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Investigation of the rapid chloride permeability test

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Distribution of Steady-State Cathodic Currents Underneath a Disbonded Coating[☆]

R. Brousseau and S. Qian^{*}

ABSTRACT

Pipeline corrosion frequently persists underneath disbonded coatings on pipelines that appear to be well protected cathodically. Application of higher cathodic potentials for improved protection may produce hydrogen gas (H₂) bubbles that block current flow underneath a disbonded coating. A project was undertaken to determine whether an increase in applied potential results in higher polarization levels on the crevice steel underneath a disbonded coating. With a higher applied potential, pH levels in a crevice should increase. Steady-state cathodic protection experiments were performed at three applied potentials in an electrochemical cell simulating the crevice steel under a disbonded coating. The recorded profiles showed that higher levels of protection underneath a disbonded coating could be achieved by applying higher cathodic potentials. Penetration of the cathodic currents underneath a disbonded coating also was more difficult in higher resistivity solutions.

KEY WORDS: cathodic protection, coatings, disbondment, hydrogen gas, pipeline corrosion, potential

INTRODUCTION

Buried or submerged pipelines usually are prevented from corroding by a combination of coatings and

cathodic protection. A coating has the basic function of isolating the steel pipe from a corrosive environment. Cathodic protection completes the defense system by preventing the electrochemical dissolution of iron (Fe) by changing its potential. This reduces the likelihood of corrosion at defective areas of the pipe coating. Proper cathodic protection can be achieved on exposed steel, but when the coating is disbonded, proper protection is hard to achieve in the void or crevice formed between the coating and pipe.

Toncre has recommended more negative potentials of cathodic protection to achieve adequate polarization beneath disbonded pipe coatings.¹⁻² This suggestion has been supported by Orton, who obtained polarization up to $-1,200 \text{ mV}_{\text{CSE}}$ 2 in. from a coating holiday when $-1.5 \text{ V}_{\text{CSE}}$ was applied to a test pipe.³ Charles obtained experimental data showing increased cathodic polarization when more negative potentials were applied.⁴

However, Fessler, et al., concluded that holiday potentials more negative than that required to form hydrogen (H₂) bubbles would cause difficulty in controlling the potential under the disbonded coating.⁵ This phenomenon is represented schematically in Figure 1. Cherry and Gould also have suggested that overprotection (e.g., a holiday potential of $-1,500 \text{ mV}_{\text{SCE}}$) is undesirable.⁶

With this information, it has been difficult to determine the proper approach to obtain adequate corrosion control on pipelines.

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FIGURE 1. H_2 bubbles formed on steel prevented OH^- ions from migrating underneath the disbonded coating.

The objective of the present work was to present additional experimental data to clarify that applying more negative potentials (up to $-1.5 V_{SCE}$) increases cathodic polarization underneath a disbonded coating.

EXPERIMENTAL

All experiments were performed in an electrochemical cell designed to simulate a crevice that is found frequently in the field between a disbonded

coating and a steel pipe (Figure 2). The cathode consisted of polished low-carbon (C) steel strips that were polarized simultaneously. The counter electrode was made with a high-grade platinum (Pt) mesh. Potential and pH measurements in the crevice were recorded using microelectrodes that were calibrated carefully before and after each experiment. All potential measurements were reported vs the saturated calomel reference electrode (SCE). A glass tube with a very fine tip was used as a luggin to extend the main reference electrode and reduce the ohmic voltage (IR) drop caused by the current concentrated at the crevice opening.

The test solution was made of distilled water and consisted of 5×10^{-4} M sodium bicarbonate ($NaHCO_3$), 5×10^{-4} M calcium chloride ($CaCl_2$), and 5×10^{-4} M tricalcium orthophosphate ($Ca_3[PO_4]_2$), unless specified otherwise. This solution was not bubbled with oxygen (O_2) or nitrogen (N_2) during the experiments.

To prevent any electrical loading by the measuring instruments on the microelectrodes, multimeters with an input impedance $> 10^{12} \Omega$ were used. Some time delay was required before measurements to ensure that the potentials were stabilized. The steady-state potentials were applied and controlled using a high-power potentiostat.

FIGURE 2. Schematic of the electrochemical cell simulating the crevice steel under a disbonded coating. Dimensions are in millimeters

(a)

(b)

(c)

FIGURE 3. Measured cathodic polarization along a simulated crevice with time when: (a) $-1.06 V_{SCE}$, (b) $-1.19 V_{SCE}$, and (c) $-1.5 V_{SCE}$ were applied at the crevice opening. Crevice depth: $\blacktriangle = 1.25$ in., $\circ = 4.25$ in., $\blacklozenge = 7.25$ in., $\circ = 10.25$ in., $+$ = 13.25 in., and $\times$ = 16.25 in.

FIGURE 4. Steel crevice potential after 250 h of cathodic polarization at the indicated voltages.

