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Laboratory Performance of Zinc Anodes for Impressed Current Cathodic Protection of Reinforced Concrete

R. Brousseau, M. Arnott, and B. Baldock*

ABSTRACT

Cathodic protection (CP) is used increasingly to mitigate steel reinforcement corrosion in concrete. The performance of zinc materials as impressed current anodes was evaluated. The anode materials investigated included rolled zinc sheets, metallized zinc, and 85% Zn-15% Al. The circuit resistance and the adhesion of the anodes was monitored with polarization time. Overall performance of arc-sprayed zinc was good. However, its adhesion to the concrete surface slowly decreased as the current density, or the polarization period, increased. Penny blank sheets and metallized 85% Zn-15% Al were found unsuitable as impressed current anodes.

KEY WORDS: *adhesion, aluminum, anodes, arc spray, cathodic protection, concrete, impressed current, polarization, reinforced concrete, steel reinforcement, zinc*

INTRODUCTION

Steel reinforcement corrosion is a serious problem for concrete structures exposed to chlorides from deicing or marine salts. Several methods exist for repairing defective concrete structures. The exercise generally is futile unless the repair provided stops the reinforcement from corroding for a long period. Reinforcement corrosion is being mitigated increasingly in chloride-contaminated concrete by cathodic protection (CP). The protective currents usually are

applied to the rebars with a rectifier and an anode. The anode consists of a conductive material that is applied on the surface of the protected concrete.

A number of anode systems have been investigated in the last two decades.¹⁻² Some of the anode systems currently used include: (a) a coke/asphalt conductive overlay with high-silicon cast iron current collectors,³ (b) a titanium mesh with concrete/shotcrete overlay,⁴ and (c) conductive coatings or paints.⁵⁻⁶ However, there is little information available on the performance of zinc-based materials as impressed current anodes, except for what has been published by the Department of Transport of California.⁷⁻⁸

The objective of the present work was to provide additional information on the laboratory performance of zinc anodes for impressed current CP of reinforced concrete.

Research Objectives

In the evaluation of impressed current anodes for CP of reinforced concrete, two factors must be considered:

— Adhesion: The anode must adhere well to the surface of the concrete for the entire service life of the CP system; and

— Driving voltage: The voltage that is required for the anode to deliver the protective current must remain low.

These two factors are influenced by degradation occurring at the anode-concrete interface as a result of the aggressive electrochemical reactions that occur when CP is applied.

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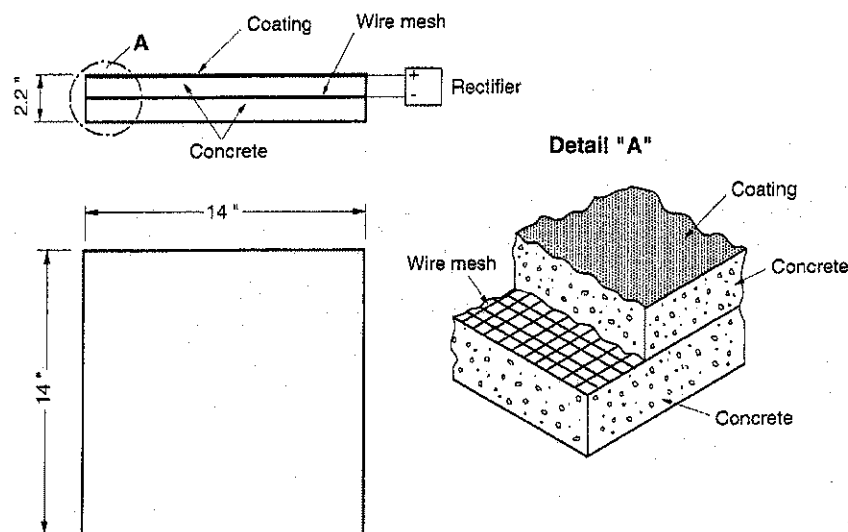


FIGURE 1. Schematic of the polarized samples.

The performance of metallized zinc, 85% Zn-15% Al, and of rolled zinc sheets was investigated. Samples were polarized at three current densities: 0 mA/m² (0 mA/ft²), 2 mA/m² (0.186 mA/ft²), and 10 mA/m² (0.929 mA/ft²).

