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SPRAYED-ZINC SACRIFICIAL ANODES FOR REINFORCED CONCRETE IN MARINE SERVICE

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ABSTRACT

The use of sacrificial anodes consisting of sprayed zinc on the surface of concrete containing corroding reinforcing steel bars has been examined by means of field tests and laboratory experiments. The anodes are sprayed directly on the external surface of spalled regions of marine substructure elements. Electrical contact between the steel and zinc can be achieved efficiently by directly spraying over exposed steel. Field tests were made in the substructure of bridges in the Florida Keys and in Tampa Bay. The installations were performed economically and were functional after as much as 5 years following placement. Protective current densities reaching 1 mA/ft² (1 µA/cm²) of the reinforcing steel were achieved routinely. Tests with reinforcing steel probes and with entire reinforcement assemblies showed steel polarization decays (upon temporary disconnection) typically exceeding 100 mV even after several years of service. The laboratory tests revealed that in the marine substructure conditions of interest concrete resistivity does not represent a main limiting factor in the performance of the galvanic anodes. However, absence of direct wetting of the anode surface can result in long-term loss of adequate current delivery, even when the concrete is in contact with air of 85% relative humidity. Periodic water contact (as caused by seawater mist, splash or weather exposure) is considered a necessary factor for long-term anode performance. The method is considered as a competitive alternative to impressed-current cathodic protection systems, and a considerable improvement over simple gunite repair of corrosion damaged substructure concrete.

Keywords: concrete, reinforcing steel, corrosion, anodes, sacrificial, cathodic protection, sprayed, zinc, galvanic, marine, bridges, substructure.

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INTRODUCTION

Severe corrosion damage often affects reinforcing steel in the substructure of highway bridges exposed to marine environments. Reinforcing steel, which is initially passive in chloride-free concrete, experiences active corrosion upon contact with chlorides ^[1]. In marine substructures the chloride from the environment permeates through the concrete. Chloride transport to the reinforcing steel surface takes place not only by diffusion, but also by capillary convection. This is facilitated by cyclic wetting and drying of the concrete at the tidal and splash zones ^[2,3]. When those zones are exposed to subtropical environments it is not uncommon to encounter chloride levels exceeding 10 pounds per cubic yard (pcy) (1 pcy = 0.59 kg/m³), at a depth of 2 inches (5 cm) below the concrete surface after 5 to 10 years of service. Under these conditions, substructure elements begin to corrode and are typically in need of repair after 12 to 15 years of service ^[4]. The severity of that environment is underscored by recent observations of widespread deterioration of epoxy-coated reinforcing steel in Florida substructures ^[5].

Common repair practice is frequently limited to patching the spalled region with new concrete. Even if the new concrete is designed for low chloride penetration, corrosion is likely to proceed at adjacent regions requiring repair there within a few years. The corrosion at adjacent regions can actually be aggravated by the development of an efficient cathode at the newly repaired portion. Repeated repair procedures are costly and do not provide a lasting solution to the problem.

Cathodic protection (CP) with impressed-current anodes can be used to stop the progression of damage. While this method can provide positive protection, implementation on a marine bridge substructure is much more complex than on a superstructure or an inland location. For example, concrete conductivity varies widely with the height above water, and tidal action can create large periodic variations in current distribution. The mechanically aggressive environment can wash away conductive polymeric coatings. Elaborate and costly anode configurations may be required to ensure reliability under these conditions ^[6,7]. Consequently, relatively few impressed current systems have been implemented for protection of reinforcing steel in marine substructure applications in the U.S.

An intermediate approach between replacement repair and costly impressed current systems, is highly desirable. The investigation described here was conducted to investigate the performance of an alternative, based on the use of sprayed zinc as a sacrificial galvanic anode. Because zinc can be sprayed on the surface of concrete, it forms an anode ideally shaped to maximize contact with the concrete and be as close as possible to the metal to be protected. In the method described here, electrical contact between the reinforcing steel and the zinc anode is achieved either by a connecting wire, or more conveniently, by direct spraying of zinc to the exposed reinforcement. This latter procedure is particularly suited to the common morphology of damage, where some reinforcement is often exposed. The common availability of spraying equipment and existing experience with concrete metallizing, coupled with low application costs, make this concept attractive ^[8].

This investigation had two main objectives. The first was to determine both the feasibility and performance of sacrificial sprayed anodes in practical field installations. To that effect, bridges at locations with aggressive service conditions (Florida Keys Tampa Bay) were selected for anode performance evaluations. The second objective was to investigate the general limits of achievable protection dictated by anode polarization, circuit resistance, anode wastage and related time evolution factors. This objective was examined by a series of laboratory experiments.

This paper summarizes the findings of extensive investigations performed under the sponsorship of national and state agencies. Complete reports on the findings of those investigations, as well as an Implementation Manual for application procedures, can be found in references ^[9,10].

PROCEDURE

Both field and laboratory anode applications used similar equipment and techniques. Procedures for zinc-metallizing the surface of concrete are well established, partly as the result of earlier experience with the use of sprayed zinc anodes for impressed-current protection systems for steel in concrete ^[8] and other early work ^[11].

