Intermittent Cathodic Protection For Steel Reinforced Concrete Bridges

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ABSTRACT

Thermal-sprayed zinc anodes are used for impressed current cathodic protection (ICCP) systems on Oregon's reinforced concrete coastal bridges to prevent chloride-induced corrosion damage. Thermal-sprayed zinc performs well as an ICCP anode but the service life of the zinc anode is directly related to the average current density used to operate the systems.

After a ICCP system is turned off, the rebar in the concrete remains passive and protected for a period of time. Intermittent operation of CP systems is possible when continuous corrosion rate monitoring is used to identify conditions when the CP system needs to be turned on to reestablish protection conditions for the rebar. This approach applies CP protection only when needed and reflects the fact that external protection may not be needed for a range of environmental conditions. In doing so, intermittent CP would lower the average current necessary to protect rebar, increase the anode service life, and reduce the lifetime costs for protecting reinforced concrete bridges.

Keywords: cathodic protection, zinc, corrosion, reinforced concrete bridges, chloride

INTRODUCTION

Cathodic protection is the primary means currently used for reducing or halting corrosion damage to steel reinforced concrete structures in the high chloride environments found on bridges along the Oregon (USA) coast and bridges where deicing salts are used. Thermal sprayed metal anodes are effective distributors of current to rebar in CP systems, both to protect the rebar cathodically and to retard migration of corrosive chloride ions to the rebar. Ongoing Oregon Department of Transportation (ODOT) sponsored research [1-6] has demonstrated that the service life of thermal sprayed metal anodes on coastal bridges is critically dependent upon interactions with the bridge environment. Atmospheric moisture is important in the anode reactions, in the maintenance of electrical conductivity across the anode-concrete interface, and in the dispersion of reaction products away from the anode before they can interfere with charge transport, with properties of the cement paste, or lead to delamination of the anode.

Research has also shown that the service life of anodes is limited by the total charge passed by the anodes (electrochemical age) and by the time available for anode reaction products to disperse from the anode-concrete interface. As used by ODOT, the service life of TS zinc anodes in ICCP systems may exceed 25 years [1-3, 6].

Rebar does not typically corrode in the high pH (pH 12-13) environment of chloride- and

carbonate-free concrete. At pH 13, a thin passive film of Fe_2O_3 and Fe_3O_4 protects iron. Surface Enhanced Raman Spectroscopy studies [7] have shown that Fe_3O_4 and $Fe(OH)_2$ are present on the rebar surface at E_{corr} and at cathodic potentials in simulated pore water solution (SPS) at pH 13. Typical reactions [8] for iron oxide formation are:

$$3Fe + 4H_2O = Fe_3O_4 + 8H^+ + 8e \qquad (1)$$
$$2Fe_3O_4 + H_2O = 3Fe_2O_3 + 2H^+ + 2e \qquad (2)$$
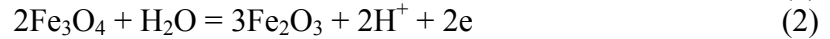
The high pH of concrete associated with hydration of Portland cement is usually sufficient to keep the protective film stable. However, chloride ions break down the protective passive film resulting in acceleration of corrosion [9-10]. Active dissolution of iron [10] proceeds in accordance with the following reaction:

$$Fe = Fe^{2+} + 2e \qquad (3)$$

This reaction is followed by hydrolysis reactions and further oxidation reactions, such as eqns 1 and 2, that decrease the pH at the rebar-concrete interface.

As a result, the rebar becomes increasingly susceptible to corrosion. Cathodic protection can be applied to reinforced concrete structures to protect rebar from corrosion. In doing so, passivation due to re-alkalization of the rebar-concrete interface can take place according to the following equation:

$$2H_2O + O_2 + 4e = 4OH^- \qquad (4)$$

Intermittent CP (ICP) can both reduce the average current needed to protect rebar in concrete structures and lengthen the time available for anode reaction products to disperse into the concrete. During the ICP "off" period, chloride ions present in the concrete disrupt the passive film to accelerate the corrosion reaction, lower the rebar-concrete interfacial pH, and move the iron potential into the corrosion region. Under these conditions, the corrosion current will increase, eventually requiring the re-application of ICCP to the rebar. During the ICP "on" period, the rebar is cathodically polarized and the pH will gradually increase. The effect of successful application of ICP will be a net decrease in the average current density for the CP system and as associated increase in the service life of zinc anodes protecting Oregon's bridges.

