Electrochemical Aging of Thermal-Sprayed
Zinc Anodes on Concrete

by

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(figures are at end of document)

Abstract

Thermal-sprayed zinc anodes are used in impressed current cathodic protection systems for some of Oregon's coastal reinforced concrete bridges. Electrochemical aging of zinc anodes results in physical and chemical changes at the zinc-concrete interface. Concrete surfaces heated prior to thermal-spraying had initial adhesion strengths 80 pct higher than unheated surfaces. For electrochemical aging greater than 200 kC/m^2 (5.2 A-h/ft^2), there was no difference in adhesion strengths for zinc on preheated and unheated concrete. Adhesion strengths decreased monotonically after about 400 to 600 kC/m^2 (10.4 to 15.6 A-h/ft^2) as a result of the reaction zones at the zinc-concrete interface. A zone adjacent to the metallic zinc (and originally part of the zinc coating) was primarily zincite (ZnO), with minor constituents of wulfingite (Zn(OH)$_2$), simonkolleite (Zn$_5$(OH)$_8$Cl$_2$·H$_2$O), and hydrated zinc hydroxide sulfates (Zn$_4$SO$_4$(OH)$_6$·xH$_2$O). This zone is the locus for cohesive fracture when the zinc coating separates from the concrete during adhesion tests. Zinc ions substitute for calcium in the cement paste adjacent to the coating as the result of secondary mineralization. The initial estimate of the coating service life based on adhesion strength measurements in accelerated impressed current cathodic protection tests is about 27 years.

THERMAL-SPRAYED ZINC ANODES are being applied as coatings to reinforced concrete bridges in coastal Oregon (and elsewhere). These coatings are used in galvanic and impressed current cathodic protection (CP) systems designed to extend the service lives of the bridges.

In coastal environments, as well as in areas where road salts are used, chloride ions penetrate the concrete and accumulate 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 iron corrosion products occupy a larger volume than the rebar consumed, which leads to a static pressure buildup at the interface that cracks the concrete,[2] causes delamination of the concrete, and leads to further corrosion damage.

The only approach that has been proven to control corrosion in high chloride environments is cathodic protection.[3] In several states zinc coatings have been thermal-sprayed on reinforced concrete bridge structures as large-area consumable anodes.[4-5] In Oregon, such coatings are used in CP systems where an impressed current is used. The Cape Creek Bridge in Oregon has been cathodically protected this way since January of 1992. Impressed current CP (ICCP) is achieved by supplying electrons to the structure to be protected.[6] An applied potential forces current from a sacrificial anode (the zinc coating) through the electrolyte (the concrete) to the cathode (the steel rebar). The oxidation reactions of

steel and zinc are:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \quad\quad (1)$$
$$Zn \rightarrow Zn^{+2} + 2e^{-} \quad\quad (2)$$
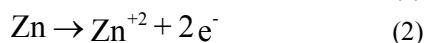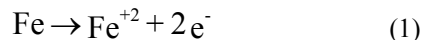
The arrival of electrons at the steel slows the reaction in Eq. 1, while removal of electrons from the zinc increases the reaction in Eq. 2. The current density requirements to achieve protection in a CP system are usually determined empirically, and a typical range for rebar in concrete is 0.1 to 0.5 mA/ft^2 (0.0011 to 0.0054 A/m^2).[6] The zinc anode consumption rate, r, can be calculated from Faraday's law:

$$r = \frac{i}{nF} \quad\quad (3)$$

where i is the current, n is the number of electrons transferred (2 for zinc in Eq. 2), and F is Faraday's constant (96,500 C/eq).

The cost of applying thermal-sprayed zinc varies from bridge to bridge. In Oregon, part of the cost is related to difficult access at the projects. Part is also related to stringent ODOT surface preparation and adhesion strength requirements resulting from the premise that high initial adhesion strength will yield coatings that remain bonded to the concrete for a longer life. Before zinc application, ODOT requires brushing and blowing down the concrete surface to remove dust. The surface under preparation must be at 70°F (21°C) or higher to keep it dry. To meet ODOT adhesion strength specifications, the contractor typically must use supplemental surface heating immediately prior to zinc application to bring the concrete surface temperature to about 250°F (120°C).[7] The additional surface preparation contributes about 16 pct to the cost of anode application.

The requirements for obtaining high initial zinc adhesion strength are based on the research of Brousseau *et al*.,[8-9] where it was shown that low or reduced initial adhesion strengths result from high moisture levels on the concrete, low concrete surface temperatures, too much exposed aggregate, and surface contamination. In this work, heating the concrete surface just prior to zinc application improved the initial adhesion strength substantially.

Initial results of the research presented here was reported for aging times corresponding to approximately 6 and 12 years.[10-11] The purpose of the current study is to extend the information on the aging process to approximately 24 years and to offer insight into the zinc anode bonding mechanism. The results provide the basis for assessing the investment in high initial adhesion strength and the impact electrochemical aging has on the service life of CP systems using large area thermal-sprayed zinc anodes.

Experimental Design

Concrete slabs were cast to physically, mechanically, and electrochemically approximate a section of bridge substructure in a typical thermal-sprayed zinc anode CP system. The concrete mix design included 5 lb/yd^3 (3 kg/m^3) of sodium chloride. A steel mesh was embedded in the slab to simulate rebar and to act as the cathode. After curing, the top surfaces of the slabs were sand blasted and prepared to receive a thermal-sprayed zinc coating following ODOT specifications. Immediately prior to thermal-spraying, the top surfaces of half of the slabs were heated to between 250 and 320°F (120-160°C). The remaining slabs were not heated prior to spraying. These are the "preheated" and "unheated" conditions. The slabs were then electrochemically aged at an accelerated rate by cathodically polarizing the steel mesh at a current density (based on the nominal concrete surface area) of 3 mA/ft^2 (0.032 A/m^2). Slabs were periodically removed from the experiment to measure the adhesion strength of the zinc coating to the concrete and to determine the chemistry of the zinc-concrete interface.