Field Investigation

Application of the zinc in the field was preceded by first removing the delaminated concrete and then cleaning the surface of the affected member by sandblasting. The concrete (and, in this method, also any exposed steel reinforcement) surface was thus thoroughly cleaned and roughened, improving adhesion of the sprayed metal. A spray gun was used with an electric arc sustained at the end of continuously fed zinc wires, operating typically at 25 V, 250-350 A DC. Compressed air atomized the zinc and deposited the droplets onto the working surface. The zinc was commercially pure (99.9%). Application was straightforward and quick. Usually two to three passes were sufficient to deposit a suitable zinc layer (0.016 inch (0.4 mm) thick, about 90% dense) at a rate of 2 ft² (0.19 m²) per minute. Complex shapes, and surfaces in any orientation could be covered effectively. For the field installations the typical installed costs (including surface preparation, etc.) ranged from \$6 to \$12 per ft² (\$65 to \$130 per m²), as compared to approximately \$40/ft² (\$370 per m²) for conventional impressed current cathodic protection systems on marine substructures based on experience by the Florida DOT.

The field installations discussed in this paper were selected piers at the following Florida Keys bridges along U.S. Highway 1: Bahia Honda, Niles Channel, Seven Mile, and Long Key. The first structure was built with plain reinforcing steel and was nearly 22 years old at the time of anode application. Severe reinforcement corrosion was taking place at the substructure. The latter three structures were built using epoxy-coated rebar, which was also severely corroding by the time of anode application (when the structures were about 10 years old). The morphology and mechanisms of corrosion in those three structures have been described in detail elsewhere ^[4, 12, 13]. Sprayed anode application at spalled zones of the corroding epoxy-coated rebar structures was chosen partly because of the ability of this method to easily effect simultaneous anode connection to various exposed rebar^[12] elements. In an epoxy-coated rebar structure, only partial rebar interconnection is normally present. As a result, conventional CP installation would have required costly wired connections to each exposed rebar element (ideally, connection to the rest of the structure not suffering spalls would also have to be made in either case, but connection to only the elements involved in a spall was deemed to be a workable compromise).

Additional field installations for this study were made in the substructure of Northbound portion of the Howard-Frankland bridge on Interstate 275 across Tampa Bay (piers 280, 281, 293, and 307). This structure was built with plain reinforcing steel and was 30 years old at the time of anode application. The anodes discussed here were applied at pile caps and underdeck beam locations where corrosion was, in general, less pronounced than in the case of the Florida Keys structures. The anodes were installed so that the spalled region and the surrounding region were metallized. Figure 1 describes the physical placement and dimensions of the installations. Selected portions of the anodes were cutout so that square regions 30 cm by 30 cm (1 ft^2) could be connected to the rest of the anode by means of a stainless steel strap. The current delivered by these "windows" could then be directly measured by replacing the strap with an ammeter. Division by the nominal area of the window provided therefore an indication of the average current density of that region of the anode. Two test spots (pile cap and a portion of the bridge underdeck) on pier 293 of the Howard-Frankland bridge were arranged so that the entire anode could be disconnected from the structural steel.

Reinforcing steel probes were also embedded in each of the sites to allow measurements of current delivery and potential shifts. The probes were lengths of 1.3 cm (1/2 inch) diameter reinforcing bars with an exposed area of 13 cm^2 (2 square inch). Each probe had a length of insulated copper wire mechanically fastened and sealed at one end of the probe. The probes were embedded in a sand-cement mortar (mixed using seawater) and the wire extended out of the surface to facilitate easy connection to the zinc anode. The probes were placed in pairs spaced vertically along the length of the metallized area to allow for both polarization and depolarization tests during monitoring. An example of the positioning of the anode windows and rebar probes is shown in Figure 1.

At each site several measurements were performed periodically as indicated in the following: Bond strength of the sprayed zinc anode was measured using an Elcometer, Model 106 fixed alignment adhesion tester using ASTM D 4541-85 test procedure. Generally, bond strength measurements consisted of three individual tests at locations corresponding to the elevation represented by the zinc windows. In instances where either partial failure of the zinc or epoxy failure was observed, the test values were not used in the average test value.

Current measurements were made using a hand held digital anumeter. Where necessary, current values were computationally corrected to compensate for meter input resistance. Current density of the anode was indirectly evaluated by measuring the current output of the anode windows. Current density of the cathode was determined by measuring the current delivery to the embedded reinforcing steel probes.

Anode and cathode half cell potentials were obtained with a 200 M Ω impedance voltmeter. The potentials were measured with respect to a copper/copper sulfate electrode (CSE) placed in contact with the surface of the concrete exposed at a small spot where the anode was removed, next to the point of exit of the probe connecting wire. Potential values were measured immediately following current interruption. The "window to structure" resistance was measured between the anode window and the rest of the steel-anode system with a Nilsson Model 400 soil resistance meter, (97 Hz square wave constant current) configured as a 2-point probe, after disconnecting the stainless steel jumper band between the window and the rest of the system

Polarization decay measurements of the reinforcing steel probes were made by disconnecting the probe from the rest of the system (interrupting the current) and measuring the potential decay (from the instant-off value) over a period of several hours.

Laboratory Investigation

The laboratory tests were conducted using two types of specimens: compact test specimens (slabs) and instrumented laboratory columns.

