

Thermal-Sprayed Zinc Anodes for Cathodic Protection of Steel-Reinforced Concrete Bridges

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ABSTRACT

Thermal-sprayed zinc anodes are being used in Oregon in impressed current cathodic protection (ICCP) systems for reinforced concrete bridges. The U.S. Department of Energy, Albany Research Center, is collaborating with the Oregon Department of Transportation (ODOT) to evaluate the long-term performance and service life of these anodes. Laboratory studies were conducted on concrete slabs coated with 0.5 mm (20 mil) thick, thermal-sprayed zinc anodes. The slabs were electrochemically aged at an accelerated rate using an anode current density of 0.032 A/m² (3mA/ft²). Half the slabs were preheated before thermal-spraying with zinc; the other half were unheated.

Electrochemical aging resulted in the formation at the zinc-concrete interface of a thin, low pH zone (relative to cement paste) consisting primarily of ZnO and Zn(OH)₂, and in a second zone of calcium and zinc aluminates and silicates formed by secondary mineralization. Both zones contained elevated concentrations of sulfate and chloride ions. The original bond strength of the zinc coating decreased due to the loss of mechanical bond to the concrete with the initial passage of electrical charge (aging). Additional charge led to an increase in bond strength to a maximum as the result of secondary mineralization of zinc dissolution products with the cement paste. Further charge led to a decrease in bond strength and ultimately coating disbondment as the interfacial reaction zones continued to thicken. This occurred at an effective service life of 27 years at the 0.0022 A/m² (0.2 mA/ft²) current density typically used by ODOT in ICCP systems for coastal bridges. Zinc coating failure under tensile stress was primarily cohesive within the thickening reaction zones at the zinc-concrete interface. There was no difference between the bond strength of zinc coatings on preheated and unheated concrete surfaces after long service times.

Keywords: zinc, thermal spray, arc spray, anode, cathodic protection, bond strength, interfacial chemistry, water permeability, pH, bridges, reinforced concrete.

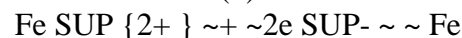
INTRODUCTION

The state of Oregon has a rugged and beautiful coastline linked by a series of bridges along US Highway 101. Conde B. McCullough was the internationally recognized designer of most of the major bridges along this section of highway. The remoteness of the coastal area in the 1920s and 1930s makes the engineering accomplishments of McCullough impressive. He used innovation and an excellent sense of aesthetics to develop an arched bridge theme. His designs extended the length of the coast highway and a number of these bridges are currently listed on the National Historic Register. McCullough probably did not envision the severe corrosion damage some of his bridges would suffer in the coastal environment. The decision to replace or to preserve these older bridges involves not only issues of public funds and public safety but historic value as well. The 1987 replacement of the Alsea Bay Bridge in Waldport, OR, resulted in public protest at the loss of a landmark McCullough bridge.

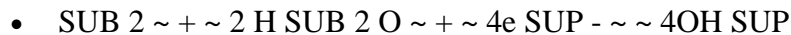
Reinforced concrete structures such as bridges are particularly susceptible to salt-induced corrosion in coastal areas. Problems arise when salt permeates the concrete and accumulates at the rebar-concrete interface. Rebar, which is normally passive in the high pH concrete environment, loses passivity and begins to corrode when a threshold level of salt is exceeded.¹ The rebar corrosion product is less than half as dense as the steel it replaces and the increased volume leads to static pressure buildup at the interface which cracks the concrete,² causes delamination of the cover concrete, and leads to further corrosion damage.

In Oregon, thermal-sprayed zinc coatings on concrete bridge substructures are used as anodes in impressed current cathodic protection (ICCP) systems. ICCP electrochemically protects the rebar by reducing the rebar corrosion rate, by regenerating an alkaline environment around the rebar, reactions 1 and 2, respectively, and by moving chloride ions away from the rebar.

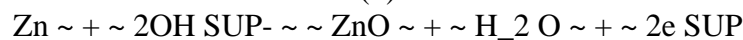
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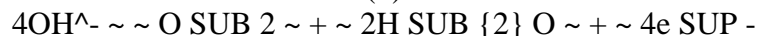
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The Cape Creek Bridge was the first Oregon Department of Transportation (ODOT) project to use thermal-sprayed zinc anodes in ICCP. The sprayed surface area was 9,500 m² (102,000 ft²) with a coating thickness of 0.5 mm (20 mils). Anode installation was completed in 1991 and the cathodic protection system has operated since January 1992. Other ODOT zinc thermal-spray projects are the Yaquina Bay Bridge in Newport and the Depoe Bay Bridge in Depoe Bay.