EXPERIMENTAL

Manufacture of the Concrete Samples

The various anode systems were applied to concrete samples manufactured according to specifications given in Figure 1. A mild steel mesh was placed 2.54 cm (1 in.) from the face on which the anode system was applied. The same concrete mix formulation was used for all samples (i.e., cement/sand/aggregate ratio = 1:2:3). Type 1 portland cement was used, with a water-to-cement ratio of 0.43. Chlorides also were introduced in the concrete mix as sodium chloride (NaCl) to better simulate aggressive environments. The chloride content was 0.6% by weight of cement. After demolding, the samples were cured in a humid room at 23°C and 100% relative humidity (RH) for 28 days. The concrete surface on which the anode was to be applied was grit-blasted using a 16-mesh silica sand at 758 kPa (110 psi). The sample surface was grit-blasted until the smooth cement paste surface created by the mold was removed and a mainly sand-cement surface remained.

Application of Thermally Sprayed Anodes

The 85% Zn-15% Al anodes were applied to the surface of the concrete samples using an electrical arc sprayer. All arc sprayings were performed with 3-mm (0.118 in.) wires, 620 kPa (90 psi) air pressure, 26 V, 300 A, and a spray distance of 15 cm (5.906 in.). An automated application system was used to travel the electric arc gun in the X-Y plane

during metallizing in order to produce a uniform coating. The metals were sprayed to a 0.4-mm (0.016-in.) thickness. The surface of all the concrete samples was preheated with radiant heat panels to 150°C immediately prior to metallization.⁹⁻¹¹ This was done to maximize adhesion of the metallized coatings during their application. If bond strengths would not have been maximized, decreasing trends in adhesion of the metallized coatings with polarization time would have been more difficult to characterize.

Fabrication of the Rolled Zinc Anodes

The rolled zinc anodes consisted of rolled zinc sheets 30.5 cm by 30.5 cm by 0.08 cm (11.811 in. by 11.811 in. by 0.031 in.) that were perforated with 25 1.27-cm (0.50-in.) holes. The sheets were attached to the concrete by applying a 0.32-cm (0.126-in.) layer of a commercial mortar overlay on the surface of the concrete samples. The perforated zinc sheets were pressed into this mortar overlay, while it was still uncured so that it could be forced up through the holes. A second layer then was applied to totally encapsulate the perforated zinc sheet.

Application of Impressed Current

Concrete samples with applied anodes were placed in individual plastic containers partially filled with a salt solution. The lower 0.5 cm (0.197 in.) of the sample always was immersed in the salt solution. The samples were wired in series and were polarized with constant current power supplies. Three current densities were investigated (i.e., 0 mA/m² [0 mA/ft²], 2 mA/m² [0.186 mA/ft²], and 10 mA/m² [0.929 mA/ft²]). Ten replicates of each anode material were tested for each of the three current densities. The voltage across each sample (i.e., between the steel mesh and the anode) was monitored continuously

using a computerized data acquisition system. The change in voltage indirectly provided information about the effective resistance changes at the anode-concrete interface induced by electrochemical oxidation of the anode. This interpretation was possible because these concrete samples were more than 3 months old when polarization commenced, and they were maintained in a controlled humidity environment. All this ensured that the resistance in the concrete portion of the sample remained nearly constant.

RESULTS AND DISCUSSION

Driving Voltages vs Time

The driving voltage, which was the potential difference between the anode and the steel mesh, is plotted as a function of time in Figures 2 and 3. These graphs illustrate the increase in effective circuit resistance occurring at the various anode-concrete interfaces. The gaps in the curves represent the time during which the current was shut off due to maintenance of the system or to measure adhesion of the metallized coating. Occasionally, individual samples developed very high driving voltages (> 30 V to 50 V). Typically, these samples had a driving voltage similar to the other samples until it began to steadily increase. The erratic sample was removed from the test circuit at that time. The driving voltage results, beginning from the point where the voltage began to increase, were not included in the calculated average. Only a few samples remained after 230 days for the 85% Zn-15% Al alloy at 10 mA/m^2 (0.929 mA/ft^2). Although discontinued from that point, it was evident that the driving voltages were increasing sharply for the 85% Zn-15% Al.