Test Slabs. The base configuration of the slabs was designed as shown in Figure 2. The zinc patch was dimensioned to have a 1:1 zinc to steel surface ratio. The rebars were size #4 (12.7 mm nominal diameter). Each slab contained a centrally placed embedded reference electrode. The concrete used for the slabs was made with Type II cement, standard Florida DOT aggregates (with maximum size restricted to 3/8 inch (1 cm)) and a water to cement ratio of 0.45. The slabs were removed from their molds after four weeks of curing and allowed to dry in laboratory air for two weeks. The specimens were then placed in a covered stainless-steel tank, and subject to daily 1-hr showers with 15% NaCl solution over a period of 40 days. Ambient outdoor air was circulated through the tank except during each salt spray. An internal electrical heater was used to achieve inner tank air temperatures that were typically 5°C higher than external air (which was under typical summer weather conditions). To further accelerate chloride ingress in the slabs, four short holes (1/2 inch diameter (1.3 cm), 1 inch (2.5 cm) deep) were drilled on the face of the slab closest to the reinforcing steel. The holes were evenly placed so that they would reach between the reinforcing steel bars but not directly expose metal. The holes were plugged with mortar after the salting procedure was completed. The specimens were metallized afterwards following a procedure similar to that used for the field specimens (but without removing any of the concrete cover). The results described here are for specimens metallized with commercially pure zinc and with no topcoat over the zinc. Variations from this base configuration have also been tested and the results are reported elsewhere ^[9].

A group of test specimens was exposed in an environmental enclosure which permitted external electrical connections to each specimen. Humidity was manually controlled to achieve 85 ± 5 % relative humidity. Another group was exposed to laboratory air with an approximate average humidity of 60%. A third group was exposed in a low humidity chamber with an approximate average humidity of 25%. The anode and rebar were normally connected to each other by means of an externally switchable connection, except for a group of control specimens which remained disconnected in the 85% R.H. environment.

Measurements performed periodically with the slabs included: 1) Galvanic current delivery, measured with a 5 ohm input resistance ammeter. 2) Instant-off potentials, measured one second after current interruption, with respect to the internal reference electrode. The internal reference electrode was periodically calibrated with respect to an external CSE. 3) Inter-element resistance, measured with an a.c. soil resistance meter while the anode and rebar were momentarily disconnected. 4) Polarization decay; for this test the anode-rebar connection was interrupted and the potentials of the reinforcing steel and the anode were determined after 1 second, 1 minute, 10 minutes, 1 hour, 4 hours and longer periods when desired. The connection between bar and anode was reestablished after the test was completed. All potentials were measured with a high impedance voltmeter.

Selected specimens were subjected to examination of the microstructure around the zinc- concrete interface. Small cores, 10 mm in diameter and 10 mm deep were removed from the specimen. After embedding the core in an epoxide resin the cores were sliced longitudinally with a diamond saw. The exposed cross section was further impregnated with epoxide and polished using standard metallographic procedures. A metallographic microscope was used for examination of the cross sections.

Surface wetting tests were performed on selected specimens after the normal exposure conditions had progressed for several hundred days. The anodes were wetted for a few seconds by applying a distilled water saturated sponge to the center of the anode surface, minimizing wetting of the anode edges. The current delivery and electrode potentials were monitored for various periods of time afterwards. The procedure was then repeated for several cycles. Instrumented Test Columns. The columns were designed as shown in Figure 3. The columns were 48 in. tall, 12 in. wide and 4 in. thick (122 X 30 X 10 cm). Horizontal #6 (2 cm nominal diameter) steel bar segments, with an effective length of 8 in. (20.3 cm), were placed in groups of three bars at various heights. The portion of the column containing the two lowest groups of bars was made of concrete containing 20 pcy (12 kg/m³) chloride ion. The three highest groups were in chloride-free concrete. The water line was positioned so that only the lowest group was fully immersed. The chloride and water distributions were intended to represent typical marine substructure exposure. Sprayed zinc was applied in patches over each of the four highest groups of bars. The bar and patch dimensions were set to obtain a 1:1 zinc-to-steel surface ratio. Internal reference electrodes were embedded facing the center of each reinforcing steel group. The wiring schematic is shown in Figure 4. Longitudinal fiberglass reinforcing bars were placed to avoid accidental cracking during handling of the columns.

The concrete used was Type I cement, standard Florida DOT aggregates (maximum aggregate size was set to 3/8 in. (1 cm) for these columns) and a water-to-cement ratio of 0.45. The chloride ions in the lower portion of the column were added by mixing in the appropriate amount of NaCl. A removable dam divided the upper and lower portions of the column during casting; the dam was removed after consolidation of the concrete was complete.

The columns were cured for four weeks before removing them from their molds. After approximately one week of air-drying, the columns were placed vertically in a tank containing a 5% NaCl solution, and only the lower 10.5 in. (27 cm) were immersed. All the bar segments were electrically interconnected in each column at that time.

The columns were removed from the tank after 40 days and the anodes were installed the next day. The columns were returned to the tank one week later.

Measurements performed periodically with the columns included: 1) Interelement currents; Figure 4 shows a schematic of the connections between the anodes and bars. Switches 1 to 8 were kept normally closed; a 5-ohm input resistance ammeter was used to periodically measure the currents through the switches. The electronic currents leaving each anode $(I_{zo1}$ to $I_{zo4})$ and entering each reinforcing steel group $(I_{B1}$ to $I_{B5})$ were calculated by the difference between the currents measured at the switches above and below the reinforcing steel group. 2) Instant-off potentials; the entire set of switches for the column was turned off at once, and potentials readings between each element and the closest reference electrode were taken within one second. 3) Interelement resistance; the anode to adjacent bars resistance was measured periodically by opening all switches and using an a.c. resistance meter. By using a three-pin measurement meter connection, the anode- and steel- to midpoint (that is, to the mid-plane containing the reference electrode) resistances were also determined. 4) Polarization decay; the entire set of switches for the column was turned off and potentials with respect to the closest reference electrode of each element were taken over an interval of several hours.