Thermal-sprayed zinc anodes have been in service only a short time (5 years) in ICCP systems in Oregon. Service life and factors affecting long-term performance are not known from field applications. Accelerated aging studies have shown that reactions occurring at the zinc anode affect the bond strength of the coating and that bond strength may be the determining factor in the service life of the coating.³⁻⁴ The two important anode reactions that occur in the zinc anode are:

Reaction 3 leads to a zinc reaction layer between the anode and cement paste that, through secondary mineralization, can react further to form an altered cement paste layer. Both reactions consume hydroxy ions and may lead to reduced pH levels at the zinc-concrete interface. This paper will show how the consumption and liberation of chemical species at the anode is responsible for changes in the bond strength of thermal-sprayed zinc coatings on concrete and in the operating characteristics of the zinc anode ICCP system.

EXPERIMENTAL DESIGN

Fifty-five concrete slabs were cast to physically, mechanically, and electrochemically approximate a section of bridge substructure in a typical thermal-sprayed zinc anode ICCP installation. The concrete slabs measured 0.23 m x 0.33 m x 0.05 m (9 in. x 13 in. x 2 in.) and were cast with steel mesh embedded near the bottom of the form to simulate the rebar and to act as the cathode. Iron wire was welded to the mesh and extended above the top surface of the form to provide an electrical connection to the mesh.

The concrete mix design (with a resulting water-cement ratio of 0.48) was intended to approximate that used in ODOT's older, corrosion damaged coastal structures.³ The concrete mix design included 3 kg/m³ (5 lbs/yd³) of sodium chloride to simulate marine exposed concrete. The slabs were cured two weeks in a moist room, then air dried. Two months elapsed before the slabs were thermal-sprayed with zinc. Immediately prior to zinc application, the top sides of the slabs were sandblasted to remove a thin layer of cement paste and produce a sound surface with adequate "tooth" for the thermal-sprayed zinc coating. The top surface of half the slabs was preheated to 120-160°C (250 -320°F) with a propane torch immediately before thermal-spraying with zinc; the remaining slabs were not preheated before spraying.

The twin-wire arc-spray process was used to apply zinc to the concrete surface. Spray parameters used to apply the zinc were: DC current of 265 amps, DC voltage of 25 volts, air pressure of 0.65 MPa (105 psi), spray distance of 150 - 230 mm (6 - 9 inches), spray angle normal to surface, a zinc wire diameter of 3.2 mm (1/8-inch). Thickness measurements were made with an eddy current device. Zinc coating thicknesses ranged from 380 to 580 µm (15 to 23 mils) over the slab surface with a standard deviation for an individual measurement of ±14 µm (0.55 mils).

More than three months elapsed from the time slabs were arc-sprayed with zinc before electrochemical aging began. The slabs were aged in a constant temperature-constant humidity room where the temperatures ranged from 70 to 90°F and relative humidities (RH) from 70 to 85%. The fifty-five slabs were divided into three groups. Each group was wired in series, with the zinc as the anode and the steel mesh as the cathode, so that the same current passed through all slabs in a group. Electrical connection to the zinc coating was made with a star washer and

lug terminal held in place with an insulated plastic molly anchor. The slabs were polarized at a current density of 0.032 A/m² (3 mA/ft²) by constant current power supplies. This current density is 15 times the 0.0022 A/m² (0.2 mA/ft²) typically used by ODOT in ICCP systems for coastal bridges.⁵ Total voltage across each group of slabs, impressed current, and laboratory temperature were recorded hourly on a data acquisition system to provide long-term performance data for the electrochemical aging (ICCP) system.

At regular intervals, a preheated and unheated slab were removed from the experiment. The slabs were equilibrated with dry air for one day and then prepared for bond strength measurements by attaching aluminum dollies, 50 mm (1.9 in.) diameter, at six predetermined locations with high-viscosity, fast-cure epoxy. The bond strength measurements were made using an Instron Model 1123 Universal Testing Machine. Original bond strengths were determined by measurements on two unaged slabs each from the group of preheated and unheated slabs, for a total of 12 measurements from each group. All subsequent bond strength values were the result of six measurements on a slab.

