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CORROSION99

CURRENT DEMAND AS A RESULT OF COATING VOID TO INTACT COATING SURFACE AREA RATIO

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ABSTRACT

Previous research has suggested that a coated steel substrate can be cathodic to boldly exposed steel in seawater. As a result logic would suggest that the corrosion rate at defects in the coating would be a function of the coating to holiday surface area ratio. To examine this hypothesis four (4) surface area ratios were tested in natural seawater. These ratios are 3:1, 10:1, 136:1 and 1176:1 (coated to exposed steel). Coated panels were painted with a MIL-P-24441 epoxy barrier coating and electrically coupled to exposed steel. During testing the current between coated and uncoated samples was monitored along with the potential between the couple and a saturated calomel reference electrode (SCE). Testing has been conducted for over one year, with each area ratio showing interesting trends.

This paper discusses the current flow of each area ratio, and how it relates to the corrosion rate of exposed steel. Whether the corrosion is anodically or cathodically controlled, and to what extent, are evaluated. Finally, "real-world" applications of this type of analysis will be discussed.

BACKGROUND

Barrier coatings are commonly used for the protection of steel exposed to corrosive environments. With proper substrate preparation and application procedures a coating system can extend the life of metallic structures for many years. However, when voids are present in such systems (whether due to damage or poor application of the coating system) a localized, premature failure of the metal can occur. For critical systems (such as fuel or chemical pipelines) these localized failures are unacceptable.

While "small" defects have long been acknowledged as sites of increased corrosion rates, there has not been much consideration given to the effect of defect to coated area ratio on the corrosion rate of the exposed steel. An experiment was designed to investigate how differences in corrosion rates are influenced by changes in the coated to exposed steel area ratios.

The corrosion rate of a steel structure is determined by the DC current discharging from its surface into the electrolyte, which in is contact with it. From Ohm's Law, $V=I*R$, we see that the current is a function of the potential difference and circuit resistance. In the subject case, V, is simply the open circuit potential difference between the boldly exposed and coated steel. The resistance, R, is actually a combination of several resistance values, i.e. the coating resistance, the polarization resistance of the bare steel and the electrolyte resistance, all in series.

From previous testing on similarly coated panels the coating resistance has been found to be approximately 10^9 ohm-cm^2. The polarization resistance of the bare steel coupon is approximately 10^3 ohm-cm^2 and the electrolyte resistance (anode to electrolyte) is approximately 10^3 ohm-cm^2. Thus, in this case the are of coated steel would primarily control the circuit resistance.

The corrosion potential of steel in natural seawater (E_{corr}) is approximately -0.7 V versus SCE. Based on other testing, the corrosion potential of coated steel samples can approach 0.0 V versus SCE.[1] Using this (0.7 V) and the resistance value of the coating (10^9 ohm-cm^2), we can calculate for the current from Ohm's Law ($i=V/R$). This gives a current density, i, of 7E-10 A/cm^2 (per square centimeter of coated steel). Polarization or the build-up of corrosion products would also limit the actual current flow in the circuit.

EXPERIMENTAL PROCEDURE

Panel Preparation

For these experiments a bare steel coupon was prepared for each coated panel examined. This coupon was set in a metallographic resin electrically isolating the entire coupon except for a 0.5 by 0.5-inch (12.7 by 12.7-mm) area. Four sizes of panels were coated with a MIL-P-24441 epoxy. These panels measured 0.5 by 0.5-inch (12.7 by 12.7-mm), 1 by 1-inch (25.4 by 25.4-mm), 4 by 4-inch (102 by 102-mm) and 12 by 12-inch (305 by 305-mm) by 1/8-inch (3.18 by 3.18-mm) thick. Triplicates of each size were coated with the epoxy system. Prior to coating them, a lead wire was attached to each sample allowing for a direct electrical path to the substrate. Table 1 lists the number of replicates, coated and uncoated panel surface areas and area ratios.

TABLE 1
PANEL SURFACE AREA RATIOS

Sample Set	Replicates	Coated Area (inch)	Uncoated Area (inch)	Area Ratio (coated/uncoated)
1	3	0.75	0.25	3 to 1
2	3	2.50	0.25	10 to 1
3	3	34.0	0.25	136 to 1
4	3	294	0.25	1176 to 1

Exposure Testing

During testing, each panel was electrically coupled to a bare coupon and immersed in natural seawater. To avoid stagnation, the seawater was replenished by trickle in. The bare coupon attached to each panel represents a holiday formed through the panel's coating. By varying the size of the painted panel we can measure the effect coated steel structures of different areas have on this size holiday.

