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ABSTRACT

Effective inhibition of a galvanic couple requires consideration of several factors. One factor is the presence of sufficient inhibitor to lower the potential of the galvanic couple. If an effective dose is being administered the corrosion rate of the anode in the couple will decline.

Various techniques were used to evaluate inhibitor effectiveness on the galvanic coupling of a corrosion resistant alloy, QT-16Cr80 to a high strength steel. This study consisted of two phases of electrochemical testing. The first phase of the testing was a potentiodynamic study of each metal individually, both inhibited and uninhibited. This involved employing linear polarization resistance (LPR) to determine the corrosion rate and a potentiodynamic scan to evaluate the pitting resistance of the alloys. The second phase involved a galvanic corrosion study using a zero resistance ammeter (ZRA) to measure the current between the two metals. In this technique the corrosion resistant alloy, Cr16 and the high strength steel were electrically connected and evaluated in both inhibited and uninhibited fluid. Visual inspection and weight loss were also used in evaluating the test specimens in all phases of the testing.

The test results showed that corrosion inhibition did not sufficiently reduce the effect of the galvanic couple.

INTRODUCTION

Alloys are sometimes specified to meet special mechanical or corrosion requirements in systems. This can create a potential for galvanic corrosion. Galvanic corrosion occurs whenever two dissimilar metals are electrically connected in a corrosive environment. The member of the pair which is lower in position in the galvanic series will suffer damage. Various electrochemical test methods can be used to experimentally determine the degree to which each member of the couple will corrode. We were asked to investigate methods of protecting a high strength steel HS-80, ASTM A606 Type 4 connected to a corrosion resistant alloy (austenitic stainless steel described as QT-16Cr80) coiled tubing in a well.

In this experiment electrochemical methods, in conjunction with gravimetric and visual analysis, were used to evaluate the galvanic coupling of QT-16Cr80 to HS-80 steel. Each alloy was tested with and without the addition of a continuous corrosion inhibitor. The first portion of the test was a potentiostatic study using linear polarization resistance (LPR) measurements to determine the natural corrosive behavior of each alloy individually. A potentiodynamic scan using cyclic potentiodynamic polarization (CPP) was then used to determine the pitting resistance of each of the alloys both inhibited and uninhibited. The second portion of testing involved a zero resistance ammeter (ZRA) study to evaluate the corrosive behavior of the alloys when coupled.

EXPERIMENTAL PROCEDURE

The experiments outlined employed the electrochemical techniques of linear polarization resistance (LPR), cyclic potentiodynamic polarization (CPP), and zero resistance ammetry (ZRA). The potentiostatic study used LPR measurements to measure the general corrosion rate of the test specimens. This technique involves monitoring the current response when a small potential is applied to the working electrode. The ratio of voltage to current yields the polarization resistance which is proportional to the corrosion rate.

In the potentiodynamic scan CPP is employed by applying a large potential to the electrode to determine the pitting resistance of the alloy. The free corrosion potential (E_{CORR}) is the potential of the specimen under freely corroding conditions. The potential at which the pits initiate on the forward scan is referred to as the pitting potential (E_{PIT}). The potential at which pits (if they occur) passivate on the reverse scan is referred to as the protection potential (E_{PROT}).

The last electrochemical test method used was the ZRA scan which was used to determine the behavior of the alloys when electrically coupled. The current flow between two dissimilar metals is measured when immersed in the same solution. The current measured is proportional to the rate of the reduction reaction on the surface of the anodic member in the couple.

In addition to these electrochemical methods, weight loss corrosion rate and visual inspection were also employed as evaluation methods. The weight loss corrosion rate is an effective method to determine the corrosion rate spanning the entire testing period as opposed to the LPR measurements which represent the corrosion rate at a specific time in the testing. Visual inspection was used to judge the type of corrosion that is occurring on the electrode surface and to confirm the presence of pitting, if any.

The autoclaves used in this testing are constructed of Hastelloy 276-C with a three electrode assembly (working, reference and counter electrodes) in a closely spaced equilateral triangle configuration. Since the alloy was supplied in the form of tubing the alloy electrodes were made in a disc configuration as opposed to a cylinder which is typically used in this testing.

The composition of the brine used was 65,000 mg/L sodium, 100,000 mg/L chloride and 100 mg/L bicarbonate. The brine was purged with CO_2 for two hours prior to filling the autoclave cells and was not pH adjusted. The second round of testing, performed at a concentration of 200 ppm corrosion inhibitor, also had an addition of 0.5% calcium chloride at the request of the client.

The testing was performed at 80°C, in cells held in a heating jacket controlled by a thermistor and stirred by a magnetic stirrer. The autoclave cells were charged to a total pressure of 850 psi, containing 1.2% CO_2, the balance high pressure methane. Refer to Table 1 for specific parameters for each phase of testing.

