CORROSION BEHAVIOR OF REBAR FOR INTERMITTENT CATHODIC PROTECTION OF COASTAL BRIDGES

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ABSTRACT

A number of reinforced concrete bridges on the Oregon coast are protected against chloride-induced corrosion damage by means of impressed current cathodic protection (ICCP). Thermal-sprayed Zn serves as the anode in these systems. Rebar in the concrete can remain passive and protected for some period of time after the CP system is turned off. The active-passive corrosion behavior of rebar in simulated pore solution (SPS) was investigated as a function of pH and Cl^- concentration as part of a study of intermittent ICCP operation. Rebar corrosion rates in SPS were determined from polarization curves by fitting the Butler-Volmer equation and the linear polarization equation. Analysis of the passive film in SPS by x-ray diffraction and surface enhanced Raman spectroscopy showed it to be largely Fe_3O_4. However, the $Fe(OH)_2$ content increased with cathodic polarization time.

INTRODUCTION

Corrosion of rebar in concrete is a major problem in highway bridges located in coastal environments and where deicing salts are used. Rebar does not typically corrode in the high pH (pH 12-13) environment of chloride- and carbonate-free concrete. A thin passive film of iron oxide is formed on the steel surface. The high pH of concrete associated with hydration of the Portland cement is usually sufficient to keep the protective film stable. However, under these conditions, a sufficient concentration of chloride ions in the concrete (the chloride ion corrosion threshold) can cause the rebar to corrode.[1,2] Carbonates in the concrete, formed from atmospheric carbon dioxide, can also cause rebar corrosion but at a slower rate than typically associated with chlorides.[3] The Oregon Department of Transportation (Oregon DOT) is using thermal-sprayed zinc anodes for impressed current cathodic protection (ICCP) systems on a number of reinforced concrete coastal bridges to prevent further chloride-induced corrosion damage.[4-9]

Literature data suggest that rebar in concrete can remain passive and protected for a period of time after the ICCP system is turned off.[10] The U. S. Department of Energy, Albany Research Center, in conjunction with the Oregon DOT, is conducting research to determine the feasibility and effectiveness of intermittent cathodic protection for protecting reinforced concrete structures. A goal of this research is to extend the service life of the zinc anode ICCP system. This paper presents early results from the research on the corrosion behavior of rebar in SPS using electrochemical and surface analytical techniques.

EXPERIMENTAL PROCEDURES

The electrochemical experiments were performed on Grade A615 reinforcing steel furnished by Oregon DOT. These rebar have a yield strength of 460 MPa (66 ksi). The chemical composition of the steel 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

The electrochemical experiments were conducted in a flat cell connected to a one liter reservoir through a peristaltic pump. A solution was circulated between the flat cell and the reservoir. All potentials were measured versus a saturated calomel electrode (SCE). Platinum was used as the counter electrode. Specimens were flat pieces with an area of 1 cm^2 exposed to the solution. Before each test, the specimen was polished with 600 grit SiC paper. Prior to each experiment, the surface of each specimen was reduced by applying a cathodic potential 300 mV more negative than the open circuit potential, E_{corr}, for 30 minutes.

The experiments were conducted in a solution of 8.33 g/l NaOH, 23.3 g/l KOH, and 2 g/l $Ca(OH)_2$, i.e., the SPS. The composition of SPS was proposed by Linfang and Sagués[11] to represent the chemistry of fluids present in the pores of concrete bridge superstructure elements. Two other solutions were used in this research based on SPS and containing chloride ions: SPS + 0.5*M* NaCl and SPS + 1*M* NaCl. All experiments were performed at room temperature, and run in triplicate to ensure experimental reproducibility.

Polarization curves were determined in potentiodynamic experiments where the potential was scanned at rates of 10 and 100 mV/min in the anodic direction from a cathodic potential 300 mV more negative than E_{corr}. Corrosion rates were determined from the polarization curves at 10 mV/min in two ways: (1) fitting the Butler-Volmer equation to the non-linear polarization data; and (2) fitting the linear polarization equation to polarization data at potentials ± 15 mV to E_{corr}.[12] Faraday's law was used to convert the corrosion current to a penetration rate.