Throughout testing the potential of this couple was monitored versus a saturated calomel electrode (SCE) along with the current flowing between the bare steel and painted panel. A Keithly Electrometer, having an input impedance of 10 Tera-ohms (10^{13} ohms), was used to measure the couple potential. The same meter was used to measure current and is capable of measuring in the pico-amp (10^{-12} amp) range. Equipment of this sensitivity are necessary to avoid errors due to the high coating resistances and low current flow typical of corrosion circuits.

Polarization Testing

Following one-year of testing a single replicate of each area ratio was uncoupled and allowed to reach a stable potential (E_{corr}). Following stabilization a polarization scan was performed on both the bare steel coupons and coated steel panel. From the intersection of these scans the corrosion potential and corrosion current can be determined. All other samples remained in test.

Polarization testing on the bare steel samples was done using an EG&G Model 273 Potentiostat/Galvanostat. A linear polarization cure was run from E_{corr} to +150 mV from E_{corr}. This is referred to as an anodic curve since it moves from E_{corr} to a more electropositive potential, thus promoting corrosion.

Polarization testing of the painted steel coupons was performed using an experimental technique developed in-house by the authors. This method applies a current to a painted steel panel, immersed in an electrolyte, to obtain a desired potential. Potentials are varied from anodic to cathodic values, with the potential and current monitored at each set point. These data points are plotted on an E vs. I (potential vs. current) graph, from which the coating resistance can be calculated. A more detailed explanation of this method is found elsewhere.[1,2]

RESULTS AND DISCUSSION

Exposure Testing

During the first year of testing regular potential and current readings were taken. Figure 1 shows the average current (from triplicate sets) between the bare and coated steel. This shows that the cell current for larger panels is higher. Earlier the current density for a coated panel was calculated as 7E-10 A/cm^2. From maximum current seen at 100 days for the largest area panel, the calculated current density is approximately 3E-10 A/cm^2.

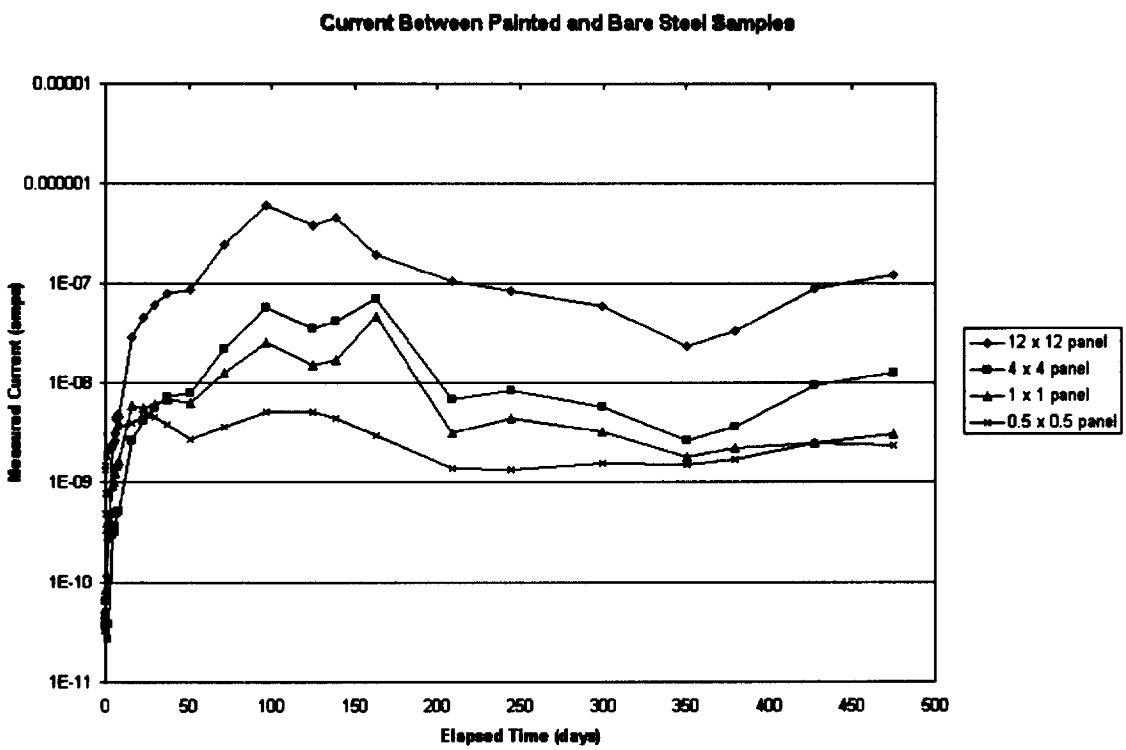

FIGURE 1 - Average Current Between Exposed and Coated Steel.