A procedure similar to that for the slab specimens was used to determine the effect of surface wetting after a stable current flow had developed in the columns.

RESULTS

Field Investigations, Florida Keys Structures

Table I shows the results (averaged over the structural member surface) of adhesion tests performed at the various test locations during a two-year monitoring period. The anode installation at Niles Channel (NC) was already 2 years old at the beginning of that period. The coating retained good adherence throughout. The external physical appearance of the sprayed surface was also well preserved, in spite of the harsh environmental service conditions at the test sites. The anodes at the oldest installation (NC) are showing signs of wastage but are still in relatively good condition at present, after about 5 years of service.

Figure 5 shows the average current delivery, as determined from the anode window current measurements, for each of the field locations as a function of the age of the anodes. The NC, Long Key (LK) and Seven Mile (SM) locations (all with corroding epoxy-coated rebar) had roughly constant average current deliveries on the order of 0.5 mA/ft^2 ($0.5 \mu \text{A/cm}^2$). The Bahia Honda (BH) anode (on a plain rebar structure) delivered about 1 mA/ft^2 ($1.1 \mu \text{A/cm}^2$) over the same period. Average steel depolarization decay (as measured by the embedded rebar probes) exceeded 100 mV at most of the test locations over the entire test period (see Table II). Anode potentials in the "on" condition varied from -0.035 to -0.835 mV CSE, attesting to zinc conditions that ranged from essentially passive behavior to clearly active surfaces. At the BH site (plain rebar) the current density delivered to the rebar probes ranged from about equal to that of the anode (NC) to as much as one order of magnitude greater (LK). In all structures, the ratio of area of concrete to area of rebar steel underneath was roughly 1:1.

The average anode-to-steel resistances at the 4 test sites were on the order of 100 Ω . Determination of instant-off potential differences between anode and steel, coupled with the value of anode current delivery, resulted in similar values of anode-steel resistance. Taking into consideration the approximate cell constant for the windows (area \approx 1000 cm², electrolyte thickness \approx 8 cm), the corresponding average concrete resistivity was on the order of 12 k Ω cm, which is in agreement with resistivity values measured by independent means at the same locations ⁽¹²⁾. This low resistivity value, coupled with the high chloride concentrations observed down to the rebar depth (sometimes exceeding 10 Kg/m² of concrete ^[13]) attest to the highly aggressive corrosion service encountered at the test sites.

Field Investigations, Howard-Frankland Bridge

The seven locations examined at the Howard Frankland (HF) location corresponded to milder corrosive service compared with those in the Florida Keys. Current density delivery by the anodes was consequently smaller. Figure 6 shows average current densities at the pier caps (as determined by anode windows) as a function of age of the anodes. The current density was typically on the order of 0.3 μ A/cm². Current delivery was even smaller (typically less than 0.1 μ A/cm²) at the underdeck beams, which were at a higher elevation and less subject to chloride contamination than the pier caps. One of the pier caps and an underdeck patch at this bridge had been fitted with a completely disconnectable anode, so that current delivery to the steel and depolarization of the steel assembly could be directly measured (as opposed to having to rely solely on embedded rebar probes). Figure 7A shows the average current density delivery for the cap and deck of pier 293 as a function of anode age. The trends of the entire structure elements follows those measured using the anode windows. Figure 7B shows the steel

depolarization decay measured with the same structure elements. The pier cap showed depolarization values well in excess of 100 mV over the test period. The underdeck portion fell somewhat below 100 mV. Figure 8 summarizes the depolarization decay measurements (using rebar probes) after about one year of anode service, as a function of the corresponding steel current density. The full-structure measurements for the two specially fitted locations are also shown. The depolarization decay exceeded 100 mV at most locations, even for several cases of small current densities.

The concrete resistivity at the HF bridge was on the order of 30 K Ω -cm to 100 K Ω -cm for the pile caps, and 70 k Ω -cm to 180 k Ω -cm for the beams. Chloride contamination at the rebar depth for those elements was on the order of 1 pcy (0.6 Kg/m³), which approximates the threshold for corrosion initiation of steel in concrete. This 30-year old structure, located in a bay with water salinity about half of that in the open sea, showed significant corrosion damage in the beam caps and in the piles. At the elevations examined the overall deterioration, the levels of chloride contamination and the concrete resistivity reflected in general conditions less severe than those encountered at the test elements chosen in the Florida Keys locations.

Laboratory Investigations

Slab Specimens. Figure 9 shows the average current densities for the slab specimens over a twoyear period. There was a continuous decrease with time (more pronounced in the low humidity environment) of the current density. Tests of the depolarization decay of the steel at various times (see Table III) indicated that significant protection was being achieved in the medium and low humidity environments even as the current density delivery decreased. However, the data in Table III indicated that the decrease with time in current delivery in the 85% relative humidity environment was accompanied by a reduction in the level of protection. This decrease in protection in the high humidity environment was not due to an increase in circuit resistance, since this magnitude did not change dramatically during the test at that humidity level (see Figure 10). Taking into account the specimen dimensions, concrete resistivity in the high humidity tests remained at about 6 K Ω -cm to 10 K Ω -cm during the test period. The specimens exposed at the lower relative humidities did experience large increases in circuit resistance (Figure 10) but this did not appear to impair the effectiveness of the protection in these specimens. In all the slab specimens, the resistances between the anode to the specimen mid-plane and from the mid-plane to the steel bars were approximately equal throughout the test duration. This suggests that any variations in total circuit resistance were mainly due to changes in the concrete (curing and/or drying, depending on the surrounding humidity) and not to changes in the anode/concrete interface.