Conditions within the experimental slabs may differ from those expected to exist within coastal bridges in two important ways. The chloride was uniformly distributed throughout the slab (obtained by dissolving NaCl in the mix water prior to mixing), rather than diffused into the concrete from the outer surface with the associated concentration gradient. The salt distribution obtained by mixing may also put chloride in locations not readily accessible by diffusion, *i.e.*, in isolated pores and blind channels. Secondly, the current density in the accelerated test is a factor of 15 higher than the approximately 0.2 mA/ft^2 (0.0022 A/m^2) used by ODOT on coastal bridges.[12] This can have the effect of altering transport processes and reactions so as to give results that vary, at least in fine detail, from those being approximated by the experiment and that may occur over much longer times on cathodically protected bridges.

Concrete Design. Concrete slabs, measuring $9 \times 13 \times 2$ inches ($0.23 \times 0.33 \times 0.05$ m), were cast with No. 16 expanded steel mesh covering the full dimension of the form bottom. Steel wire was welded to the mesh and extended above the top surface of the form to provide electrical connection to the mesh. A thin layer of concrete was spread in the bottom of the form prior to placing the mesh to ensure that there were no voids behind the mesh. The cover concrete over the steel mesh was 1.25 inches (3.2 cm) thick.

The concrete mix design was intended to approximate that used in ODOT's older coastal bridges and was published elsewhere.[10] The resulting water to cement ratio of 0.48 is similar to that of Oregon's older coastal bridges. The coarse aggregate size was 4.75 to 6.4 mm (0.20 to 0.25 inches), and is smaller than aggregate typically used in bridge construction. This change in aggregate size was necessary to obtain uniform current distribution in the slab between the zinc anode and the steel mesh cathode, something that was not possible with the larger aggregate. The slabs contained 5 lb/yd^3 (3 kg/m^3) of NaCl.

Surface Preparation. Following ODOT specifications, the slabs were cured two weeks in a moist room, then air dried for one week. Prior to applying the zinc coating, the tops of the slabs were sandblasted to remove any weak cement paste on the surface, expose a small amount of aggregate, and give the surface a medium sandpaper texture. Half of the slab

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surfaces were preheated to between 250° and 320°F (120-160°C) with a propane torch immediately prior to thermal-spraying; half remained unheated before spraying.

Thermal-Spray Process. The twin-wire arc-spray process was used to apply zinc to the concrete surface. The spray parameters were: 265 amps (DC), 25 volts (DC), air pressure of 105 psi (0.65 MPa), a spray distance of 6-9 in (0.15 - 0.23 m), a spray angle normal to the surface, 3/16 inch (4.8 mm) diameter zinc wire, and a spray rate of 32 lbs/hr (14.5 kg/hr) of zinc. A custom designed and constructed programmable X-Y traversing system was used to control the movement of the spray head to obtain a nominal zinc coating thickness of 0.020 inches (0.5 mm).

Electrochemical Aging. Electrochemical aging of the slabs was conducted in a warm, high humidity room to keep the slabs from drying out. The temperature was about 75°F and the relative humidity was about 80 pct. The slabs were randomly divided into three groups. The slabs in each group were wired in series, the zinc as the anode and the steel mesh as the cathode. The slabs were polarized at a current density of 3 mA/ft^2 (0.032 A/m^2) using constant current power supplies. The total voltage across each group of slabs, the impressed current, and the laboratory temperature were recorded hourly on a data acquisition system to provide long-term performance data for the system.

Even in the high humidity room, the slabs would tend to dry out and the voltage needed to maintain the current density of 3 mA/ft^2 (0.032 A/m^2) would rise. Therefore, the slabs were sprayed as needed with deionized water; midway in the experiment they were being sprayed every day or every other day. The wetting and drying cycles resulted in voltage cycles similar to those observed on the zinc-coated, cathodically protected, Cape Creek Bridge during and after rainfall.[8]

Adhesion Strength Measurements. Preheated and unheated slabs were removed from the experiment at regular time intervals following the passage of a given total charge through the zinc coating. The slabs were equilibrated with dry air for one day, then prepared for adhesion strength measurements by attaching aluminum dollies to the zinc coating at six predetermined locations using epoxy. The aluminum dollies, 1.9 inches (50 mm) in diameter, are identical to those used with portable adhesion testers on Oregon bridges. A high viscosity, high strength, short cure time (300 sec) epoxy was used to eliminate failures at the epoxy-dolly interface and to prevent epoxy penetration through the coating to the concrete. Zinc adhesion strength measurements were made using a universal tensile testing machine. In preliminary measurements, scoring of the zinc coating around the dollies did not improve the reproducibility of adhesion strength measurements and was not used further.

Initial zinc adhesion strengths were determined by measurements on two preheated and two unheated slabs, for a total of 12 measurements for each condition. All subsequent adhesion strengths were the result of six measurements each time a slab was pulled from the experiment.

Interfacial Chemical Analysis. X-ray diffraction analysis was used to identify crystalline phases in the reaction products formed by electrochemical dissolution of the zinc anode and by secondary mineralization. Phase and lattice parameter analysis were performed using a Philips APD 3720 diffractometer system. The samples examined were reaction products taken from the zinc concrete interface and from the surface of the zinc coating, and included samples taken from both laboratory slabs and from the Cape Creek Bridge.