Considering the surface area of the bare steel coupon we can calculate the average current density at this surface. Figure 2 shows that the average current density on the bare steel coupons increases with painted surface area. The higher current densities with increasing bare to coated surface area ratios suggest increased corrosion rates of bare steel at coating holidays.

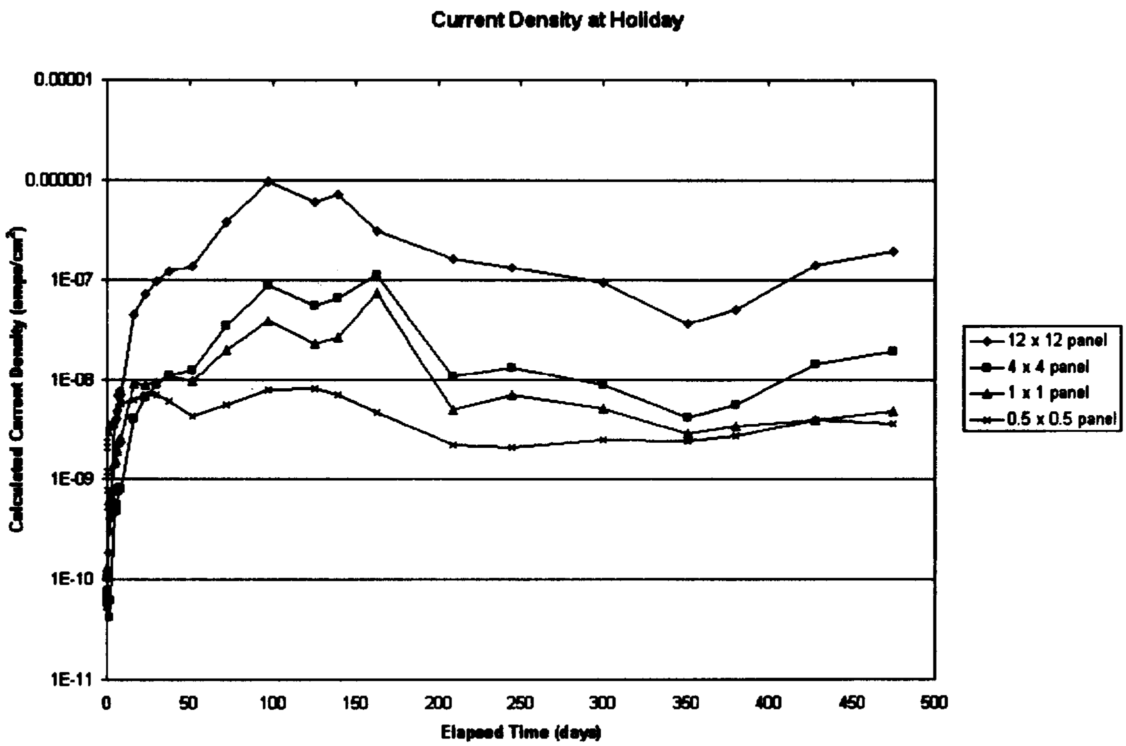

FIGURE 2 - Calculated Average Current Densities at Coating Holidays.

Polarization Testing

Figure 3 shows the anodic and cathodic polarization scans for one steel coupon and the 4 by 4-inch (102 by 102-mm) and 12 by 12-inch (305 by 305-mm) painted panels. Consider the intersection points of the 4 by 4 and 12 by 12-inch panels, we see that the current density increases as the area of the coated panel increases. This agrees with the mixed potential theory. This also confirms the results of the "galvanic" coupling measurements discussed in the previous section. The corrosion rate (which is a function of current density) of the holiday is directly proportional to the area of the intact coating. The corrosion rate is under cathodic control.