The objective of this study is to determine the technical basis, reliability, and effectiveness of intermittent cathodic protection for protecting reinforced concrete bridges and to provide design and operating guidelines for its application. The U.S. Department of Energy, Albany Research Center, in collaboration with the Oregon Department of Transportation, in performing the research in three phases: (1) evaluate corrosion rate measuring and monitoring instrumentation, (2) develop a fundamental understanding of the operation of intermittent cathodic protection, and (3) conduct a field trial of a fully integrated remote-monitoring, thermal-sprayed-zinc-anode intermittent CP system. In this paper, the monitoring of rebar corrosion in simulated concrete pore water, simulated concrete pore water plus sand, and in concrete is discussed.

EXPERIMENTAL

Electrochemical and gravimetric experiments were performed to measure corrosion rates of

rebar. The rebar was No. 12, Grade A615, reinforcing steel rebar furnished by ODOT with a yield strength of 460 MPa (66 ksi). The chemical composition is shown in Table 1.

Table 1. Chemical composition of Grade A615 reinforcing steel.

Element	C	Mn	Si	Cu	Ni	Cr	Mo	P	Fe
weight %	0.31	1.36	0.25	0.41	0.14	0.081	0.27	0.013	bal

Experiments were conducted in the solutions shown in Table 2. The basic solution was a simulated pore water solution (SPS) with a pH of 13. Linfang and Sagués [11] proposed the SPS as representative of the chemistry of fluids present in the pores of concrete bridge substructure elements. Modifications of this pH 13 solution were made by the addition of 0.5 and 1M Cl, as would occur on bridges exposed to salt deposition along marine coastlines. Two pH 7 solutions were prepared with nominal chemistries of 0.5 and 1.0 M Cl, by adding NaCl, KCl, and $CaCl_2$. Measurements were made in solutions deaerated with nitrogen and aerated with oxygen, and in quartz sand saturated with these solutions

Table 2. Simulated pore water solution compositions.

Solution	PH	Cl conc.	NaOH	KOH	Ca(OH)$_2$	NaCl	KCl	CaCl$_2$
		M	gms/liter					
SPS	13	0.0003	8.33	23.3	2.0			
SPS + 0.5 M Cl	13	0.49	8.33	23.3	2.0	29.2		
SPS + 1.0 M Cl	13	0.99	8.33	23.3	2.0	58.5		
(Na,K,Ca)Cl (0.5 M Cl)	7	0.54				17.0	15.5	1.5
(Na,K,Ca)Cl (1.0 M Cl)	7	1.32				34.0	31.0	3.0

Gravimetric Experiments

Samples cut from rebar were degreased and polished to a 240-grit finish on SiC paper for gravimetric measurements. The tests were conducted in Erlenmeyer flasks with extended necks and condensers. The solutions were deaerated with N_2 or aerated with O_2. A temperature of 25^{0}C was maintained by immersing the flasks in a circulating water bath. Triplicate samples were suspended by Teflon thread to permit full exposure of the samples to the test solution. Each flask held 1000 ml of "solution only" or "solution + sand." Samples were exposed for 108 days (N_2) and 126 days (O_2). After exposure, the samples with visible corrosion layers were first rubbed with a rubber stopper to gently remove corrosion product. Additional corrosion product was chemically removed by immersion in a 50% HCl solution containing 0.35% Rhodine 95 inhibitor for 2 to 4 minutes, rinsed with distilled water, then methanol, and dried with a heat gun. Samples were weighed before and after exposure to accuracy of 0.1 mg.