The effect of temporary surface wetting of the anode surfaces (near the end of the test period) is shown in Figures 11 A and B. The spikes in the current density or potential corresponds to brief anode wetting events. Each event was followed in each case by a recovery that lasted from several hours to days. The current density upon anode wetting experienced a momentary increase of over one order of magnitude. The anode potential changed from about -500 mV (typical of the static anode potentials after one year of service) to a momentary value of about -800 mV. The steel (instant-off) potential experienced a concurrent momentary displacement from about -400 / -500 mV (typical static value) to -500 mV immediately after anode wetting. The anode-steel resistance of the slab specimens was virtually unchanged by the brief anode wetting procedure.

Metallographic examination of the anodes revealed a structure typical of arc-sprayed metal (Figure 12 A). The dark regions and thin lines are porosity resulting from impact and solidification of

consecutive droplets on the sprayed surface. The deposited zinc closely followed the concrete surface. Cement paste and aggregates can be seen underneath. The coating on the specimen shown was about 250 μ m thick. Figure 12 B shows the microstructure of a zinc deposit after approximately 200 days of galvanic service in the 85% relative humidity environment. Porous deposits were present on the outer (top)surface. Zinc corrosion had taken place at the porous pockets between zinc layers and, to a lesser extent, between the zinc and the concrete (same magnification as in Figure 12 A).

<u>Laboratory Columns.</u> Figures 13 A and B show the effect of connecting the anodes to the steel in a laboratory column. Before connection, the column showed the typical macrocell current distribution expected from a partially submerged reinforced concrete system ^{i14]}. In such pattern, the lower bars in the chloride-contaminated concrete (B4, B5) behave as net anodes, while the upper bars behave as net cathodes. Upon connection of the anodes, the entire bar system shifted to a cathodic regime. Examination of the current delivered by the anodes (Figure 13 B) shows that most of the protecting current flowed form the lowest anode (ZN4), which is on chloride-rich concrete and closest to the water line.

Figure 14 A shows the average current delivered to each set of bars (at each of the column levels) as a function of time. At each column level, the area of steel or zinc anode was about 500 cm² (0.5 ft²). Figure 14 B shows the average instant-off potential (SCE scale) of each set of bars as a function of time. Unlike the case of the slab specimens, current delivery to an area of high corrosion (level 4) remained high (at about 0.6 μ A/cm² (0.6 mA/ft²)) after nearly two years of service. The effectiveness of the protection was confirmed by polarization decay measurements (Table IV), showing values that amply exceeded 100 mV for levels 3 and 4 throughout the test period. The polarization of levels 1 and 2 was small, but these bars were in chloride-free concrete where protection was not required. At level 5 (the region below water), the 4-hour polarization decay was expected to be small and slow, because of restricted oxygen access to the fully submerged steel. This condition, addressed in detail in References^[15], results from the low diffusivity of oxygen in water-saturated concrete. The long term current demand for the bars below water was likewise expected to be small.

The resistance between anode and steel at each of the column levels experienced a small increase increased with time at level 4 (chloride rich concrete and just above the water line), and a much larger increases elsewhere. Unlike the case of the laboratory slabs, as the top of the columns dried the resistance at levels 1 to 3 (chloride free concrete) between the anode and the section midplane became about one order of magnitude larger than the steel-to-midplane resistance. Such disparity was not encountered at level 4.

Anode wetting experiments on the upper levels of the columns resulted in anode current delivery spikes (and negative potential excursion spikes) similar to those observed in the slab specimens. At levels 1 to 3 (chloride free concrete), the spikes were accompanied by a reduction by about half an order of magnitude of the anode-to-midplane resistance.

DISCUSSION

Field Experience

The behavior of the metallized structures in the field has been encouraging. The coatings have remained in place and retained reasonable physical integrity after nearly 5 years of service in the harsh

subtropical environment of the Florida Keys, and have shown excellent condition in the two years testing to date in Tampa Bay. Adhesion between the coating and the concrete has remained high at all test locations.

As expected from field testing conditions, current density measurements on the test windows were complicated by the difficulty of maintaining reliable long-term electrical contacts at numerous test points. Nevertheless, the results indicate that protective current delivery has been maintained over 4.5 years at about 0.5 mA/ft² (0.5 μ A/cm²) of concrete in structures containing corroded epoxy-coated reinforcing steel at the Florida Keys. Current densities about twice as high were obtained during the 2 year test interval at the uncoated steel Bahia Honda site also in the Keys. A current density of 1 mA/ft² (1.1 μ A/cm²) or less is typical for protection in mature impressed current systems on corroded plain reinforcing steel ^[16]. The current delivery on corroding epoxy-coated reinforcing steel members was smaller, but quite significant considering that coated steel is involved. While there is little evidence at this time as to the current density levels necessary to protect epoxy-coated reinforcing steel, design values for corrosion of buried pipeline steel with a coating in poor condition are typically one tenth or less of those specified for bare steel ^[17]. The protecting current values measured at the Florida Keys bridges meet or exceed those requirements.