Cross-sections of electrochemically aged slabs were also examined using an analytical scanning electron microscope (SEM) to determine physical, chemical, and mineralogical characteristics of the zinc-concrete interface and changes that may be associated with electrochemical aging and that affect adhesion strength and operation of CP systems. Cross-sectional samples were cut from the aged slabs at predetermined locations adjacent to those used from adhesion strength measurements. The cross-sections, measuring $1 \times 1 \times 0.5$ inches ($2.5 \times 2.5 \times 1.2$ cm), were cut with a water-cooled diamond blade and then dried over night in a 100°F (38°C) oven. To keep the concrete from crumbling during grinding and polishing, the samples were embedded in ring forms using a 5:1 ratio epoxy, infiltrated under vacuum, and then cured overnight to a pressure tank. The samples were polished to a 1 µm diamond finish.

The cross-sectioned samples were carbon coated prior to imaging. Chemical analysis was performed using a wavelength dispersive (WDS) x-ray analyzer with 4 crystals, and an energy-dispersive x-ray analyzer (EDS) with atmospheric thin window for low atomic number elements. The results were ZAF corrected (Z is atomic number, A is x-ray absorption, and F is fluorescence) and converted into atomic percent. Zinc, Cl, S, Ca, and O were analyzed by WDS with accuracies of 0.1, 0.1, 0.1, 0.1, and 2 wt pct absolute. Aluminum, Fe, K, Na, and SI were analyzed by EDS with accuracies of about 2 wt pct absolute. Pure element standards were used with the following exceptions: Ca used CaCO$_3$, Cl used NaCl, and S used FeS$_2$. The NaK$_\alpha$ and ZnL$_\alpha$ lines overlap, causing errors in the Na values in high-zinc regions.

Adhesion Strength

Zinc Pull-Off Failure Mechanism. A back-scattered SEM photomicrograph of a cross-section of the zinc concrete interface from a preheated slab aged an equivalent of 13.2 years (1100 kC/m^2 or 28.3 A-h/ft^2) is shown in Fig. 1. The white and light gray zones are areas with high atomic number

Fig. 1 - Back-scattered SEM micrograph of an electrochemically-aged zinc-concrete interface showing voids in the coating and failures along the interface. Reaction zones 1 and 2 are shown. Preheated with an effective aging time of 13.2 years.

elements (primarily zinc). The brightest zone is the zinc coating. Voids and delaminations between the zinc splats typical of thermal-sprayed zinc are evident within the coating. The figure shows the zinc coating followed the topography of the concrete surface. There was no obvious difference between the interfaces for the preheated and unheated slabs. The reaction zones identified in Fig. 1 are discussed later.

The primary failure mode when the coating is pulled from the concrete substrate was cohesive fracture within a thin layer of the concrete immediately adjacent to the zinc. As failure occurs, cracks propagate through the hardened cement paste and around sand particles, causing some pull-out of the particles. The layer of concrete where failure occurs is roughly 0.05-0.20 mm (0.002-0.008 inches) thick. This failure zone coincides, as will be shown later, with zones affected by the zinc reaction products. In contrast, tensile failure of the underlying concrete, using the same test technique, produced massive pullout of the concrete matrix.

Experimental Results. Adhesion strength as a function of charge passed during electrochemical aging is shown in Figs. 2-3 for the preheated and unheated zinc-coated slabs.

Fig. 2 - Adhesion strength of electrochemically-aged arc-sprayed zinc on preheated concrete slabs as a function of aging charge. A multiplying factor of 0.0257 converts kC/m^2 to A-h/ft^2.

The six individual measurements from each test slab are given for the purposes of showing the scatter in the data. The lines though the data arise from the model described below. The scatter in adhesion strength values is typical of measurements on these types of samples. In spite of the scatter, it is evident that there are several trends associated with the data. To aid interpretation, 200 kC/m^2 (5.2 A-h/ft^2) is roughly equivalent to 3 years of service for the zinc anode ICCP systems used by ODOT.

The average initial adhesion strength, S_i, was 2.06 MPa (299 psi) for the preheated slabs and 1.15 MPa (167 psi) for the unheated slabs. Each of these values is based on 12 measurements and have standard deviations of 0.38 MPa (preheated) and 0.19 MPa (unheated). These strength values show the benefits gained from preheating the concrete, at least in terms of initial adhesion strengths. Values for the preheated slabs are 80 pct higher than for the unheated slabs. This benefit is consistent with the results of Brousseau *et al.*[13]

Fig. 3 - Adhesion strength of electrochemically-aged arc-sprayed zinc on unheated concrete slabs as a function of aging charge. A multiplying factor of 0.0257 converts kC/m^2 to A-h/ft^2.

With charge transfer across the zinc-concrete interface, Figs. 2-3 show the adhesion strength decreases during the early stages of aging for both the preheated and unheated slabs. This decrease is more pronounced for the preheated slabs. The adhesion strength reaches a minimum for both types of slabs at about 50 kC/m^2 (1.3 A-h/ft^2) and then begins to increase for larger values of charge. The minimum corresponds to roughly nine months for the ICCP systems used by ODOT.

For charge values of about 200 kC/m^2 (5.2 A-h/ft^2), adhesion strengths for the preheated and unheated slabs are nearly identical. The adhesion strength then continues to increase for larger values of charge. This increase concludes at strengths greater than the initial adhesion strengths--strengths of about 2.5 MPa (363 psi) at 400 to 600 kC/m^2 (10.4 to 15.6 A-h/ft^2).