Cross-sections of the coating from electrochemically-aged slabs were examined by scanning electron microscopy (SEM) to determine physical, chemical, and mineralogical properties of the zinc-concrete interface, and changes that may be associated with aging effects on bond strength, operation of the ICCP system, and water permeability of the coating. Sample cross-sections were cut from aged slabs at locations adjacent to those used for bond strength measurements. To stabilize the sample cross-sections, they were first infiltrated with epoxy under vacuum and cured. They were ground and polished to a 1 μm diamond finish; then carbon coated before imaging. Chemical analyses of the cross-sections were performed using a wave-length dispersive (WDS) x-ray analyzer with 4 crystals, and an energy-dispersive x-ray analyzer (EDS) with atmospheric thin window for imaging low atomic number elements.

pH of the zinc-concrete interface was measured as a function of aging time using a micro combination pH electrode. The coating was lifted from the concrete surface at selected locations to expose areas for analysis. All pH measurements were made in solutions comprising only one or two drops of water. Concrete pH was measured in a slurry formed from scrapings removed from the concrete surface; zinc pH was measured *in situ* on the underside of the zinc coating after wetting the surface with several drops of water.

The rate of water permeation through the zinc coating and into the concrete was measured on small areas of aged and unaged coatings. Water under constant pressure was applied to the surface using a buret and an inverted glass funnel sealed to the zinc surface by silicone adhesive. Water flow through the coating was measured with the buret as a function of time for up to 14 days. Water permeation rates were computed from the initial slope of the water volume-time curves.

RESULTS and DISCUSSION

Laboratory Measurements

Zinc coating bond strength as a function of electrical charge passed (equivalent to service time in an ICCP system) during electrochemical aging is shown in Figure 1 for preheated and unheated slabs. These curves represent the overall trends in bond strength from over 300 measurements on over 50 slabs.⁴ The average original bond strength for the preheated slabs was 2.06 MPa(299 psi); it was 1.15 MPa(167 psi) for the unheated slabs. The original bond strength was increased 0.91 MPa or 80 pct by preheating the slab surface immediately before thermal-spraying with zinc. This advantage from heating is consistent with the results of Brousseau *et al.*⁶

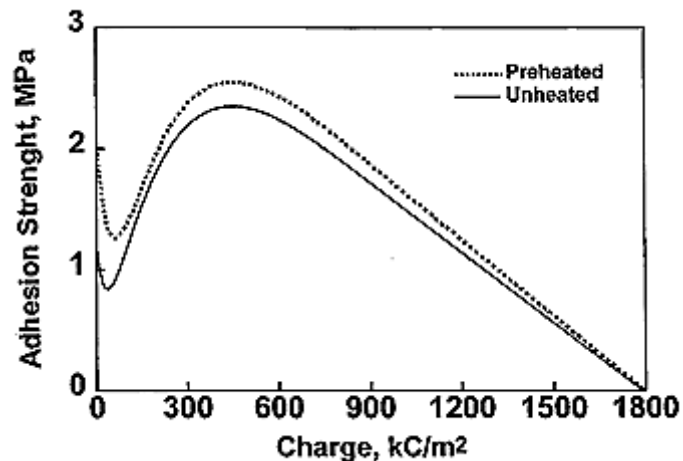


Figure 1 - Bond strength of electrochemically-aged Zn thermal-sprayed on preheated and unheated concrete slabs as a function of aging charge.

Initially the bond strength of coatings on both preheated and unheated slabs decreased with the passage of charge across the zinc-concrete interface. Because of the higher original bond strength, this decrease was more pronounced for the preheated slabs. Bond strength reached a minimum at a charge of approximately 50 kC/m²(1.3 A-h/ft²) for both types of slabs and then began to increase for larger values of the charge. At approximately 600 kC/m²(15.5 A-h/ft²), the bond strength reached a maximum and began decreasing for higher charge values, approaching zero at about 1800 kC/m²(46.5 A-h/ft²). After the initial decrease, bond strength values for the preheated and unheated slabs were not significantly different. At the accelerated aging rate, 1800 kC/m²(46.5 A-h/ft²) was equivalent to roughly 27 years service at the current density of 0.0022 A/m² (0.2 mA/ft²) typically used by ODOT for ICCP on coastal bridges.

Cross-sections of the zinc-concrete interface prior to aging showed that the zinc coating closely matched the topography of the sand-blasted concrete surface. There was no visual difference between the interface for preheated and unheated slabs. The coatings had a significant amount of porosity but there were relatively few through pores connecting the outer coating surface to the concrete. The elongated grain structure of the coating was typical of that produced by molten metal droplets splatting and freezing on a cooler surface.