The reinforcing steel probes provided additional evidence of promising field systems performance at the Florida Keys locations. The average current density on the probes in the bare bar structure (Bahia Honda) was comparable with that obtained from the adjacent anode windows. Since the ratio of anode surface to that of the underlying reinforcing steel was typically near 1:1, the observations suggest that the current densities delivered by the anodes to the reinforcing steel and to the reinforcing steel probes were comparable. Therefore, it appears that the polarized condition of the probes was a good indicator of the polarization on the reinforcing steel, at least when the reinforcing steel was uncoated.

In the structures with epoxy-coated reinforcing steel the steel probes also gave a reasonable indication of how the anode would protect an uncoated steel system. The lower current demand of the coated steel is likely to increase the relative amount of protective current flowing to the probe. This increase does not appear to have been important at the Niles Channel test site, where the probe and anode current densities were comparable. However, probe current densities were noticeably larger than those of the anode at the Long Key and Seven Mile locations. Within the limitations just discussed, the polarization decay measurements on the reinforcing steel probes (typically exceeding 100 mV over as little as 1 hour, even after many months of service) are an additional indication that considerable protection was being provided by the galvanic anode systems in the bare bar structures, and that the sprayed anodes remained functional over long service times.

Indirect indication of positive protection by the galvanic anodes is also emerging. Florida DOT maintenance records indicate that gunite repairs on other piers in the Niles Channel bridge last typically two years before external signs of corrosion develop again. Increasing damage has been reported in the piers left without any treatment. In contrast, few instances of cracking or other corrosion related damage of concrete have been observed over the last 4 1/2 years at the locations fitted with the sacrificial sprayed anodes.

The corrosion conditions of the structural members examined at the Howard Frankland bridge were less severe than those for the Florida keys structures. It is possible that because of both high concrete resistivity and a lesser degree of activation of the anodes, average current density delivery was significantly smaller than in the Florida Keys. The depolarization behavior of the rebar probes suggested nevertheless that significant potential shifts in the protective direction (exceeding 100 mV in most cases) were being obtained. The data from the structures that could be completely disconnected from the anode confirmed this general observation, at least for the pile cap for which corrosion severity was greater. The lesser current demand for polarization is likely to have resulted from the lower level of chloride contamination encountered in the portions of the Howard Frankland bridge that were investigated.

The results from both the Tampa Bay and Florida Keys structures indicate that the anode application can be performed satisfactory in the field using commonly available technology, and that reasonable levels of protection are obtainable over a range of corrosion severity conditions. Both installations indicate that anode durability of several years (at least 4 1/2) can be obtained in real field operating conditions. Because the cost of the sprayed anode application is roughly the same as that of a conventional repair, these anodes are an attractive alternative to simple gunite patching.

Laboratory Study

The laboratory experiments with the test columns replicated and confirmed the findings from the field test sites. Long-term current delivery could be obtained with anodes near the waterline in which the concrete was contaminated with chloride ions and kept moist by the proximity of regions in contact with water. The anodes on the chloride-free regions of the laboratory columns had very low current delivery throughout the test exposure. This was due in part to the high bulk concrete resistivity in these areas, where the concrete was dryer. In addition, the resistance between the anode and the midpoint in these areas was significantly greater (specially when the air relative humidity was low) than the resistance between the reinforcing steel and the midpoint. These observations suggest that the current delivery of the column anode sections in the chloride-free regions was reduced by the combined effects of passivation of the zinc (no chloride ions) and the high resistance between the anode and the concrete.

Figure 15 summarizes the combined potential vs current behavior of the zinc anodes (average of the three columns) over the entire test period. The three upper anodes delivered currents consistently less than 0.1 mA and typically about 0.01 mA (current densities of approximately 0.2 to 0.02 mA/ft² (0.22 to 0.022 μ A/cm²)), while maintaining potentials between -200 and -500 mV vs SCE. The current densities and potentials are typical of zinc in the passive condition ^[18].

In contrast, the lower anode had current densities one to two orders of magnitude greater, and potentials typically in the -500 to -700 mV range vs SCE, consistent with active zinc. In addition to having been placed over chloride-rich concrete (20 pcy (12 Kg/m^2) initially), this anode was very close to the saltwater level.

The columns developed a ring of salt deposits 1 to 3 inches (2.5-7.5 cm) above the waterline. This ring was the result of water capillary rise and evaporation which leads in turn to high chloride ion accumulation in the concrete ^[15]. The high moisture and high chloride conditions were the main factors in retaining consistently high current delivery in that anode segment. It is also expected that similar conditions were responsible for the long term high current delivery inferred from the field measurements.

The slab specimens in all three humidity test conditions delivered initial current densities on the order of $1 \text{ mA/ft}^2 (1.1 \mu\text{A/cm}^2)$ or higher, comparable with those observed in the field and in the lower anodes on the laboratory columns. The current delivery dropped rapidly and continually with time at 25 and 60% relative humidity due to increases in anode-to-steel resistance associated with water loss and possible reduction in anode activity. The specimen drying is also expected to have reduced the rate of

corrosion of the steel ^[19]. This may explain that although concrete resistance and anode activity decreased with time, the extent of steel depolarization measured in the 25 and 60% relative humidity specimens was still significant (Table I).