With further charge transfer, the adhesion strengths of both preheated and unheated slabs decrease. This is in contrast to Brousseau et al.[8] where adhesion strengths decreased rapidly after much smaller values of charge were passed. It is in good agreement with the experience of the California Department of Transportation, where some delamination of zinc coatings has occurred after roughly 11 years of service.[14]

Adhesion strengths near zero, observed in the later stages of aging for both preheated and unheated slabs, occur when there is significant delamination of the coating from the concrete. One such slab is shown in Fig. 4 where half of the coating was removed to expose the concrete and delaminations along the coating-concrete interface. The exposed concrete has a mottled appearance produced by a mosaic of white reaction products and gray concrete (representing remaining points of attachment for the coating).

Fig. 4 - A delaminated electrochemically-aged arc-sprayed zinc coating on concrete. There are patches of a white corrosion product where the coating was removed. Preheated sample with an effective aging time of 22 years.

Many of the remaining points of attachment were characterized by "fingers" of the zinc coating projecting deeply into the concrete at locations of deep narrow surface hollows. The nonhomogeneous distribution of the corrosion products undoubtedly results in much of the scatter found in the adhesion strength measurements.

Empirical Model. An empirical model was developed to describe the adhesion strength data shown in Figs. 2-3 and to predict long-term adhesion strengths. The model uses four parameters (1 directly measured and 3 fitted) to describe the data:

For $C \leq 2C_f$:

$$S = S_i \exp\left(-\frac{C}{C_m}\right) + S_u\left(\frac{C}{C_f}\right)\exp\left(1 - \frac{C}{C_f}\right) \quad (4)$$

For $C \geq 2C_f$:

$$S = \frac{S_u}{e}\left(4 - \frac{C}{C_F}\right) \quad (5)$$

The first term of Eq. 4 describes the initial stages of electrochemical aging through an exponential decay function starting at the initial adhesion strength, S_i. S_u is the adhesion strength at the maximum that occurs at charge C_f, and C_m is the charge associated with the weakening of the initial mechanical bond. Specifically, C_m is the charge where the first term of Eq. 4 contributes S_i/e to the total strength (e $\approx$ 2.72). The relationships between the shape of the curve and the parameters are shown in Fig. 5. The first decay in adhesion strength describes a weakening of the initial mechanical bond. The first term in Eq. 4 becomes negligible after about 400 kC/m^2 (10.4 A-h/ft^2). The second term in Eq. 4 describes the rise and subsequent fall in adhesion strength.

Fig. 5 - Adhesion strength model of electrochemically-aged arc-sprayed zinc coatings as a function of aging charge. Model parameters are shown in relation to the curve shape.

This rise and fall in adhesion strength results from the growth of an adhesive reaction layer produced by secondary mineralization at the zinc-concrete interface. At charges greater than $2C_f$ (the inflection point of the second term in Eq. 4), Eq. 4 trails off more gently than the data indicates, so Eq. 4 is replaced by the linear decline of Eq. 5. Equation 5 reaches an adhesion strength of zero at $4C_f$. For both the preheated

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and unheated slabs, $4C_f$ occurs at about 1800 kC/m^2 (47 A-h/ft^2), which corresponds to 27 years of service at the levels of charge used by ODOT. Table I shows the results of applying the model to the data from both the preheated and unheated experiments.

The estimated mean squared error in Table I is the sum of the squared residuals divided by N-m, where N is the number of data points and m is the number of independent parameters. The value of m is 3 in this case because S_i (one of the four parameters) is experimentally measured and not determined by fitting Eqs. 4-5. The number of data points is 144 (6 pull tests for 24 slabs). The estimated error is simply the square root of the estimated mean squared error, and is used to plot the dotted lines in Figs. 2-3 that straddle the fitted solid curve and represent 70 pct confidence limits. The pseudo R^2 values arise from 1 minus the ratio of the sum of the squared residuals to (N-1) times the variance. If the non-linear model fits the data less well than the mean, then the pseudo R^2 would have a negative value. Pseudo R^2

Table I - Results of Applying Model to Adhesion Data. The Zinc Thickness Values Represent the Amount of Zinc Consumed. The Times Associated with the Charge Data are for Applied Currents of 0.0022 A/m^2 (0.2 mA/ft^2).

Variable or Statistic	Model parameters	
	Preheated slabs	Unheated slabs
S_i	2.06 MPa (299 psi)	1.15 MPa (1.67 psi)
S_u	2.54 MPa (369 psi)	2.35 MPa (341 psi)
C_m	40 kC/m^2 (1.0 A-h/ft^2) 1.9 µm Zn (0.08 mil Zn) 7.1 months	31 kC/m^2 (0.80 A-h/ft^2) 1.5 µm Zn (0.06 mil Zn) 5.5 months
C_f	450 kC/m^2 (11.6 A-h/ft^2) 21 µm Zn (0.84 mil Zn) 6.7 years	448 kC/m^2 (11.5 A-h/ft^2) 21 µm Zn (0.84 mil Zn) 6.6 years
$4C_f$ (lifetime)	1800 kC/m^2 (47 A-h/ft^2) 86 µm Zn (3.4 mil Zn) 27 years	1792 kC/m^2 (47 A-h/ft^2) 85 µm Zn (3.4 mil Zn) 27 years
$\sum$ Residuals^2	56 MPa^2	47 MPa^2
Variance	0.90 MPa^2	0.87 MPa^2
Estimated mean squared error	0.40 MPa^2	0.34 MPa^2
Estimated error	0.63 MPa	0.58 MPa
Pseudo R^2	0.57	0.62

values of 0.58 and 0.63 suggest a moderately good fit, especially considering the overall scatter in the data.