The change of the driving voltages with time for the metallized coatings were quite different at the two current densities. The driving voltages at 2 mA/m^2 (0.186 mA/ft^2) remained relatively constant at < 1 V. Initially, the driving voltages were slightly lower for the 85% Zn-15% Al alloy than for pure zinc. However, the driving voltages for both metallized coatings were equal after 350 days of polarization, and remained similar thereafter. Interruptions in current, for maintenance or testing, did not affect the driving voltages across these samples.

A polarized potential survey for the two metallized coatings is presented in Table 1. Generally, the polarized potential of the metallized coatings became more electropositive with higher applied current densities and/or with longer polarization times. This partially explained why the driving voltage of both metallized coatings became much higher and more erratic at 10 mA/m^2 (0.929 mA/ft^2) than at 2 mA/m^2 (0.186 mA/ft^2). The values tended to increase during uninterrupted periods of polarization, similar to that found previously.⁸ The driving voltage usually

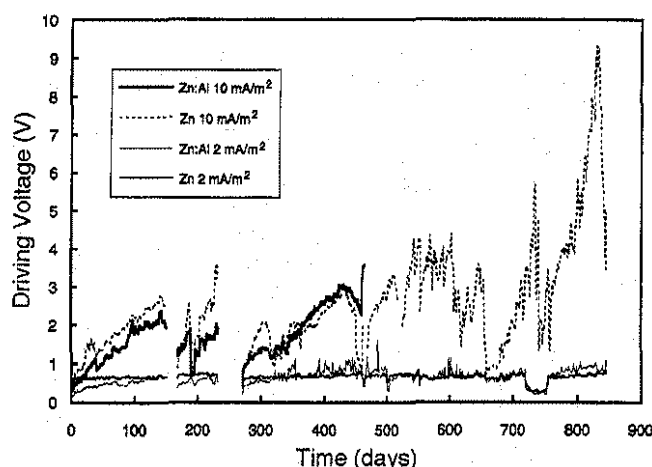


FIGURE 2. Average voltage drop across arc-sprayed anodes.

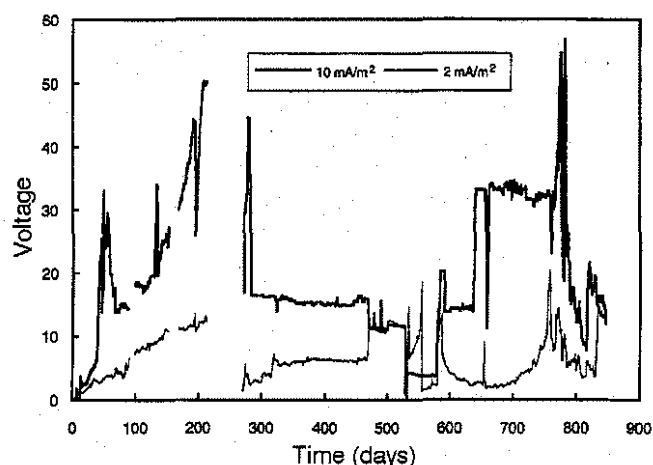


FIGURE 3. Driving voltage, zinc sheet anodes, powered at 2 mA/m^2 (0.186 mA/ft^2) and 10 mA/m^2 (0.929 mA/ft^2).

dropped significantly after a current interruption of at least a few hours. It then took a significant amount of time for the driving voltage to surpass that recorded prior to the interruption of the polarizing current. It was believed that the zinc oxidation products did not have sufficient time to diffuse away from the electroactive sites at the interface when the current density was too high. This resulted in a higher overvoltage at the interface unless the current was interrupted for a certain period of time. This hypothesis on diffusion polarization was supported by the absence of this phenomenon for the current density 2 mA/m^2 (0.186 mA/ft^2). The driving voltages following current interruption still remained higher than the initial "0-day" driving voltage. This suggested nonreversible changes to the system, including the formation of metallic oxides.