The current delivery in the specimens at 85% relative humidity also decreased rapidly and continually with service time. The current decrease was also associated with decreasing amounts of steel depolarization. This indicated that the current decrease was due to increasingly poorer performance of the protecting system, and not to lesser demand on the part of the steel (as it could have happened, for example, if the cathodic current had created over time a substantial decrease in chloride content around the steel). Further evidence of the decay in performance was that after long exposure the steel potential was about the same as the disconnected control specimens.

The anode to steel resistance in the compact specimens at 85% relative humidity changed relatively little during the test. Moreover, the resistance between the anode and specimen midpoint was always comparable to that between the steel and midpoint. This suggests that the decay was not due to the simple buildup of a resistive material between anode and concrete, as it may have been in the case for the anode patches on the chloride-free portion of the test columns.

Microstructural examination of the zinc-concrete interface revealed that, although some wastage had taken place, significant amounts of unreacted zinc remained on the anode after the current delivery had dropped (Figure 13). Therefore, anode wastage did not appear to be the cause of the decay. Further examination showed no conclusive evidence of the formation of a poor conductance zone between the anode and the concrete, thus supporting the conclusions suggested by the resistance measurements.

Examination of the remaining possible causes of current decay suggested that direct wetting of the anode surface may be a key factor. Both the laboratory columns and the field installations contain anode portions that are in direct contact with saltwater at some time. The wetting of the compact slabs resulted in a large increase in current delivery. Current increases were observed even when the anodes in the chloride-free portions of the laboratory columns were wetted with distilled water.

These observations confirm the importance of direct surface wetting (as it may result in the field from exposure to seawater spray or weather) on increasing anode current delivery. The precise mechanism by which this takes place is not known at this time. One possibly important factor is an increase upon wetting of the fraction of the anode surface which is in direct contact with an electrolyte. This is likely since, even in an apparently dry anode, a certain amount of condensed water must exist within the fine porosity of the anode and the concrete, due to capillary depression of the local equilibrium vapor pressure. Thus, the anode delivers current at an effective rate consistent with the fraction of metal surface in contact with electrolyte. Upon wetting, the fraction would increase sharply with consequent increase in current delivery.

The anode-to-concrete resistance and its variation upon wetting is also expected to play some role on the extent of current delivery. As shown earlier, that role may not be very important in the case of the compact specimens in the 85% relative humidity environment. Moreover, in both the 85% and 60% relative humidity compact specimens the anode-to-midpoint resistance values did not vary significantly upon temporary wetting. On the other hand, the anode-to-midpoint resistance in the chloride-free portion of the laboratory columns (in room air) was much greater than the anode-tomidpoint resistance of the slab specimens exposed to 60% relative humidity (also room air). The anode-to-midpoint resistance in the columns was also much more sensitive to wetting than that of the

This difference in behavior appears to be the result of the concrete in the slab slab specimens. specimens being rich in chloride ions (from the salting procedure). While the increase in conductivity due to chloride contamination is moderate in bulk concrete ^[20], the effect can be important if some concrete carbonation or anodic acidification had taken place directly below the zinc coating during In carbonated or otherwise reduced-pH concrete the conductivity of the chloride-free pore service. solution can be very low, and in that case, the differences due to chloride contamination would likely be more notable ^[20]. Therefore the electrolyte in the pores of the concrete, in direct contact with the zinc, might be expected to be much more conductive in the compact specimens than in the chloride-free portion of the columns. A related factor is that the presence of hygroscopic salts at the concrete surface could increase the equilibrium amount of water present at the anode-concrete interface. In summary, anode-to-concrete resistance in the chloride-contaminated specimens appears to be low enough (with or without direct surface wetting) that current limitation occurs by other mechanisms. In the chloridefree surfaces reduction of anode-to-concrete resistance by direct wetting may be an important factor in increasing current delivery.

Surface wetting also resulted in sharp negative excursions of the anode potential during wetting. These effects could have resulted from solution dilution with consequent lowering of the zinc/zinc ion redox potential, phenomena involving loss of passivity in previously wetted surfaces, and the behavior of freshly wetted portions of the metal surface. The complicated interplay of surface electrochemical behavior, ohmic changes, and the amount of wetted surface area cannot be determined with the information available. In general, the field and laboratory tests indicated that performance of galvanic anodes is likely to be best under conditions where direct wetting occurs. Thus, the concept is promising for protecting the splash zone on marine substructure components, which are also the areas that most often need corrosion protection.

CONCLUSIONS

1. Field installation of the galvanic anodes in the field was achieved rapidly and economically with existing technology on marine bridge substructures in subtropical environments at the Florida Keys and in Tampa Bay.

2. The anodes have continued to show physical integrity after up to 4 1/2 years of service in a harsh marine environment.

3. In the Florida Keys locations, field current density measurements over 4 1/2 years indicate that typically 0.5 mA/ft² (0.54 μ A/cm²) has been maintained on structures containing corroded epoxy-coated rebar. On the order of 1 mA/ft² (1.1 μ A/cm²) was maintained over two years on structures containing corroded ordinary rebar. In the Tampa Bay structure elements examined corrosion conditions were less severe and current densities on ordinary rebar were on the order of 0.1 mA/ft² to 1 mA/ft² (0.11 μ A/cm²) to 1.1 μ A/cm²).