The charge parameters, C_m and C_f, can be viewed as time constants for the processes of weakening the initial mechanical bond, and of reaction product layer growth at the zinc-concrete interface. Assuming 100 pct current efficiency and 100 pct coating density, the charge parameters are also given in Table I as the equivalent thickness of zinc consumed during these processes (using Eq. 3) and as the times required to consume this equivalent thickness based on ODOT ICCP current densities for coastal bridges. Expressed in this way, they suggest the coating thicknesses involved in each process.

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Specifically, only a thin layer of zinc needs to be dissolved by the anodic current to degrade the mechanical bond between coating and concrete. On the other hand, dissolution of roughly 20 µm (0.8 mil) of coating provides sufficient zinc ions, when acted on by periodic wetting and drying and the associated secondary mineralization, to form an adherent layer between zinc and concrete. The total zinc consumption over the predicted lifetime of the coating (until detachment) of 1800 kC/m^2 is 86.4 µm (3.4 mil). This is much less than the 500 µm (20 mils) of zinc in the initial coating, and suggests that a thinner coating of 210-250 µm (8-10 mil) should be sufficient. And since Howell[15] reports that zinc coatings thicker than 230 µm (9 mil) reduce adhesion strengths by a buildup of thermal stress during application, the tendency for detachment may also be reduced--thereby extending the life of the coating past 27 years.

Zinc-Concrete Interfacial Chemistry

The zinc-cement interface in Fig. 1 was characterized by WDS and EDS analyses. Two reaction zones, "zone 1" and "zone 2", are observed in Fig. 1 between the zinc and cement paste.

Zone 1 is primarily Zn and O in roughly equal amounts of each. Zone 1 was also found to be enriched in Cl and S. Silica particles in zone 2 (the roundish dark areas) serve as markers for the original location of the cement paste in contact with the zinc. The presence of these silica particles shows that zone 1 formed from the original zinc coating and zone 2 formed from the original cement paste.

Zone 2 is cement paste enriched in Zn and depleted in Ca. The presence of Zn within this zone indicates reactions where Zn has modified the mineralogy of the original cement paste during repeated wetting and drying cycles. This modification of the original cement paste with Zn is termed "secondary mineralization".

The thickness of these zones show significant variation within aged samples. Nevertheless, observations of several samples (shown in Table II) indicate that the zones develop over time and that zone 1 forms prior to zone 2. Also listed in Table II are similar observations from cores taken from the

Table II - Thicknesses of Zones 1 and 2 Found Between the Zinc Coating and Cement Paste. Determined from WDS Scans Across the Zinc-Concrete Interface. The C_f and $4C_f$ Values Refer to the Bond Strength Model.

Sample	Effective Aging (yr)	Zone 1 Width (mm)	Zone 2 Width (mm)
Preheated	0.6	< 0.02	0
Preheated	1.2	< 0.02	0.18
Preheated	4.1	0.11	0.41
C_f (Preheated)	6.7	N/A	N/A
Preheated	9.4	0.15	0.61
Preheated	13.2	0.38	0.63
Preheated	13.2	0.39	0.19
Preheated	15.4	0.08	0.50
Preheated	15.4	0.13	0.49
$4C_f$ (Preheated)	27	N/A	N/A
Unheated	0.7	0.02	0
C_f (Unheated)	6.6	N/A	N/A
Unheated	9.8	0.09	0.56
Unheated	15.4	0.31	0.49
$4C_f$ (Unheated)	27	N/A	N/A
Cape Creek Bridge[a]	3.7[d]	0.07	0
Cape Creek Bridge[b]	3.7[d]	0.02	0
Cape Creek Bridge[c]	3.7[d]	0.05	0.20

[a] from south side of west column, 30 ft (9.1 m) below the deck, zinc on existing concrete.

[b] from west side of west beam, zinc on existing concrete.

[c] from south side of east column web, 15 ft (4.6 m) below the deck, zinc on deep concrete patch.

[d] Actual years of exposure at 0.2 mA/ft^2 (0.0022 A/m^2).

Cape Creek Bridge. The Cape Creek samples show evidence of zones similar to those found in the laboratory samples (zone 1 and one case of zone 2). However, in the laboratory, accelerated aging takes place without accelerated diffusion (from concentration gradients). So the mass transport mechanisms associated with Zn enrichment and Ca depletion that define zone 2 may bear a somewhat different relationship

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to the electrochemical processes at the Cape Creek Bridge.

The white corrosion products underneath the detached zinc coating shown in Fig. 4 were examined with x-ray diffraction. X-ray diffraction revealed that the corrosion product was primarily zincite (ZnO). Also present as minor constituents were wulfingite ($Zn(OH)_2$), simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$), and hydrated zinc hydroxide sulfates ($Zn_4SO_4(OH)_6 \cdot xH_2O$). The presence of the zincite phase supports the WDS and EDS results where the corrosion product in zone 1 has a one-to-one Zn-to-O ratio.

White corrosion products were also formed on the surface of the zinc coatings on both the laboratory slabs and on the Cape Creek Bridge (after 3.7 years of ICCP). Simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) was found in the Cape Creek Bridge samples. Simonkolleite was also the primary constituent of the samples from the laboratory samples. Also present were hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and $Zn_4SO_4(OH)_6 \cdot xH_2O$. The presence of $Zn_5(OH)_8Cl_2 \cdot H_2O$ as the major surface corrosion products from both the Cape Creek Bridge and the laboratory samples suggests a good correspondence between the conditions in the natural and accelerated aging processes.

