6,000	
20	10,000	7,000	5,000	
40	6000	7,500	4,000	
	,	Accelerated Exposure - 1 ye	ear	
10	8,200	8,000	5,000	
20	9,000	6,000	3,500	
40	· 	<4,000	2,000	

Table 5 - Incidence of Corrosion - Tidal Zone Exposure (Swamy 1991)

Type of Bar	Cover in mm	Frequency of Rust %		
,		1 year	3 Years	
	20	95	46	
Uncoated	40	10	38	
	70	2	8	
	20	Negligible	1.5	
Galvanized	40	Negligible	1.0	
	70	Negligible	Negligible	

Table 6 - Incidence of Corrosion - Accelerated Exposure (Swamy 1991)

Type of Bar	Cover in mm	Frequency of Rust %		
••		1 year	3 Years	
<u></u>	. <u>.</u>			_
	20	80	100	
Uncoated	40	25	98	
	70	8	75	
	20	15	72	
Galvanized	40	7	8	
	70	5	6	

Table 7 – Coating Thickness Measurements from Bermuda Cores

	Core #1 (Small Bar)	Core #2 (Large Bar)
Average	7.1 mils	4.9 mils
Range	4.7 - 9.8 mils	0 - 7.4 mils

Table 8 – Stoichiometric Results from SEM-EDX Analysis of Bermuda Core #2

ZnO	55.08%
Fe₂O₃	5.78
CaO	31.71
CI	0.25
SO₃	0.82
SiO ₂	4.63
Al_2O_3	1.72

Table 9 – X-ray Diffraction Analysis of Corrosion Product from Bermuda Core #2

Major	calcium carbonate (Calcite)
Major	zinc oxide (zincite)
Minor	calcium zinc hydroxide hydrate
Minor	calcium carbonate (Vaterite)
Trace	zinc hydroxide (Wulfingite)
Probable Trace	FeO and Fe ₂ O ₃ (Goethite and Hematite)

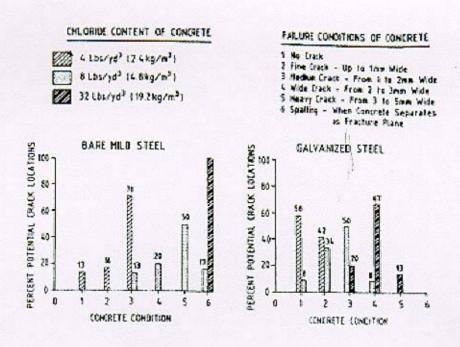


Figure 1 - Effect of Coating Type and Chloride Content on Concrete Failure (from Rasheeduzzafar, et al. 1992)



Figure 3 - Core #1



Figure 4 - Core #2

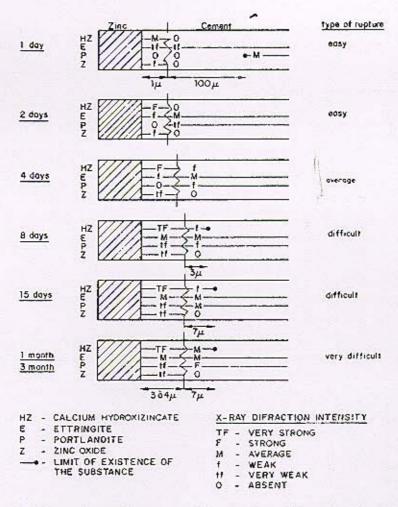


Figure 2 - Formation of Layers on Zinc Surface (from Duval and Arliquie)



Figure 5 - Core #1 Bar "Away"



Figure 6 - Core #1 Bar "Toward".



Figure 7 - Large Bar from Core #2

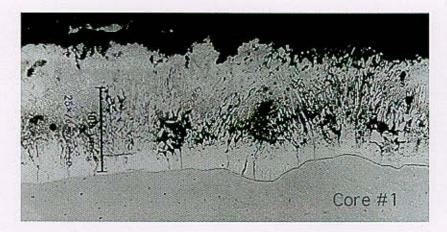


Figure 8 - Coating Cross-Section from Core #1

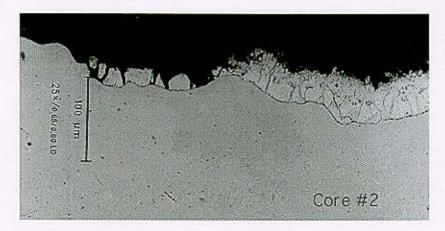


Figure 9 - Cathodic Protection Provided on Core #2



Figure 10 - SEM Photo of Bar/Coating/Concrete Interface of Bar #1

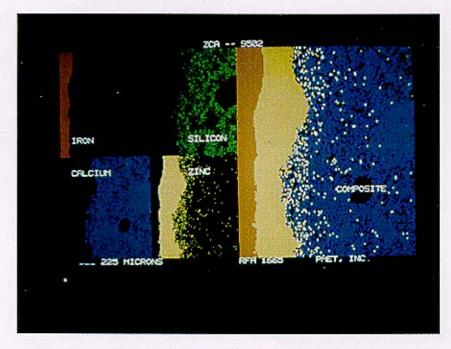
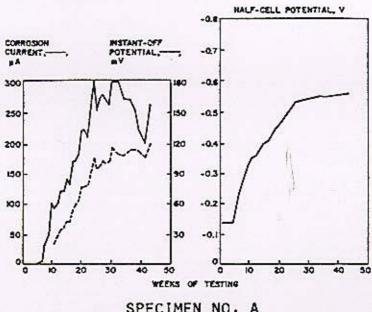