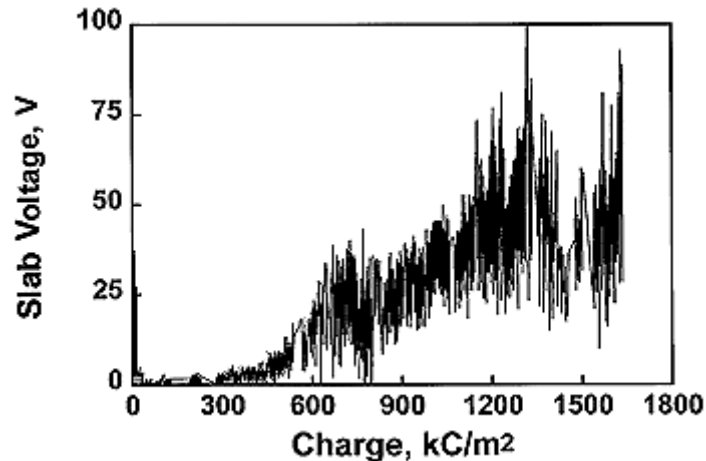


Figure 2 - Potential of individual slabs as a function of aging charge.

The voltage required to maintain a constant current through the slabs rose continually throughout the experiment. This occurred even though the slabs were kept in a humidified room to prevent them from drying. To minimize IR heating of the slabs and to avoid exceeding the operating range of the constant current power supplies used in the experiment, the zinc coatings were periodically wetted with deionized water. Wetting was done by spraying a fine mist on the coating surface. This was similar to what others have referred to as "activating" the coating, and is what occurs in nature as the result of irregularly occurring, but seasonal, rain, dew, fog and ocean spray.

The potential-time record for the test slabs is shown on a per slab basis in Figure 2. The saw-tooth pattern is a result of the wetting and drying cycles; the drop in the slab potential occurred after wetting and the rise in potential occurred during drying. Important features of the potential-time record are the rise in the minimum slab potential following each wetting cycle as aging progressed, and the increase in the rate of voltage rise during each drying period. Within the first 300 kC/m² (7.8 A-h/ft²) of charge passed, the slab potentials typically fell to a low value approaching zero when wetted. Beyond that charge value, the minimum voltage rose substantially and the rate of potential rise increased to several volts or more per day. At the same time that minimum voltages began to rise, the ability of water to soak through the zinc coating became more restricted, and free water pooled on the coating surface and remained for longer periods after wetting.

The primary failure mode, when the coating debonded from the concrete substrate, was cohesive fracture within a thin layer of reaction product lying along the original zinc-concrete interface. The fracture propagated along the interface, through basic zinc reaction product and through cement paste chemically-altered by zinc reaction products. The fracture zone was roughly 20-50 μm (1-2 mils) thick.

Adhesion Behavior

Based on Figure 1, the effect of aging on zinc-concrete bond strength can be divided into three distinct stages. In the first stage the bond strength decreases with charge, from zero to

approximately 50 kC/m²(1.3 A-h/ft²). In the second stage the bond strength increases to values greater than the original non-aged bond strength. This stage extends to approximately 600 kC/m²(15.5 A-h/ft²) of charge. In the third stage bond strength decreases finally to zero at a charge of roughly 1500-1800 kC/m²(38.7-46.5 A-h/ft²). (As a point of reference, 200 kC/m²(5.2 A-h/ft²) is equivalent to roughly three years of service for the zinc anode ICCP system used by ODOT on Oregon coastal bridges.) The change in bond strength reported here is in good agreement with the practical experience of the California Department of Transportation where loss of bond strength and some delamination of zinc coatings occurred over 11 years of service.⁸

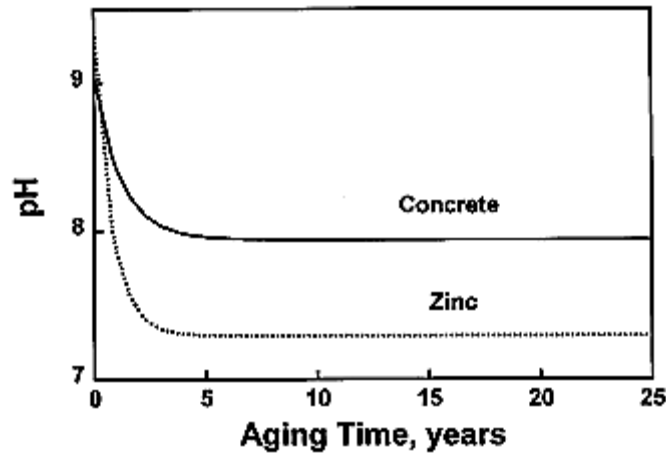


Figure 3 - Effect of aging on pH of the zinc-concrete interface. Stage I (0 to 50 kC/m²) -