Potentiodynamic Polarization Experiments

Potentiodynamic polarization experiments in solutions without sand were conducted at room temperature in a flat cell connected to a two-liter reservoir through a peristaltic pump. The solution was circulated between the flat cell and the reservoir. The experiments in sand were conducted in a typical 1 L polarization cell. All potentials were measured versus a saturated calomel electrode (SCE). Platinum was used as the counter electrode. Samples were flat pieces cut from rebar with an area of 1 cm^2 exposed to the solution. Samples were ground to a 240-grit finish on SiC paper prior to each experiment. Samples were exposed to the test

solution at open-circuit for 30 minutes prior to beginning the polarization experiment. The potentiodynamic polarization measurement was made at a rate of 0.167 mV/s in the anodic direction starting at potential 300 mV more negative than the open circuit (or corrosion) potential, E_{corr}. The scan was terminated at a potential 600 mV positive to E_{corr}. The linear portion of this polarization curve, approximately $\pm$ 15 mV of E_{corr}, was fit linearly to determine the R_p [12]. The R_p was then converted to the corrosion current using a B value of 26mV and the corrosion current value was converted to corrosion rate using Faraday's law.

Polarization Resistance: Long-term

Polarization resistance measurements were used to take corrosion rates over a three-month exposure period. These electrochemical experiments were made in SPS plus sand and conducted in a typical 1 L polarization cell. All potentials were measured versus a saturated calomel electrode (SCE). Platinum was used as the counter electrode. Samples were flat pieces cut from rebar and embedded in epoxy with an exposed area of 5.13cm^2. The samples were ground to a 240-grit finish on SiC paper prior to each experiment. The samples were exposed to the test solution at open-circuit for 30 minutes at the beginning of an experiment. Then polarization resistance measurements were made with laboratory instruments –25 mV to +25 mV vs. E_{corr} at a scan rate of 0.167 mV/s. Polarization resistance measurements were also made using a commercial corrosion rate monitoring device (CRMD) that measured E_{corr}, and R_p. The R_p values were converted to corrosion currents using a B value of 26mV. Corrosion current values were then converted to corrosion rate using Faraday's law.

Intermittent Cathodic Protection (ICP)

Cylindrical concrete samples were cast from a mortar mix with sand as fine aggregate, no large aggregate, no air, and a water/cement ratio of 0.5. The cylinders contained 3 kg Cl/m^3 (5 lbsCl/yd^3) of concrete. The steel rebar was located on the cylinder axis. The cylinders received a 28 day cure in a moist room before corrosion measurements. The cylinder ends were masked off with epoxy paint to prevent end effects. Counter electrodes were made from galvanized steel conduit sections 10.2 cm (4 in.) in diameter. Sponges were used to make contact between counter electrodes surrounding the cylinders and the concrete surfaces. They kept the concrete wet but not saturated and allowed oxygen to diffuse into the concrete. Sponges were initially wetted with the SPS solution to maintain current flow, but subsequent moistening was done with water. Potential measurements were made versus a saturated copper/copper sulfate electrode (CSE). In these first experiments, the cylinders were exposed to a simple regimen of unmonitored impressed current intermittent cathodic protection. This involved polarizing the rebar cathodically for 24 hours at a current density of 1.1 A/cm^2 (based on the rebar surface area), then 24 hours of open circuit depolarization. Fifteen cycles of polarization and depolarization were conducted.

RESULTS

Gravimetric Experiments

Rebar corrosion rates for the gravimetric experiments in solution and solution plus sand are shown in Table 3. Corrosion rates ranged from 0.001 to 20 mils per year (mpy). The corrosion rates in solutions of SPS, SPS + 0.5M Cl, and SPS + 1M Cl at pH 13 were low and the rebar was essentially passive in N$_2$ deaerated and oxygenated solutions. Corrosion rates were also low for rebar embedded in sand. At pH 7, the rebar the corrosion rates were higher

in oxygenated solutions than in N_2 deaerated solutions. Corrosion rates were significantly lower when the rebar was embedded in the sand.