Raman spectra were obtained on rebar samples in-situ in SPS and SPS + 0.5*M* NaCl as a function of applied potential and time using a specially designed spectroelectrochemical cell and a Spex (Edison, NJ) Model 1877 Triple spectrometer. The 514.5-nm line of a Coherent (Santa Clara, CA) Innova 307 Ar ion laser was used for excitation and the detector was Princeton Instruments (Trenton, NJ) LN/CDD detector. The slit with was 400 μm and the typical exposure time was 100 s. Spectral analysis was performed using Galactic Industries (Salem, NH) Grams 386 software. The estimated uncertainity of the peak frequencies was ± $1 cm^{-1}$. Sample preparation procedures for Surface Enhanced Raman Spectroscopy (SERS) are discussed in several references. [13]

RESULTS AND DISCUSSION

The anodic polarization curves for rebar in the SPS, SPS + 0.5*M* NaCl, and SPS + 1*M* NaCl solutions are shown in Figure 1. In each of the solutions, the rebar specimens exhibited only passive behavior. Over the potential range of the measurements, the lowest current values were observed in the SPS solution. The addition of chloride ions to the SPS, as in SPS + 0.5*M* NaCl and SPS + 1*M* NaCl, increased the current values substantially. The current values for the two chloride-containing solutions were not greatly different from each other.

Corrosion rates for rebar in the solutions are given in Table 2. There was good agreement between corrosion rates computed from the Butler-Volmer equation and by linear polarization in the one case where this was done. The values of corrosion rate increased substantially with increasing chloride concentration, doubling going from 0 to 0.5*M* NaCl and doubling again going to 1*M* NaCl. The corrosion rate measured for rebar in the SPS+1*M* NaCl solution is comparable to the corrosion rate for low carbon steel in a solution containing 13 wt % KOH and13 wt % KCl reported in the literature as 0.013 mm/yr (0.5 mpy).[13]

Table 2. Corrosion rates for rebar in SPS with and without chloride ions.

Solution	**Corrosion rates, mm/yr (mpy)**	
	Butler-Volmer equation	**linear polarization equation**
SPS	2.9×10^{-3} (0.12)	2.5×10^{-3} (0.10)
SPS + 0.5*M* NaCl	6.6×10^{-3} (0.26)	--
SPS + 1*M* NaCl	12×10^{-3} (0.47)	--

X-ray diffraction (XRD) analysis confirmed the presence of the oxide films formed in the potentiodynamic experiments. The result obtained for the film formed in the SPS +0.5*M* NaCl solution indicated that magnetite, Fe_3O_4, was present on the steel surface, Figure 2. Magnetite is a protective oxide film. According to the potential-pH diagram for the Fe-H_2O system,[14] magnetite forms at the high pH values typically present in concrete and the SPS, Figure 3. Kinetics of protective films are usually controlled by concentration polarization. Figure 4 shows the effect of the scan rate on corrosion behavior of rebar in SPS + 1*M* NaCl. The current decreased with decreasing scan rate in the passive region and E_{corr} shifted to more positive potentials. This indicates that diffusion of the species responsible for passivity is the slowest step and controls the passivation behavior of the rebar in SPS.

The electrochemical experiments were followed by scanning electron microscopic (SEM) examination of the oxidized steel surface. Figure 5 shows an SEM photomicrograph for rebar anodically polarized in SPS. The surface remained smooth as expected for a passive surface. Figure 6 shows an SEM micrograph for rebar anodically polarized in the SPS +1*M* NaCl solution. The rough surface texture is evidence of passive film breakdown, breakdown that disrupts the film that would normally protect the steel in the high pH solution. Passive film breakdown is responsible for the higher currents seen in the polarization diagrams for solutions containing chloride ions, Figure 1 .

Surface Enhanced Raman Spectroscopy (SERS) was applied to in-situ corrosion products on rebar specimens as a function of polarization and solution composition. Application of silver particles (1 minute) to the surface appreciably enhanced the Raman shift without evidence of changes in surface electrochemistry. The polarization experiments were performed in the following solutions: SPS and SPS + 0.5*M* NaCl. The polarization experiments were conducted at E_{corr} and at a cathodic potential -300 mV from E_{corr}. Additional experiments were conducted at anodic potentials of +250 mV vs SCE (saturated calomel electrode) and + 450 mV SCE.

The SERS studies showed that Fe_3O_4 and $Fe(OH)_2$ were present at cathodic potentials and at E_{corr} in both solutions. The Fe_3O_4 peak (670 cm^{-1}) was substantially more intense in SPS than in SPS + 0.5*M* NaCl. In both solutions, as the time of cathodic polarization increased, the Fe_3O_4 peak diminished in intensity and the $Fe(OH)_2$ peak (550 cm^{-1}) increased (Figure 7). The Fe_3O_4 and $Fe(OH)_2$ peaks disappeared altogether in SPS at anodic potentials leaving an unidentified peak at 430 cm^{-1}. In contrast, the Fe_3O_4 peak disappeared leaving the $Fe(OH)_2$ peak at anodic potentials in SPS + 0.5*M* NaCl.