Strengthening and Weakening Mechanisms

Initial Adhesion Strength. The initial bonding of the zinc to the concrete is purely mechanical. The "tooth" given to the concrete by sand blasting and by surface porosity allows the zinc to mechanically adhere. Preheating the concrete prior to spraying increases this initial adhesion strength.

Early Decline in Adhesion Strength. The early decline in adhesion strength is from the degradation of some of the initial mechanical bonding. The current passing through the concrete follows paths of least resistance. Other things being equal, these paths would be where the zinc is closest to the rebar--at the recesses of surface roughness. These places would tend to be the first places to react to form zone 1. This reaction is Zn oxidizing to ZnO. Since ZnO has a volume a factor of 1.6 larger than Zn, this expansion loosens the mechanical grip and reduces the adhesion strength. Other constituents have even larger volume ratios. For example, the volume of $Zn(OH)_2$ is a factor of 3.5 larger than Zn.

This tendency of the concrete to channel current (another example would be around aggregate) would lead to "hot spots" where current densities are higher and more zinc is reacted. The nonhomogeneous nature of the location of corrosion products in Fig. 4 supports the notion of "hot spots."

Since both preheated and unheated slabs decline to the same strength levels (preheated strengths decline more), the advantages of preheating are lost. It may be that the extra strength provided by preheating is from the same locations that are degraded by the first reactions to form ZnO.

Rise in Adhesion Strength. The subsequent increase in adhesion strength results from secondary mineralization. Secondary mineralization (the dissolution and reprecipitation of zinc reaction products) allows cracks and pores within the cement paste to fill. This filling of cracks and pores eliminates stress-risers within the cement paste, as well as increasing the effective cross-sectional area under stress. No significant differences between preheated and unheated samples were observed.

Later Decline in Adhesion Strength. The volume expansion in forming ZnO (1.6), combined with the nonhomogeneity in the thickness of the ZnO layer (from "hot spots"), results in local stresses at the coating-concrete interface. The stresses increase with increasing electrochemical aging. Cracking within zone 1 and between zone 1 and zone 2 (Fig. 1) results from these stresses and leads to a reduction in adhesion strength. Eventually, the cracks lead to widespread delamination of the coating. No significant differences between the preheated and unheated samples were observed.

The presence of cracks at the coating-concrete interface would presumably cause delamination much sooner in applications where freeze-thaw cycles exist. Water, when present in the cracks, would freeze and expand, adding further stresses to the coating-concrete interface.

Conclusions

Adhesion Strength. The initial thermal-sprayed adhesion strengths for the preheated concrete slabs were 80 pct higher than for the unheated concrete slabs. The adhesion strength decreased with the initial application of current, at which point the differences between preheated and unheated concrete disappeared. At an effective aging time of 6 or 7 years, the adhesion strengths increased to a maximum value higher than the initial strength. Aging beyond this lowered the adhesion strength until essential little bonding remained.

Empirical Model. A four parameter (one directly measured and three fitted) empirical model was developed to describe the adhesion strength changes with time. The model gave lifetime predictions of 27 years for both the preheated and unheated concrete.

Interfacial Chemistry. Two reaction zones were identified between the zinc coating and the cement paste. Zone 1 was zinc that had oxidized to form zincite (ZnO), with wulfingite ($Zn(OH)_2$), simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$), and hydrated zinc hydroxide sulfates ($Zn_4SO_4(OH)_6 \cdot xH_2O$). as minor constituents. Zone 1 was enriched with Cl and S. Zone 2 was cement paste that had undergone secondary mineralization in which Zn had replaced Ca. These zones were also found on the Cape Creek Bridge in Oregon.

Adhesion Mechanism. The initial zinc coating had a purely mechanical bond to the concrete. The preheated concrete allowed for a tighter bond and thus a higher initial adhesion strength. Upon electrochemical aging, the ZnO that formed decreased the mechanical bonding due to a volume expansion. With additional aging, secondary mineralization locally strengthened the bond at the coating-concrete interface and led to an increase in adhesion strength. With increased electrochemical aging, inhomogeneities in the ZnO thickness (from "hot spots") created stresses and cracking within zone 1 and at the zone 1-zone 2 interface. The cracking eventually decreased the adhesion strength of the zinc coating to zero.

Recommendations. Decrease the thickness of the applied zinc from 20 to 10 mils (500 to 250 µm). This re-

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duction in zinc thickness should save money on zinc costs, decrease residual stresses,[15] and still allow adequate zinc coverage (since only 3.4 mils (86 µm) are consumed from electrochemical reactions in 27 years with an applied current of 0.2 mA/ft^2 (0.0022 A/m^2).

Heating of the concrete surface prior to thermal-spraying with zinc is not required for long-term coating service life when all other aspects of surface preparation are properly performed.

Investigate the effect of freeze-thaw cycles on the long-term performance of thermal-sprayed zinc anodes on concrete.