The driving voltages for the zinc sheets are shown in Figure 3. The driving voltage for this type of

TABLE 1

*Polarized Potential Survey of the Metallized Coating
Anodes vs the Saturated Calomel Reference Electrode*

Anode Coating	Current Density (mA/m ²)	Potential at 231 Days (mV _{SCE})	Potential at 845 Days (mV _{SCE})
Zinc	0	-437	-455
Zinc	2	-263	-297
Zinc	10	2,072	5,140
85% Zn-15% Al	0	-751	-575
85% Zn-15% Al	2	-502	-203
85% Zn-15% Al	10	2,109	103,000

anode system was much higher and exhibited the largest fluctuations. Such high driving voltages are unacceptable for CP of reinforced concrete. The overlay and rolled zinc sheets delaminated. In general, a poor bond was found between the rolled zinc sheets and the encapsulating mortar. Large areas of the zinc appeared to have little or no contact with the underlying mortar. The first delamination of the encapsulating overlay occurred after 55 days of polarization. The delamination likely was caused by the expansion force generated by the zinc oxidation products. The lack of intimate surface contact between the rolled zinc and mortar overlay was believed to have promoted the excessively high driving voltages observed.

Oxidation Products at the Metallized Coatings

Zinc oxidation products were found on samples polarized at 10 mA/m² (0.929 mA/ft²) for 845 days. A white powdery material was observed on the surface of the concrete after the zinc was pulled off in adhesion measurements. The formation of zinc oxides, hydroxides, and chlorides also was supported by scanning electron microscopy (SEM) and optical microscopy (OM) examinations of the zinc-concrete interface. A typical SEM photograph in the back scatter mode is presented in Figure 4. The paler areas represent unoxidized zinc, while the pockets of darker gray reveal the oxidized zinc products. The very dark regions correspond to the concrete. There was an absence of oxidation at the interface between the zinc and aggregate. A possible explanation was the absence of anodic current flow through the dense aggregate relative to the cement paste. Transverse cuts through the interface examined by OM revealed white deposits formed at the zinc-concrete interface (Figure 5). There were insufficient amounts of this white powder to conduct an analysis.

Attempts were made to detect any migration of zinc into the concrete using energy dispersive x-ray analysis (EDXA). However, no detectable amounts of zinc were seen to migrate into the concrete matrix. It appeared that the zinc oxidation products remained at the interface until they dissolved and migrated to

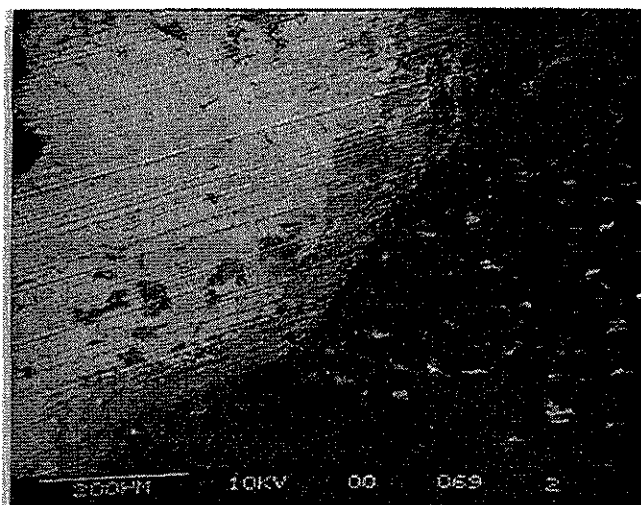


FIGURE 4. Backscattered SEM micrograph of zinc-concrete interface from a sample polarized at a current density of 10 mA/m² (0.929 mA/ft²) for 845 days. (Magnification = 150x).