Potentiodynamic polarization

Electrochemical corrosion rates computed from the corrosion current measured by potentiodynamic polarization are shown in Table 3. While the corrosion rate values measured by electrochemical methods were substantially higher than by gravimetric methods, the trends were similar. Corrosion rates at pH 13 were low in the solution only and solution plus sand in both N_2 deaerated and oxygenated conditions. At pH 7, the rebar exhibited measurable corrosion under all exposure conditions. Corrosion rates were significantly higher in oxygenated solutions than in N_2 deaerated solutions. Corrosion rates were lower when the rebar was embedded in the sand. The reduction was about 10-fold for N_2 deaerated solutions and about 100-fold for oxygenated solutions. When rebar was embedded in sand, the corrosion rate in N_2 deaerated solution at pH 7 was only marginally higher than that in the pH 13 solutions.

Table 3. Rebar corrosion rates for rebar measured gravimetrically and electrochemically.

Solution	pH	N_2		O_2	
		solution	solution + sand	solution	solution + sand
Gravimetric corrosion rates, mpy					
SPS	13	0.001	0.017	0.002	0.003
SPS + 0.5 M Cl	13	0.002	0.001	0.006	0.005
SPS + 1.0 M Cl	13	0.010	0.004	0.019	0.009
(Na,K,Ca)Cl (0.5 M Cl)	7	1.011	0.179	17.7	0.284
(Na,K,Ca)Cl (1.0 M Cl)	7	0.648	0.113	12.8	0.440
Electrochemical corrosion rates, mpy					
SPS	13	0.12	0.12	0.41	0.09
SPS + 0.5 M Cl	13	0.30	0.25	0.33	0.20
SPS + 1.0 M Cl	13	0.25	0.16	0.31	0.18
(Na,K,Ca)Cl (0.5 M Cl)	7	4.7	0.62	157	2.5
(Na,K,Ca)Cl (1.0 M Cl)	7	4.1	0.52	234	1.3

Polarization Resistance: Long-term

Polarization resistance was used to measure corrosion rates over a three-month exposure period in SPS, (Na, K, Ca)Cl +0.5 M Cl, and (Na, K, Ca)Cl +1.0 M Cl with sand. The measurements were made using a potentiostat and a corrosion rate measuring device (CRMD). The measurements were made in N_2 deaerated and oxygenated solutions plus sand. Corrosion potentials, corrosion currents, and corrosion rates at the end of the 3 month exposure are shown in table 4. The corrosion current and corrosion rate in oxygenated SPS at pH13 was the lowest and the corrosion potential the most passive. Corrosion rates for all the N_2 deaerated and oxygenated solutions at pH 7 were higher than at pH 13 and the corrosion potentials more active. Corrosion rates were higher in the oxygenated solutions than in N_2 deaerated solutions.

Table 4. Comparison of corrosion data measured by laboratory instrumentation and by a commercial CRMD after 3 months exposure.

| Solution + sand | pH | N₂ | | | O₂ | | |
| | | Laboratory instrumentation | | | | | |
		E_{corr}, Vsce	I_{corr}, :A/cm²	CR mpy	E_{corr}, Vsce	I_{corr}, :A/cm²	CR mpy
SPS	13	NA	NA	NA	-0.111	3.63	1.68
(Na,K,Ca)Cl)0.5 M Cl)	7	-0.720	17.3	7.99	-0.678	22.3	10.3
(Na,K,Ca)Cl (1.0 M Cl)	7	-0.636	13.4	6.19	-0.621	42.2	20.8
		Commercial CRMD					
SPS	13	NA	NA	NA	-0.117	3.10	1.43
(Na,K,Ca)Cl (0.5 M Cl)	7	-0.717	15.8	7.32	-0.679	15.8	9.27
(Na,K,Ca)Cl (1.0 M Cl)	7	-0.608	26.5	9.72	-0.617	26.5	12.5