Figure 11 - Elemental Map of Section of Bar #1 in Figure 10



SPECIMEN NO. A

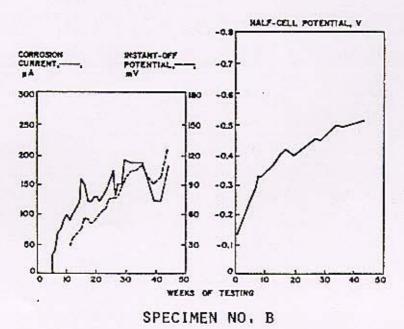
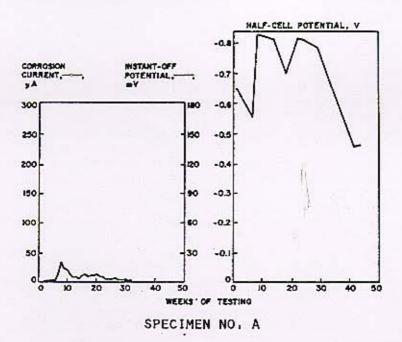


Figure 12 - System 1 - Black Bar Both Mats (from Pfeifer et al)



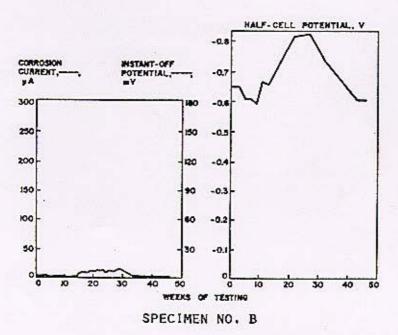


Figure 13 - System 4 - Galvanized Bar Both Mats (from Pfeifer et al)

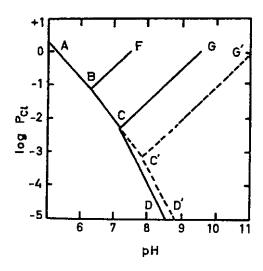


Figure 14 - pCl - pH Diagram for Zinc (from Feitknecht)

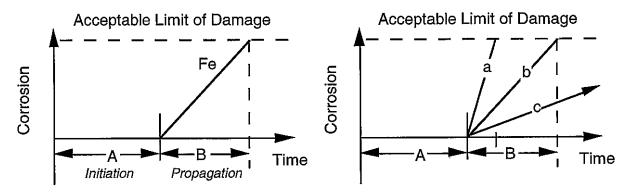


Figure 15 – "Tuutti" Diagram Rates (a,b,c)

Figure 16 - Various Corrosion

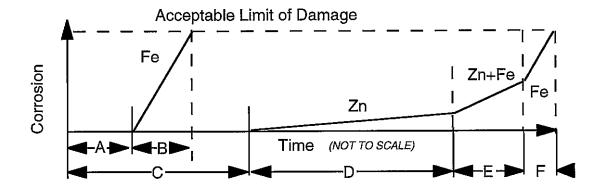


Figure 17 - Kinetics of Black vs. Galvanized Rebar (Adapted from Yeomans)

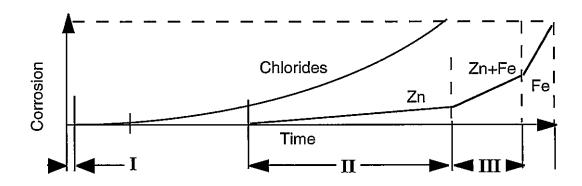


Figure 18 -Kinetics of Galvanized Rebar (Adapted from Yeomans and Barton)

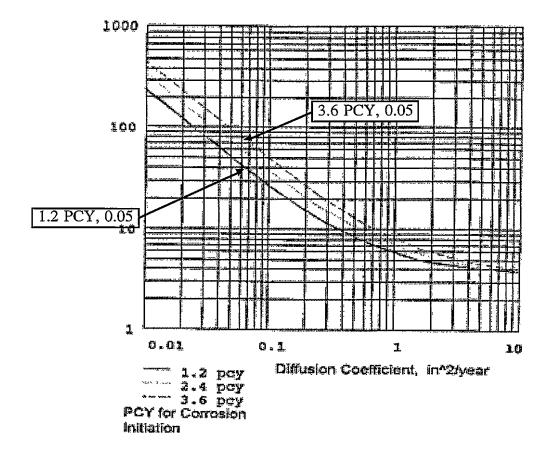


Figure 19 - Years to Spall - 4 inch Cover (adapted from Sagues 1994)

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