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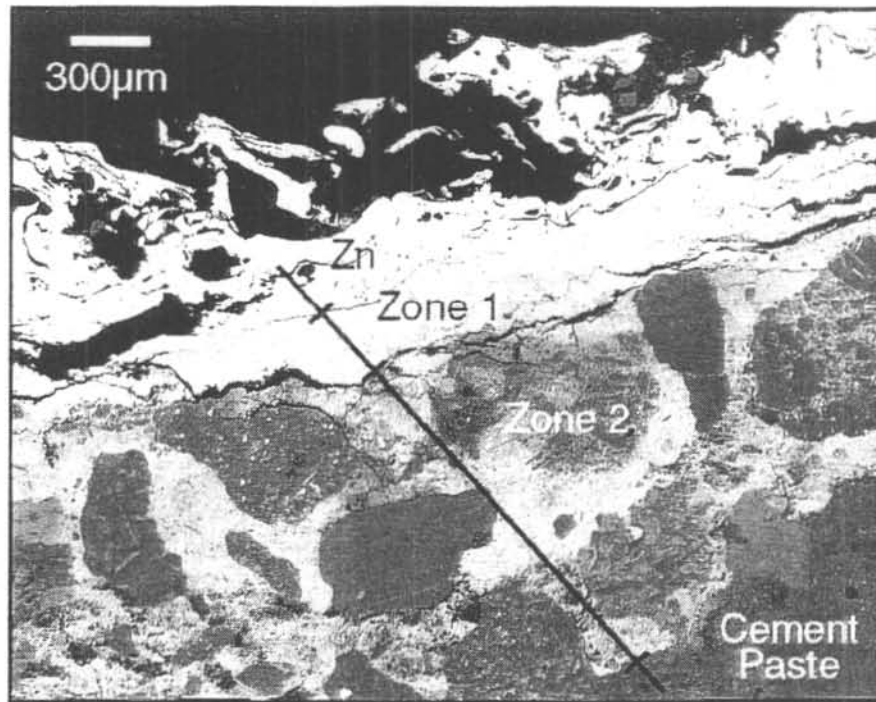Holcomb, Bullard, Covino, Cramer, Cryer, and McGill

Fig. 1 - Back-scattered SEM micrograph of an electrochemically-aged zinc-concrete interface showing voids in the coating and failures along the interface. Reaction zones 1 and 2 are shown. Preheated with an effective aging time of 13.2 years.
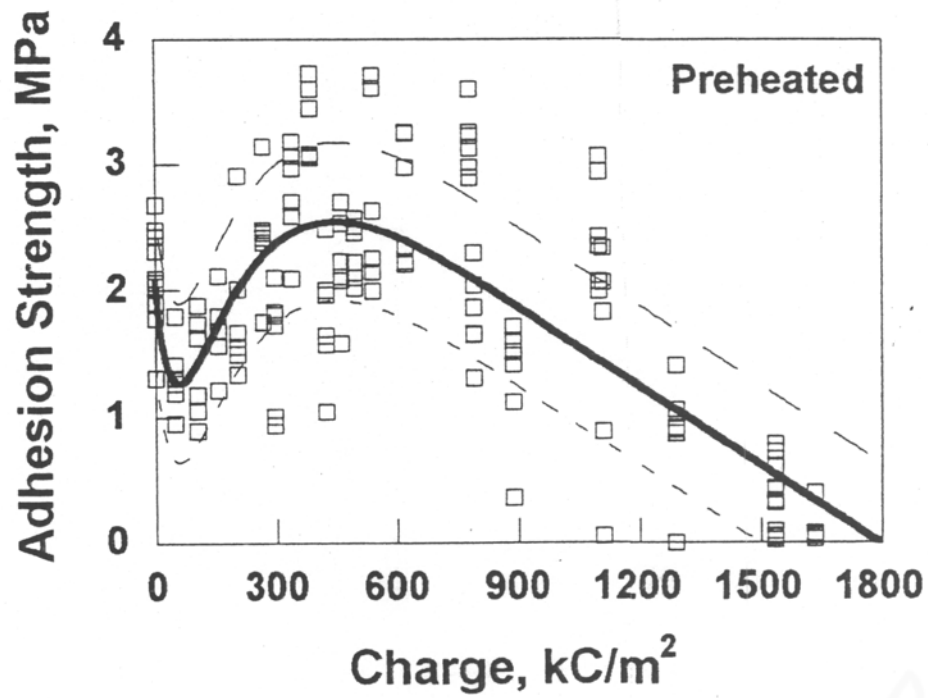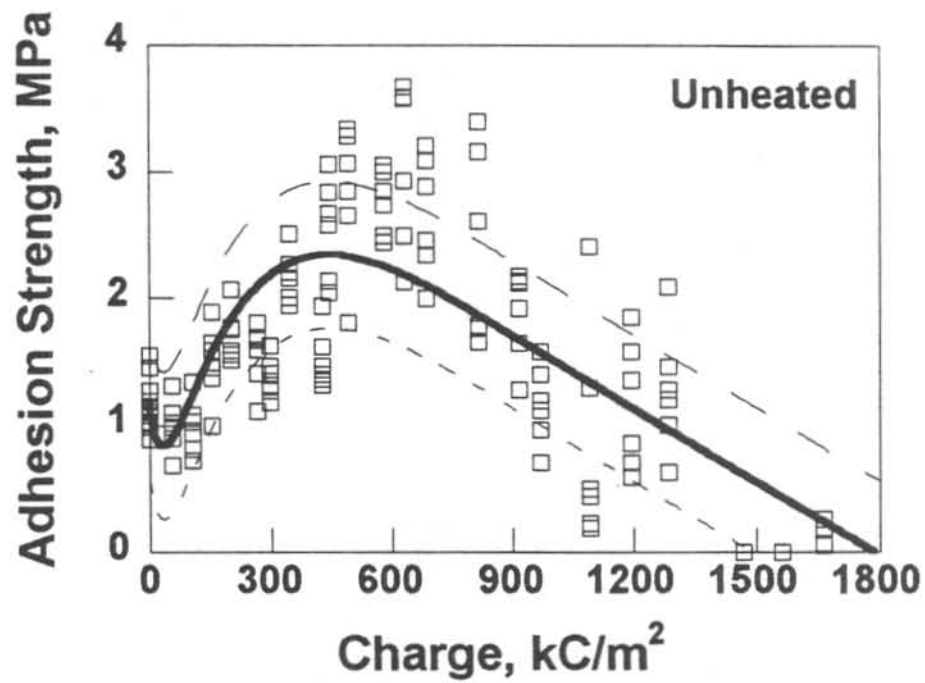
Fig. 2 - Adhesion strength of electrochemically-aged arc-sprayed zinc on preheated concrete slabs as a function of aging charge. A multiplying factor of 0.0257 converts kC/m^2 to $A\text{-}h/ft^2$