Intermittent Cathodic Protection

Fig. 1 shows that as the rebar in the concrete cylinder is polarized by ICCP, the potential to shifted in the cathodic direction from -0.25 to –0.5 V vs CSE. When the current was turned off, the potential became more active.   As long as the concrete was kept moist, the off and on cycles of the applied current fluctuated between –0.5 and –0.25 V vs CSE.   When the concrete began drying out, the potential range shifted to more negative potentials.
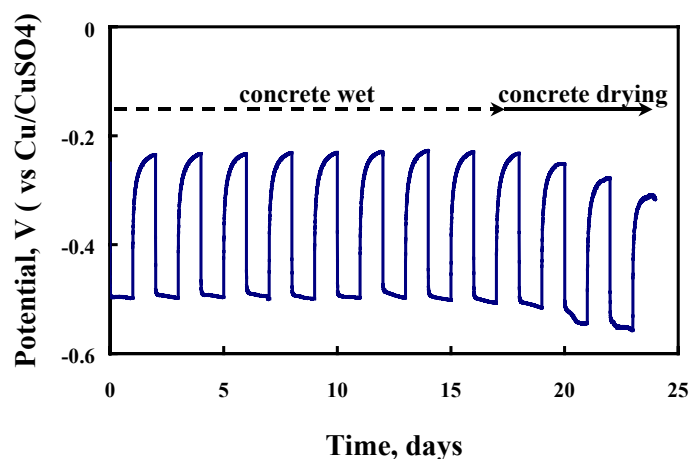

Fig. 1 - The off and on cycles of an applied current to a rebar in a concrete cylinder.

DISCUSSION

Potentiodynamic polarization curves for rebar in N₂ deaerated solutions of the simulated pore solutions are shown in Fig. 2. The decrease in pH and increase in chloride concentration shifted the corrosion potential in the active direction. At pH 13, the rebar specimens exhibited passive behavior and at pH 7 active behavior. Potentiodynamic polarization curves for rebar in O₂ oxygenated solutions of all the simulated pore solutions are shown in Fig. 3. Passive behavior was observed for the rebar polarization curves in oxygenated solutions at pH 13 with essentially the same passive currents for each of the solutions. The curves show that rebar was passive in pH 13 solutions regardless of chloride concentration. The curves show similar behavior at pH 7. The corrosion potential remained the same regardless of pH and chloride concentration in oxygenated solutions.

Table 3 shows that the corrosion rates in solution plus sand are considerably lower than in solution only. This apparently was due to the more restrictive transport of reactants to and from the rebar, particularly the elimination of convective transport, when the rebar was embedded in the sand.   Table 3 also shows that the corrosion rates measured order of
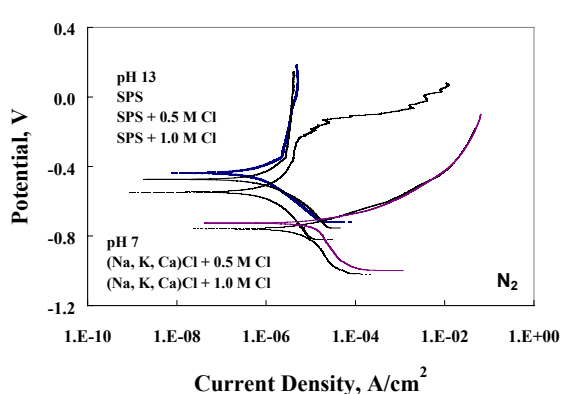
Fig. 2 - Polarization curves in N$_2$ deaerated simulated pore solutions at pH 13 and 7.
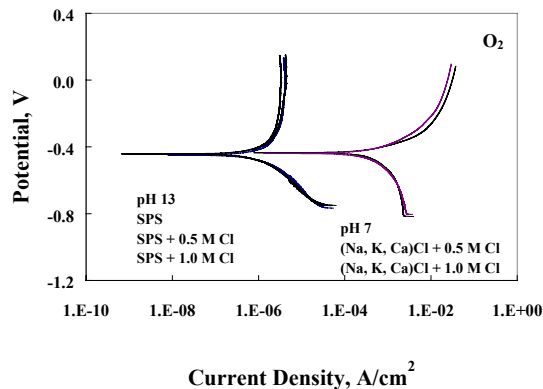
Fig. 3 - Polarization curves in oxygenated simulated pore solutions at pH 13 and 7

electrochemically were an magnitude higher than those gravimetrically. The difference in corrosion rates measured by the two methods is probably due to the surface condition of the samples at the time the measurements were made.