FUTURE WORK

Three month gravimetric measurements have begun to determine the corrosion rate of rebar at open circuit potential E_{corr} as a function of solution composition (chloride concentration), aeration, pH, and with and without isolation in quartz sand. The quartz sand simulates to some extent the environment the steel will experience when embedded in concrete. The six test solutions are SPS, SPS + 1.0*M* NaCl, SPS + 0.5*M* NaCl, SPS (pH 7 using HCl), 1.0*M* NaCl (pH 7 using HCl), and 0.5*M* NaCl (pH 7 using HCl). Further gravimetric experiments will be run in concrete partially infused with the six tests solutions. The linear polarization constant B will be determined by combining the results from these measurements and those by potentiodynamic polarization to show how well linear polarization can measure the corrosion rate of rebar in concrete bridge superstructure elements.

CONCLUSIONS

- Rebar exhibits passive behavior in the SPS solution and the SPS chloride containing solutions.

- The passive film on the rebar is Fe_3O_4 and $Fe(OH)_2$, depending upon conditions of polarization.

- The corrosion rate of rebar increases with increase in chloride concentration, doubling going from 0 to 0.5*M* NaCl, then doubling again going to 1*M* NaCl.

- Passive film breakdown leading to a rough steel surface is responsible for the higher currents observed in the anodic polarization of the rebar in chloride-containing SPS.

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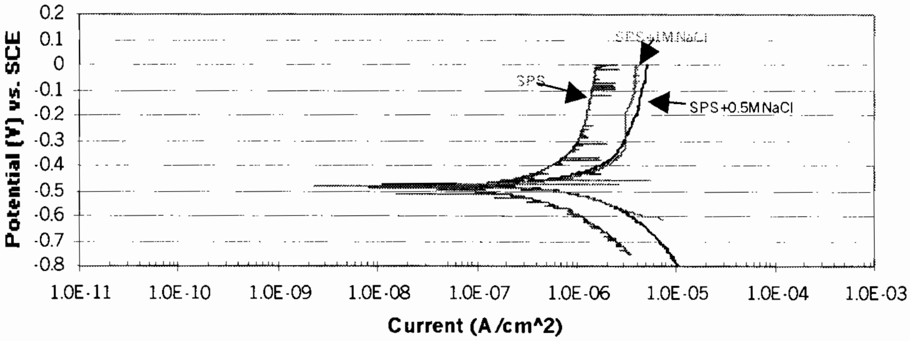

Figure 1. Anodic polarization curves for rebar in SPS, SPS+0.5M NaCl, and SPS+1.0M NaCl at 10 mV/min.

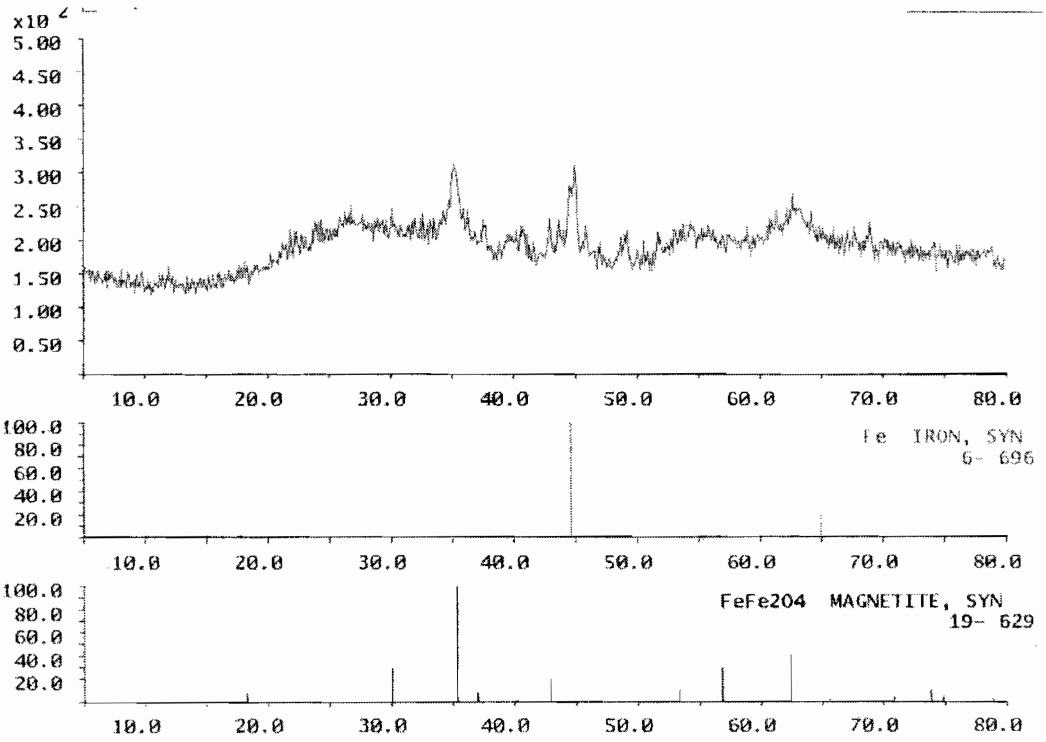

Figure 2. Results of X-ray diffraction analysis of passive film formed on rebar in SPS+0.5 M NaCl.