The bond strength of coatings on both the preheated and unheated slabs dropped below the original values after the initial passage of charge. This lowering of the bond strength is caused by the dissolution of zinc at the zinc-concrete interface, particularly dissolution of the fine zinc structure that mechanically locks the coating to the concrete surface. Furthermore, zinc dissolution and reaction 4 leads to a reduction of the pH at the interface compared to that of cement paste, pH 12-13, figure 3. The dissolved zinc forms a thin layer (<0.02 mm) of zinc oxide and/or zinc hydroxide (zone 1, figure 4). Zone 1 is the only reaction product layer present in Stage I and is not thick enough to significantly affect water permeability of the zinc coating nor minimum slab voltage requirements after wetting of the zinc surface.

Stage II (50 to 600 kC/m²) -- Analyses of the interface show that there is a thickening of the ZnO/Zn(OH)₂ layer (zone 1) at the zinc-concrete interface to about 0.1-0.2 mm. Figure 3 shows

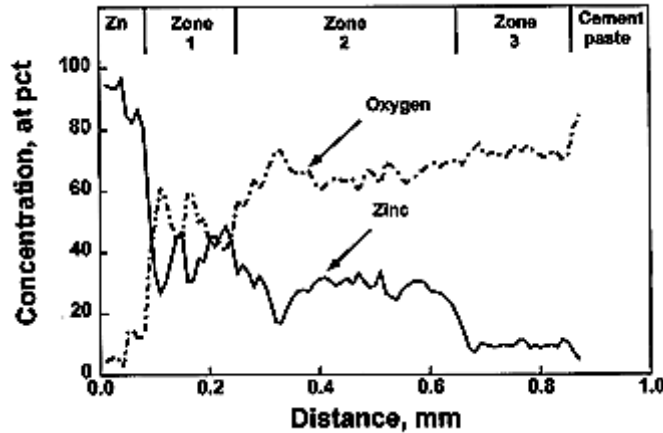


Figure 4 - Zn and O concentrations showing three reaction zones along a microprobe scan.

the interfacial pH is in the range 6.5-9.0. Thermodynamic calculations indicate that ZnO, Zn(OH)₂, and zinc hydroxychlorides and hydroxysulfates are stable in this pH range. Previously reported pH values for arc-sprayed zinc on concrete were 8.5-10.0 using indicator dyes to measure the pH rather than a glass electrode.⁹ At approximately 4 mm below the zinc-concrete interface, the pH was in the range of pH 10-12, representing a transition from cement paste altered by zinc dissolution products to unaltered cement paste.

Zones 2 and 3, Figure 4, begin to form in Stage II, with the zinc dissolution products interacting with the original cement paste over many wetting and drying cycles to partially (zone 3) and totally (zone 2) substitute Zn for Ca in the silicates and aluminates of the cement paste.³⁻⁴ This process allows cracks and pores at the zinc-concrete interface to be filled and leads to the formation of mineral structures across the interface that improves bonding of the zinc coating to the concrete. No significant differences between the bond strengths of preheated and unheated samples were observed in stage II. In this stage, however, water applied to the zinc coating began pooling on the surface due to a decrease in water permeability. Water permeation rates dropped from 31.2 ml/m²-day for the unaged coating to 4.2 ml/m²-day for a coating aged 83 kC/m². This occurred as the result of thickening of zone 1 and the development of zones 2 and 3. At this point in the aging of the coating, the minimum voltage requirements increased with increasing charge passed.

Stage III (600 to 1800 kC/m²) -- This stage begins at the maximum bond strength recorded for the coating, and continues until the bond strength approaches zero. For both the preheated and unheated slabs, bond strengths dropped to about zero at about 1800 kC/m² (46.5 A-h/ft²), which corresponds to 27 years of service at the level of current density typically used by ODOT on coastal bridges. Characteristics of the zinc-concrete system in stage III were: water permeability through the coating was substantially lower than for the unaged coating; interfacial pH was similar to that in stage II; and operating voltages were high, even after wetting the concrete. The need for water in the slab was apparently due to the more insulating nature of the zinc reaction products at the zinc-concrete interface when they were dry. However, resistive heating at the interface did not appear to be a significant factor. Temperature measurements showed less than a 0.5 oC temperature rise at the surface due to current flow through the zinc-concrete interface.