4. Rebar probe measurements consistently showed typical steel polarization decay values that typically exceeded 100 mV in as little as one hour. This extent of depolarization was observed both in the Florida Keys and the Tampa Bay sites.

5. Anodes placed near the waterline on laboratory test columns replicated the current delivery and polarization decay observed on the field structures. Anodes placed in dryer, chloride-free portions of the same columns did not contribute significantly to the overall protection.

6. After nearly two years of testing the current density delivery by the active anodes in the laboratory was on the order of $1 \text{ mA/ft}^2 (1.1 \mu \text{A/cm}^2)$. Steel polarization decay, in the area of expected highest corrosion, continued to exceed 100 mV within 4 hours.

7. The compact laboratory specimens exposed to medium (near 60%) and low (near 25%) relative humidity environments showed significant and continuous decreases in current delivery as a function of time. The decrease was more pronounced the dryer the environment. However, appreciable amounts of steel polarization decay were attained with these specimens, probably because the corrosion rate of the steel is much less in dry concrete.

8. The compact laboratory specimens placed in the 85% relative humidity test environment showed also a pronounced decrease in current delivery with time. Steel polarization decay test results indicated a corresponding reduction of protection of the steel in these specimens.

9. The loss of efficiency in the compact laboratory specimens in the 85% relative humidity environment was primarily a consequence of long-term polarization of the anode. Polarization of the steel, increase in concrete resistance, or anode wastage were found to be only of secondary importance in causing the long term loss of efficiency.

10. Current delivery on the compact specimens exposed to 85% relative humidity and on the laboratory columns was increased dramatically by direct wetting of the anode surface. Direct wetting of the anode (by seawater splashing or misting in the field, or by capillary rise in laboratory columns) is proposed to be a key factor in achieving high protective current delivery.

11. The results support the use of the sprayed galvanic anode technique for locations such as the splash-evaporation zone of marine bridge substructures, where high relative humidities and intermittent wetting of the surface are prevalent (coinciding usually with the region in greatest need of corrosion protection). The findings support indications that sprayed zinc sacrificial anodes are an attractive economic alternative to conventional spall patching in marine substructure service.

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Table I Average Bond Strength (psi), Florida Keys Test Sites

Anode Age (Months)*	BH	LK	SM	NC *
1.4	180	111	123	315
6.9	170	120	112	215
12.4	170	123	120	171
24	175	103		_

* Add 30 Months to the NC site anode ages.

Table II Average Depolarization Decay (mV), Florida Keys Test Sites

Probe Age (Months)	BH	LK	SM	NC
1.4	169		218	118
6.9	170	154	84	112
12.4	101	195	131	77
24	145	125	353	143



	Exposure Time				
Average Relative Humidity	80 days		212 days		350 days
	4h	24h	4b	24h	4h
85%	60	60	14	14	5
60%	110	120	85	95	-
25%	110	130	95	110	90

 TABLE IV

 4 Hour Polarization Decay Tests, Laboratory Columns Average Potential Shift (mV)

Bar Level	Exposure Time			
	345 Days	363 Days	650 Days	
1	30	60	27	
2	60	90	45	
3	160	220	127	
4	260	310	252	
5	-	-	3	



Figure 1: Schematic of test site at Seven Mile Bridge (1 in = 2.54 cm; 1 ft = 30.5 cm).





515/17



Figure 3: Instrumented test column (1 in = 2.54 cm).



Figure 5: Average anode current density.



Figure 6: Average current densities of test windows at each pier pile cap as a function of time the anodes were in service $(1 \text{ mA/sf} = 1.09 \ \mu\text{A/cm}^2)$.



Figure 7A: Average steel current density (from disconnecctable anode) at the pile cap and deck locations of pier 293 as a function of time.



7B: Depolarization decay at the pile cap and deck locations of pier 293 as a function of time (1 mA/sf = $1.09 \ \mu$ A/cm²).



Figure 9: Average current densities of the galvanic test specimens in the three relative humidity (RH) environments $(1 \text{ mA/ft}^2 = 1.1 \mu \text{A/cm}^2).$



Figure 8: Depolarization decay as a function of current density of each individual rebar probe (and the structure locations at pier 293) after about 1 year of anode service $(1 \text{ mA/sf} = 1.09 \ \mu\text{A/cm}^2)$. The highest current density values correspond to the beam at bent 280.



Figure 10: Average anode-to-steel resistance of galvanic specimens in the three relative humidity (RH) environments as a function of exposure time.



Figure 11A: Average anode current density of galvanic test specimens during the anode wetting sequence as a function of time $(1 \text{ mA/ft}^2 = 1.1 \mu\text{A/cm}^2;$ RH =relative humidity).







- Figure 12A: Metallographic cross-section of the sprayed zinc coating on the concrete substrate. The coating thickness is $\approx 250 \ \mu m$ thick.
- Figure 12B: Microstructure of the coating after approximately 200 days of service in the 85% relative humidity test. chamber. (Same magnification as Fig. 12A).



Figure 13A: Example of effect of anode connection on current distribution patterns. Electronic current consumed or generated at each rebar level, before and after connection of the anodes.





Figure 14A: Average current from each anode on the laboratory columns as a function of time.



Figure 14B: Average current to each set of bars on the laboratory columns as a function of time. Bi denotes bar at level i.



Figure 15: Average polarization behavior of the anodes of the laboratory columns throughout the entire exposure period. All currents are anodic.