FIGURE 5. OM photograph of the zinc-concrete interface after being polarized for 845 days at 10 mA/m² (0.929 mA/ft²). (Magnification = 45x).

imperfections in the zinc coating. Evaporation of the moisture originating from underneath the coating resulted in crystallization of the products on the external surface of the coating. This explained the "anthill" of white deposits that was found on the external surfaces of the zinc and 85% Zn-15% Al coatings. Formation of white powdery crystals at surface defects on the zinc coating also was observed in the field. This is shown in Figure 6, which is a photograph taken on the Cape Creek bridge in Oregon, where 10,000 m² (93,000 ft²) of concrete was zinc-metallized. A white powdery material was noticeable at surface holes and voids 2 y after the impressed current CP was applied.

In the laboratory, the powdery material was more noticeable on the samples polarized at a higher cur-

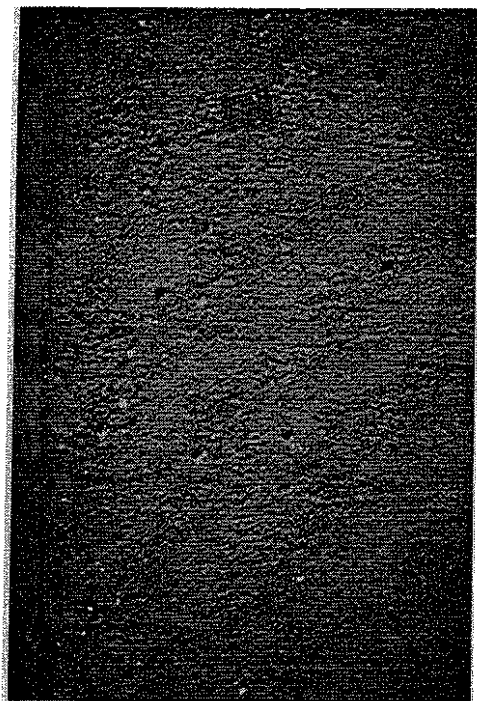
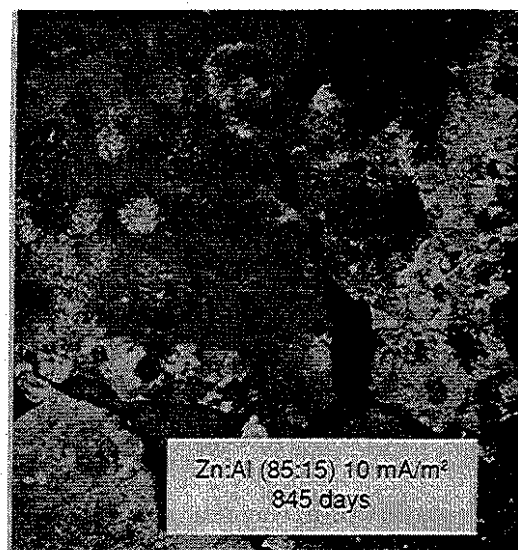


FIGURE 6. Cape Creek bridge in Oregon showing formation of white deposits at surface defects of the metallized zinc coating. (Scale = 1:10).

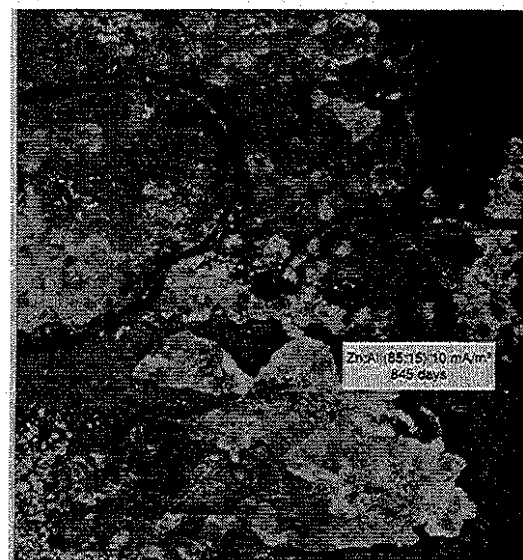
rent density, or for a longer polarization period. However, the presence of white deposits on the unpowered samples suggested some self-corrosion of the zinc that did not contribute to the CP process. The deposit was analyzed by x-ray diffraction (XRD), and determined to be a complex mixture of zinc chloride and hydroxide compounds.