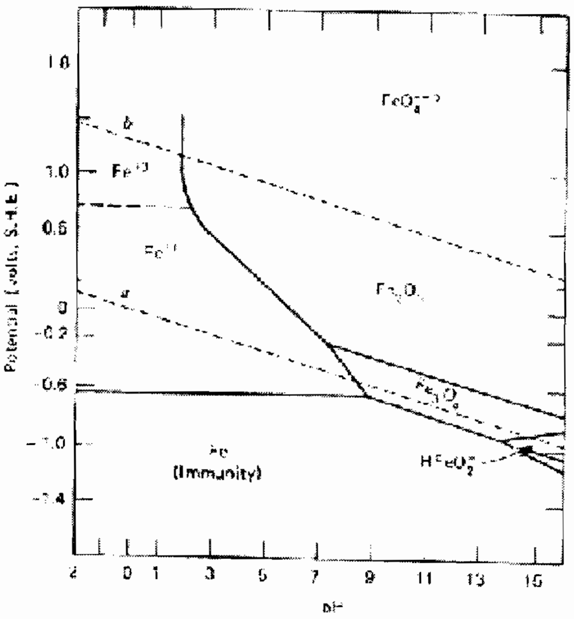

Figure 3. Potential – pH diagram for iron.

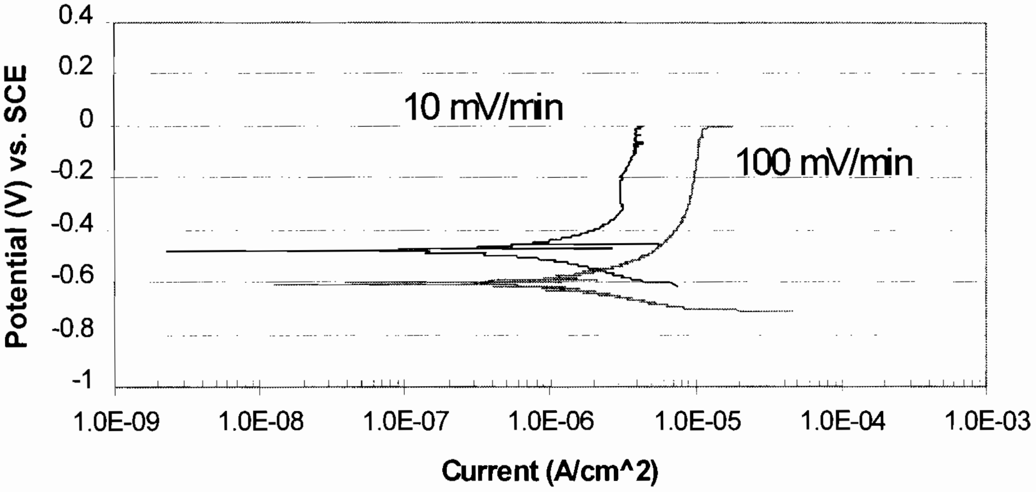

Figure 4. Anodic Polarization Curves for Rebar in SPS+1.0M NaCl at Scan Rates **of 10mV/min and 100mV/min**

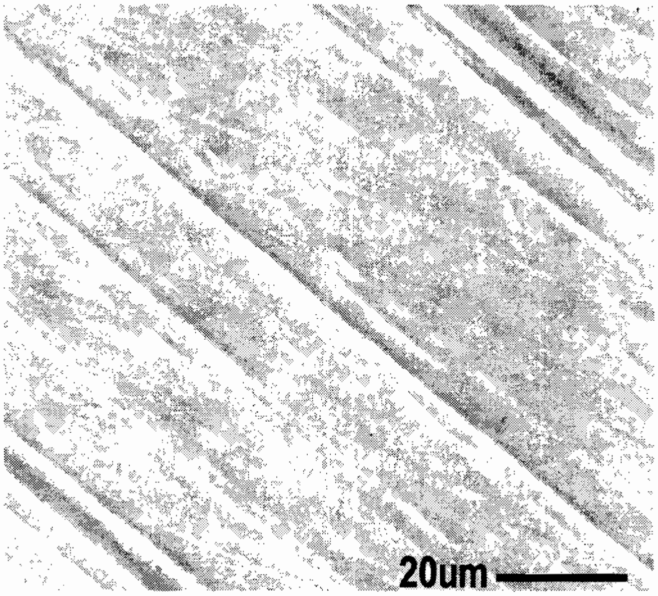

Figure 5. SEM Micrograph of Rebar Surface after the potentiodynamic experiment in SPS.