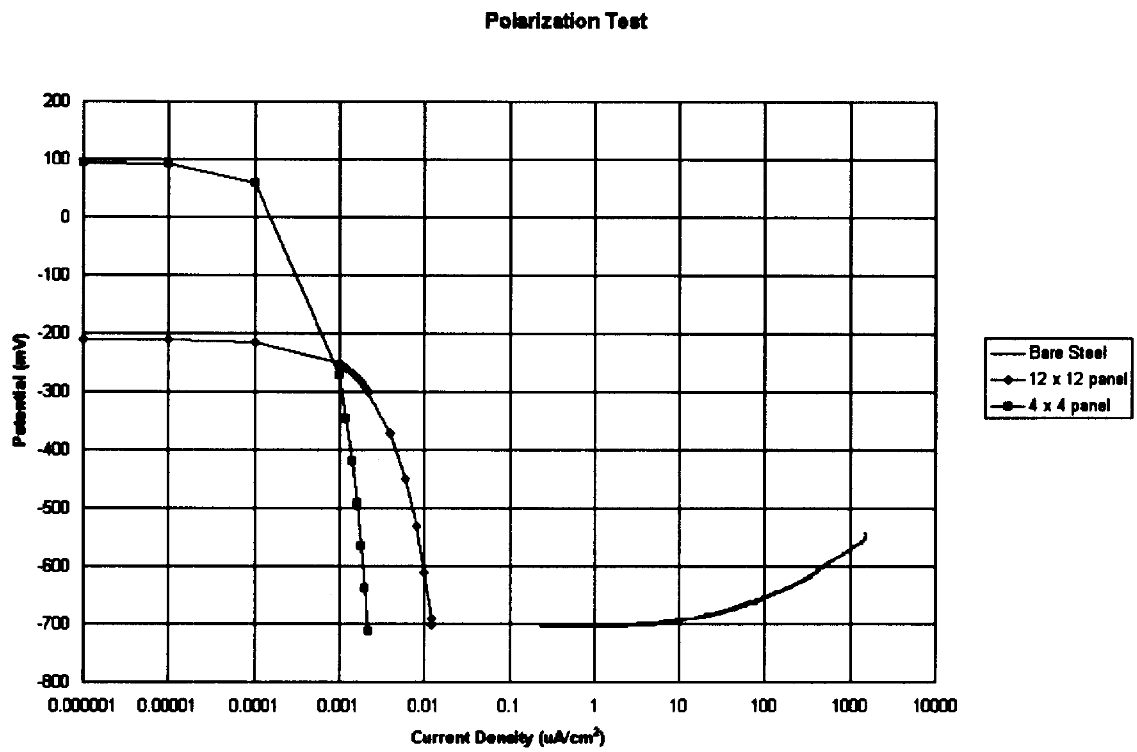

FIGURE 3 - Polarization Scans of Bare and Coated Steel.

In the subject testing the galvanic current flowing from the bare steel coupon equates to a corrosion rate of approximately 0.012-mpy at the highest current density (using the estimation of 1-mpy for every 1-$\mu A/cm^2$).[3] This is insignificant compared to typical steel corrosion rate of 5-10 mpy in seawater. However, consider the range of area ratios tested. The maximum cathode to anode area ratio was 1176:1. In an actual ballast tank of some 10,000-ft^2 (929-m^2) surface area, a holiday similar to that in the current program of 0.25-in^2 (162-mm^2) could theoretically see a cathode to anode area ratio exceeding 1,000,000:1. Casual observation of the above polarization data shows that the galvanic corrosion rate would increase three orders of magnitude. Eventually the corrosion rate would also tend to become limited by anodic polarization. Thus the galvanic corrosion rate should increase from approximately 0.012-mpy to exceed the local action rate. This remains to be confirmed through additional laboratory testing.

CONCLUSIONS

1. The electrochemical data obtained during this experiment supports the theoretical assumptions and calculation this experiment was designed to test.
2. Corrosion rates at coating holidays can be increased by galvanic interaction with the coated steel surfaces.
3. These findings should be considered in the design of coating undercutting experiments. The data may also explain high corrosion rates at holidays in large, otherwise well-coated tanks.

REFERENCES

1. K. Cramer, J. Ellor, J. Repp, "Novel Mothods for Evaluating Epoxy-Barrier Coatings for Seawater Service," U.S./Pacific Rim Workshop of Emerging Non-Metallic Materials for Marine Environments, Honolulu, HI, 1997.

2. J. Ellor, "Novel Coating Analysis Practices," Navel Sea Systems Command Corrosion Control Division (Code 03M1), December 1995.

3. Mars G. Fontana, Corrosion Engineering (New York, NY: McGraw-Hill Book Company, 1986), p. 464.