Physical Appearance

The overall appearance of the pure metallized zinc remained excellent throughout the 3-y research program. The appearance of the 85% Zn-15% Al coating initially was very similar to that of the zinc. The surfaces of the samples were smooth after thermal spraying and followed the contours of the surface of the concrete. The 85% Zn-15% Al coating began to blister near the edges of the concrete, and voids beneath the metal were formed after powering for ≈ 240 days. This eventually destroyed the coating for the 85% Zn-15% Al samples powered at 10 mA/m^2 (0.929 mA/ft^2), as shown in Figure 7. The coating appeared to blister from the concrete. No material or deposits were found beneath the bubbles to cause this. A possible explanation of why blistering occurred on the 85% Zn-15% Al may have been that the aluminum was preferentially oxidized as part of the anodic reactions. This could have induced internal stress in the metallized coating. An attempt was made to determine whether there was any preferential leaching of the zinc or of the aluminum. Results



(a)



(b)

FIGURE 7. Metallized 85% Zn-15% Al anode after polarization at 10 mA/m^2 (0.929 mA/ft^2).

were inconclusive because of the high content of aluminum normally found in concrete.

Bond Strength Measurements

Bond strength measurements were made using 50-mm- (1.969-in.-) diam dollies and a pneumatic adhesion tensile testing instrument. This larger dolly size provided for an averaging of any inconsistencies of the concrete surface and produced more reproducible results. The average bond strength values for the two metallized coatings are listed in Table 2.

Generally, the bond strength of all the unpowered samples, after 845 days of testing, was similar or higher than the initial bond strength values. The higher bond strengths of the 85% Zn-15%

TABLE 2
Bond Strengths for the Metallized Anodes (kPa)

Day	Zinc			85% Zn-15% Al		
	0 mA/m ²	2 mA/m ²	10 mA/m ²	0 mA/m ²	2 mA/m ²	10 mA/m ²
0 ^(A)	3,475	3,475	3,475	3,434	3,434	3,434
150 ^(B)	3,737	2,337	1,303	4,764	2,806	917
234 ^(C)	3,530	1,889	745	4,992	2,193	648
460 ^(C)	3,310	1,786	496	—	2,916	331
845 ^(D)	3,268	2,254	965	4,971	2,992	214

^(A) Average of 18 pull tests, 6 pull tests taken from 3 different samples.

^(B) Average of 3 pull tests, 1 pull test from 3 different samples.

^(C) Average of 6 to 10 pull tests, 3 to 5 tests from 2 different samples.

^(D) Average of 15 pull tests, 5 pull tests taken from 3 different samples.

Al may have been due to chemical reactions between this metallized alloy and the concrete. Aluminum is known to react chemically in higher pH environments because of its amphoteric oxides. The strength limiting factor for many of the bond strength tests on the unpowered samples was the tensile strength of the concrete. Failure often occurred in the concrete (cohesive failure).

The bond strengths for all the powered samples decreased over the course of the experiment.

Samples powered at the higher current density experienced larger decreases in bond strength. It is suggested that high current densities not be used in the field. The loss of adhesion of the metallized coating under impressed current most likely is related to the fact that the molten metal that penetrated into the pores of the concrete during metallizing is most susceptible to oxidation because of intimate contact with the pore solution of the concrete.

CONCLUSIONS

- ❖ Metallized zinc performed well as an impressed current anode over a 900-day test period.
- ❖ There was a loss of adhesion for coating anodes with higher anodic current densities and longer polarization times. Since this also applied to metallized zinc, the application procedure must produce the best adhesion possible to the concrete substrate.
- ❖ Metallized 85% Zn-15% Al should not be used as an impressed current anode based on the severe disbondment and blistering observed.
- ❖ Zinc sheets encapsulated in mortar performed poorly and, therefore, are not recommended for use as impressed current anodes.
- ❖ There was an increase in the effective circuit resistance as metallized zinc was oxidized (i.e., the driving voltage for the metallized samples increased with the applied current density and polarization time).

❖ The zinc oxidation products did not diffuse in the porous matrix of concrete. Some of the oxidation products chemically reacted to form zinc chloride compounds at the concrete interface. These frequently diffused out through surface defects of the metallized coating.

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