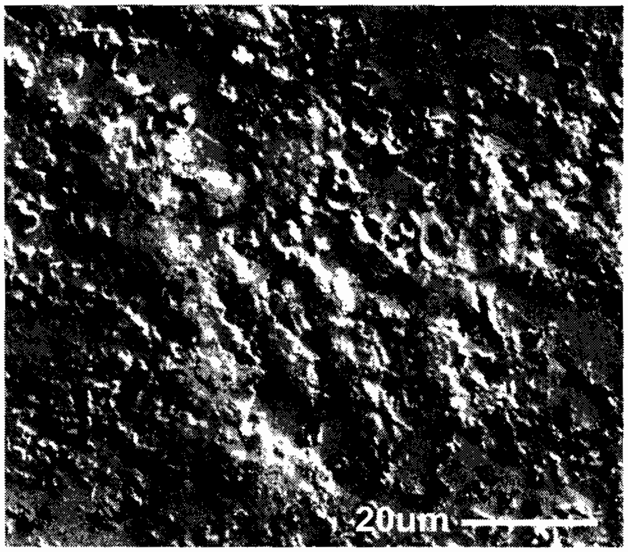

Figure 6. SEM Micrograph of Rebar Surface after the potentiodynamic experiment in SPS+0.5M NCl.

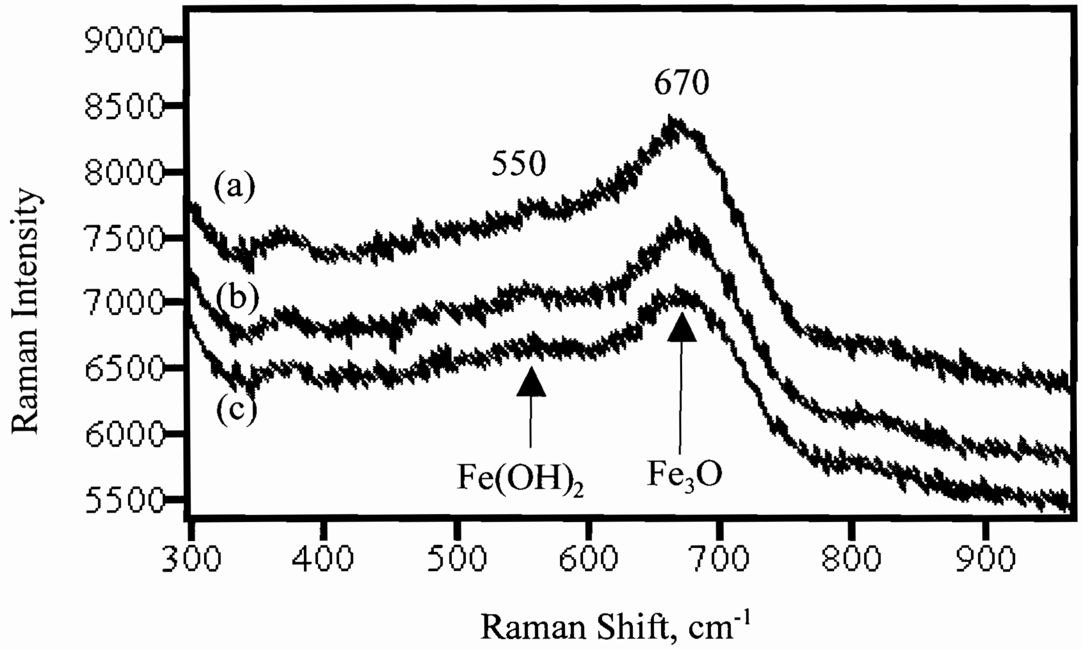

Figure 7 In-Situ Surfaced-Enhanced Raman Spectrum of Rebar Sample in SPS (a) at OCP, (b) after 300 s at -0.3 V_{OCP}, and (c) after 600 s at -0.3 V_{OCP}. Spectra show an increase in the Fe(OH)$_2$ band relative to the Fe$_3$O$_4$ bandwith increasing time of cathodic treatment.