Also, calculations show that consumption of water at the cathode, reaction 2, can not account for the increased demands for water.

Analytical SEM analyses of the interface in Stage III showed that the ZnO/Zn(OH)₂ layer (zone 1) grew to about 0.4 mm while the layer of cement paste altered by zinc (zones 2 and 3) had stabilized at about 0.4 mm. A significant amount of chloride and sulfur concentrates in zones 1 and 2. Reaction products observed at the zinc-concrete interface were analyzed using x-ray diffraction (XRD) analysis. The results showed the presence primarily of zincite (ZnO), with minor amounts of wulfingite (Zn(OH)₂), simonkolleite (Zn₅(OH)₈Cl₂·H₂O) and hydrated zinc hydroxide sulfates (Zn₄SO₄(OH)₆·xH₂O). The presence of the last two compounds accounts for the significant increase in the chloride and sulfur concentration in the interfacial region. XRD analyses of reaction products removed from the surface of the Cape Creek Bridge showed the presence of simonkolleite, zinc hydroxysulfates, and hydrozincite, a carbonated form of zincite. This represents an excellent correlation between laboratory and field results.

Bond strengths near zero, observed in the latter stages of aging for both preheated and unheated slabs, occurred when there was significant delamination of the coating from the concrete. ZnO has a molecular volume 1.6 times that of Zn and Zn(OH)₂ has a molecular volume 3.5 times larger than Zn. The presence of these and related compounds produces stress at the zinc-concrete interface that damages the bond between the zinc and concrete and would appear to account for the long-term reduction in the coating bond strength.

On the other hand, the zinc was still attached to the concrete at isolated points where the coating had penetrated into deep pits in the original concrete surface. These points of attachment would appear to be sufficiently durable to last long after the coating had debonded from the rest of the concrete surface.

Cape Creek Bridge Measurements

If the observations in the laboratory concerning the operating characteristics of the electrochemical aging (ICCP) system are to have practical significance, similar features should be observed in the current-voltage record of ICCP systems in service on the Oregon coast. The thermal-sprayed zinc anodes on the Cape Creek Bridge have the longest record of service (5 years). The cathodic protection system consists of independent anode zones where the current density in each zone is adjusted to meet the 100 mV depolarization criteria.

The Cape Creek Bridge polarization data 4 show that the ICCP zones respond to climatic conditions. Low voltage values were, on average, associated with days with significant precipitation. High voltage values were associated with dry days. The voltage values were cyclic, with the lowest values observed during the Oregon wet season of late fall and winter when coastal storms and fog repeatedly wet the bridge, and when the sky was continually overcast, preventing drying of the bridge surface. High voltage values were typically observed during the Oregon dry season of summer and early fall when precipitation was infrequent and coastal days were warmer. The bridge zones also respond to the unstable weather conditions of spring and early summer when drying trends take hold and voltage values rise.

Furthermore, minimum operating voltages at Cape Creek were observed to occur during the wettest time of the year and increased with aging of the zinc coating. This was similar to effects observed in the laboratory for charges greater than 300 kC/m² (7.8 A-h/ft²), figure 2. It suggests that changes at the zinc-concrete interface are beginning to affect the performance of the Cape Creek ICCP system.

CONCLUSIONS

Preheating concrete prior to thermal spraying of zinc causes an 80 pct increase in bond strength between the zinc and the concrete. This benefit decreases after a short period of use in an ICCP system. Zinc coatings on both preheated and unheated concrete are predicted to have a useful lifetime of approximately 27 years at a current density of 0.0022 A/m² (0.2 mA/ft²) before significant areas of the zinc become disbanded. During this period of use, changes occur to the zinc anode that affect its operating characteristics. Voltages necessary for operating the system at constant current are lowest when wet. The ability of water to penetrate the zinc coating becomes restricted as more charge is passed during ICCP. The pH at the zinc-concrete interface changes from 12-13, typical of concrete, to values of 6.5-9 where zinc reaction products are more stable. Most of these effects are well correlated with results from the Cape Creek Bridge. They occur primarily because of changes in the chemistry of the zinc-concrete interface, involving up to three reaction product zones created by zinc and the cement paste.

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