Fig. 3 - Adhesion strength of electrochemically-aged arc-sprayed zinc on unheated concrete slabs as a function of aging charge. A multiplying factor of 0.0257 converts kC/m^2 to $A\text{-}h/ft^2$.
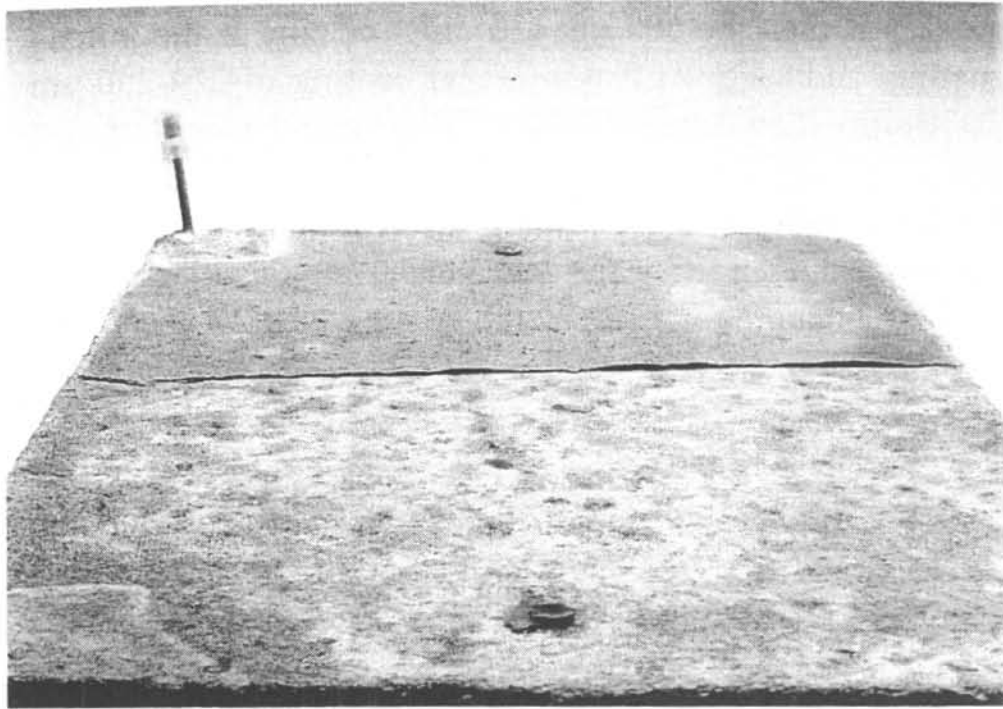
Fig. 4 - A delaminated electrochemically-aged arc-sprayed zinc coating on concrete. There are patches of a white corrosion product where the coating was removed. Preheated sample with an effective aging time of 22 years.
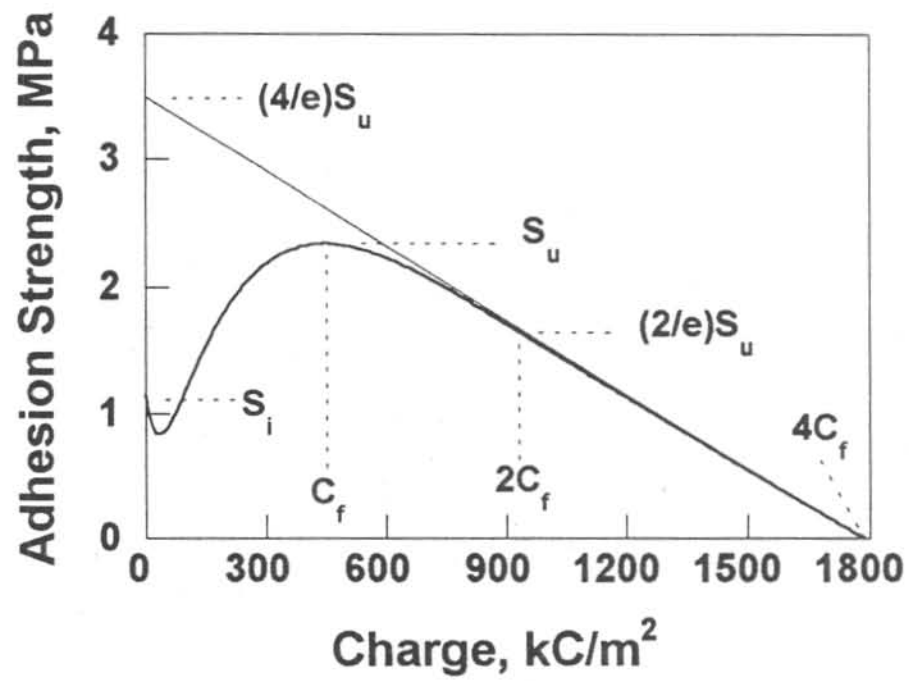
Fig. 5 - Adhesion strength model of electrochemically-aged arc-sprayed zinc coatings as a function of aging charge. Model parameters are shown in relation to the curve shape.