RESULTS AND DISCUSSION

Effect of Higher Applied Cathodic Voltages

The potential-vs-time profiles recorded by microelectrodes along a crevice are plotted in Figure 3. Three cathodic potentials were applied at the crevice opening (i.e., $-1.06 V_{SCE}$, $-1.19 V_{SCE}$, and $-1.5 V_{SCE}$). A rapid increase in cathodic polarization was evident in the first 80 h of the test period. The increase was more accentuated near the crevice opening. This was followed by a leveling of the potential to a constant value. The levels of polarization decreased with increasing distance from the crevice opening. Higher applied potentials promoted higher cathodic polarization along the entire crevice (Figure 4). Potential values were recorded after 250 h of cathodic polarization. Polarization increases with higher applied potentials were evident for all the steel segments, including those furthest from the crevice opening.

Effect of IR on Penetration of Cathodic Currents

Pipelines surrounded by a disbonded dielectric coating in high resistivity waters can be difficult to protect adequately by cathodic protection. A higher electrolyte resistivity will reduce the penetration depth of the cathodic currents underneath a disbonded coating because of the larger IR drops.

Two steady-state experiments with an applied potential of $-1.19 V_{SCE}$ were conducted using two solutions with different resistivities. The more concentrated solution described in the experimental procedure had a resistivity of $5,070 \Omega\text{-cm}$. The

(a)

(b)

FIGURE 5. Potential-vs-time profile along a crevice polarized at $-1.19 V_{SCE}$. The solution in (b) was 10 times more dilute than in (a).

second solution was 10 times more dilute, with a resistivity of $31,250 \Omega\text{-cm}$. Voltage time profiles are displayed in Figures 5(a) and (b). The cathodic polarization penetrated the crevice more easily when the resistivity of the solution was lowest.

Figure 6 shows the potential values recorded after 388 h of cathodic polarization for the two solutions. Results were in agreement with the observation that the cathodic currents also penetrated deeper in the crevice when the resistivity of the solution was lowest. These current readings were taken from the individual steel segments used to make up the steel cathode in the electrochemical cell (Figure 1). Because of the rather large spread of the values, two scales were used to display the data in Figure 7.

Crevice pH Changes During Cathodic Protection

When steel is polarized cathodically in aerated waters, the thermodynamically favored electrode reaction is O_2 reduction, which proceeds as:

FIGURE 6. Potential along a crevice after 388 h of cathodic polarization at $-1.9 V_{SCE}$. One of the solutions was 10 times more dilute than the one described in the experimental procedure.

However, when the applied voltage is more negative than $-1.2 V_{SCE}$, a competing reaction also can occur at an appreciable rate, particularly in the absence of O_2 . Then, H_2 is evolved according to the reaction:

These electrochemical processes involve the production of hydroxyl (OH^-) ions (i.e., a rise in pH).

In the present study, pH values rose much more rapidly to a plateau near the crevice opening than in deeper regions. The highest pH values were obtained near the opening and at higher applied cathodic potentials.

The pH profiles in a crevice were believed to depend strongly on the current densities, which were proportional to the rate of production of OH^- ions. The pH change in the crevice over time is plotted in Figure 8. The crevice coating in the experiments was impermeable to O_2 , which is not always the case on buried pipelines.

Although results in Figures 8(a) and (b) are rather erratic, a distinct progression of pH in the crevice with time is shown in Figure 8(c). The longer times involved for the increase in pH for the deeper areas also implied a certain amount of diffusion of the OH^- ions. The concentration gradient was such that OH^- ions built up at the opening slowly migrated away to eventually reach the deeper ends, as was found similarly by Payer, et al.⁷ However, it was anticipated that the rate of diffusion of the OH^- ions at

FIGURE 7. Current along segments of steel cathode after 388 h of cathodic polarization in the two solutions. Inset shows current on an expanded scale.

the end of a crevice would depend greatly on its geometry and the availability of O_2 . O_2 -permeable coatings might improve the capacity of cathodic protection to move the pH in the crevice into a passive region.

CONCLUSIONS

- ❖ Higher applied cathodic voltages were shown to induce a deeper penetration of the cathodic currents underneath a disbonded dielectric coating. However, excessive cathodic protection is not necessarily advisable because of the possibility of H embrittlement of the pipeline steel or cathodic disbondment of the coating system.
- ❖ Voltage drops as a result of IR always favored a higher proportion of the cathodic currents to be collected by the steel at the crevice opening.
- ❖ The cathodic currents penetrated less deeply under the disbonded coating in higher resistivity solutions.
- ❖ The chemical diffusion of the OH^- ions helped to increase pH in the more remote sections of a crevice.

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(a)

(b)

(c)

FIGURE 8. pH-vs-time profile of a simulated crevice under a disbonded coating when steady-state cathodic polarization was applied at: (a) $-1.06 V_{SCE}$, (b) $-1.19 V_{SCE}$, and (c) $-1.5 V_{SCE}$. Crevice depth: $\blacktriangle$ = 1.25 in., $\bigcirc$ = 4.25 in., $\blacklozenge$ = 7.25 in., $\circ$ = 10.25 in., $+$ = 13.25 in., and X = 16.25 in.