Electrochemical measurements were made within hours after sample surfaces were polished and represented an initial corrosion rate. Gravimetric measurements were determined in three-month exposures and represent the average corrosion rate over that period. Accumulated corrosion products over the three-month mass loss exposure can substantially reduce the average corrosion rate compared to the initial corrosion rate if the corrosion products are even partially protective. However a linear relationship exists between corrosion rates measured by the two techniques above a corrosion rate of 0.01 mpy as measured gravimetrically. This relationship suggests that linear polarization can be used on coastal bridges to monitor the condition of rebar during intermittent cathodic protection and determine when the ICCP system should be energized to return rebar to a protected state

Polarization Resistance: Long-term

Linear polarization was used to measure corrosion rates over a three-month exposure period identical to that used in the mass loss experiments. These corrosion rates are shown in table 4 at the end of the 3 month exposure period. Although the corrosion rates are lower than those determined by potentiodynamic polarization, they are not as low as those measured gravimetrically. The corrosion rates showed little change over time in both N^2 deaerated and O^2 oxygenated solutions. Table 4 also shows that the corrosion rates determined by laboratory instrumentation and the commercial CRMD are in good agreement. The CRMD is to be used in a field trial to control and monitor intermittent CP on a coastal bridge using the ODOT onsite data transmission infrastructure

Intermittent Cathodic Protection

The 24 hour off cycle for the rebar in the concrete cylinder may also be considered a 24 hour depolarization measurement (Fig. 4). Depolarization measurements are used to measure how effectively the CP system is protecting the rebar from corrosion. The depolarization standard of 100 mV in 24 hours or less is commonly used to indicate adequate protection of the rebar from corrosion. All potential decay measurements were greater than 200 mV after 24 hours for each of the 15 cycles of the test. This indicates more than adequate protection of the rebar in the chloride-contaminated concrete. A similar level of protection continued as the concrete

began to dry. The simple intermittent CP regimen described here was equivalent to reducing the anode current density by half. In long-term service, such a result could double the zinc anode service life.
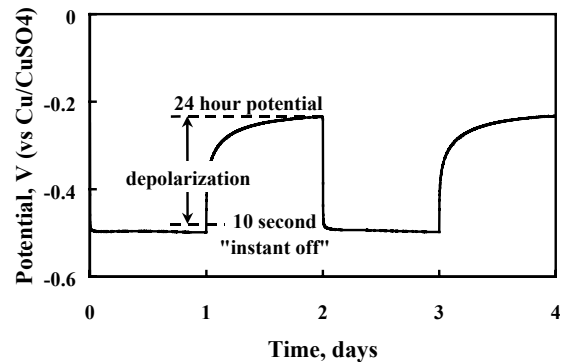
CONCLUSIONS

Fig. 4 - Twenty-four hour depolarization of rebar.

☞Rebar was passive in N_2 deaerated and oxygenated pH 13 pore water and sand saturated with pore water solutions regardless of chloride concentration.

☞Rebar readily corroded in N_2 deaerated and oxygenated pH 7 pore water solutions at chloride ion concentrations of 0.5 to 1.0 M Cl. In sand saturated with pore water solution, the corrosion rates decreased by orders of magnitude because of the restricted transport of reactants to and from the rebar surface.

☞Polarization resistance measurements by the CRMD were equivalent to those made using laboratory instruments.

☞Polarization resistance measurements showed very little change over a 3-month period.

☞A simple unmonitored intermittent CP regimen provide adequate protection of the steel in chloride-contaminated concrete while reducing by half the anode current density. In long term service this result could double the zinc anode service life.

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