RESULTS

The LPR results from the potentiostatic scan (refer to Figure 1) showed that the uninhibited high strength steel corroded severely under these conditions. The corrosion rate peaked at approximately 200 mpy (5.08 mm/year) at the eight hour mark and declined gradually, leveling out at about 50 mpy (1.27 mm/year) for the duration of the testing. The addition of 50 ppm of continuous corrosion inhibitor reduced the corrosion rate, however the level of protection achieved was still considered unacceptable at about 15 mpy (0.381 mm/year).

The corrosion resistant alloy initially exhibited a fairly low corrosion rate. The film began to break down at about the six hour mark and the rate began to steadily increase to 20 mpy (0.508 mm/year). This passive film was unable to be restored on the electrode surface and the high rate was maintained for the last 48 hours of the testing period. The addition of 50 ppm of continuous corrosion inhibitor was very effective at lowering the corrosion rate of the corrosion resistant alloy. There was a slight breakdown in the film during the first 24 hours but the film was restored and an acceptable corrosion rate of 1 mpy (245 μm/year) was maintained for the remainder of the test period.

The potentiodynamic scan was used to evaluate the pitting resistance of each of the alloys. The scan could not be run on the high strength steel as the current density exceeded the instrument settings. This indicates a very severe corrosion rate as the electrode was unable to be polarized. This is congruent with the high corrosion rate encountered throughout the testing. The 50 ppm inhibited high strength steel hysteresis loop did not close indicating a moderately high pitting potential; this was confirmed through visual inspection (refer to Figure 6).

The potentiodynamic scan on the uninhibited corrosion resistant alloy (refer to Figure 7) showed hysteresis on the reverse scan. The loop did close and was over 200 mV greater then Ecorr, suggesting that pits, once formed may passivate. The scan on the 50 ppm inhibited corrosion resistant alloy (refer to Figure 8) showed that the hysteresis loop did not close, but was nearly 300 mV greater then Ecorr suggesting that once the pits are formed they may not passivate. The area within the loop is larger than the uninhibited scan, indicating a greater amount of pitting damage is occurring in the inhibited sample. The amount of pitting visible on the inhibited sample correlated with this observation (refer to Table 2).

The initial current of the ZRA scan for the uninhibited cell (refer to Figure 3) was 1.6 milliamps indicating a high initial corrosion rate in the high strength steel. The current quickly declined to 0.2 milliamps and fluctuated between 0.2 and 0.3 milliamps for the duration of the testing. This value becomes useful when judging the effect that the addition of a corrosion inhibitor has on the anodic member of the galvanic pair. The ZRA scan completed at the 50 ppm dose (refer to Figure 4) of continuous corrosion inhibitor yielded a lower initial current, 1.2

milliamps, opposed to 1.6 milliamps in the uninhibited cell. Throughout the duration of the testing period (1 week), the current dropped to a lower level than in the uninhibited cell, approximately 0.1 milliamps, compared to 0.2 milliamps in the blank cell.

A second phase of inhibition testing was performed in which the inhibitor dosage was increased to 200 ppm. It should be noted that at the request of the client, there was a slight change to the brine composition. Based on LPR measurements (refer to Figure 2), the increased inhibitor dosage effectively lowered the corrosion rate of each of the alloys to approximately 1 mpy (245 μm/year). No breakdown in the film was detected at any point in the testing period. This increased dosage had a significant effect on the high strength steel, lowering the LPR corrosion rate to 1 mpy (254 μm/year). This is a dramatic improvement from the 50 ppm inhibited test in which the corrosion rate only declined to 15 mpy (0.381 mm/year). The corrosion resistant alloy performed similarly at both dosage levels with the LPR corrosion rate being about 1 mpy (245 μm/year) at each dose. The visual and gravimetric results from the potentiostatic scan can not be interpreted as representative of the corrosion rate that occurs under these testing conditions as the potentiodynamic (CPP) scan is performed on the same test specimens and can initiate pitting. This pitting can induce a higher weight loss corrosion rate on the test specimens than would have actually been present at the conclusion of the potentiostatic test period.

The cyclic scan on the high strength steel for the dose of 200 ppm corrosion inhibitor (refer to Figure 9) was much improved. The hysteresis loop nearly closes, and the area enclosed by the loop is much smaller, indicating relatively less localized attack. This observation is confirmed by examining the gravimetric and visual data in which the weight loss corrosion rate decreased from 14.9 mpy (0.378 mm/year) for the 50 ppm inhibited electrode to 4.7 mpy (0.119 mm/year) for the 200 ppm inhibited electrode. While the extent of the visual damage was less on the electrode with the higher inhibited dose, the same type of damage, etching and crevice corrosion, was still apparent.

The CPP scan for the corrosion resistant alloy (refer to Figure 10) at the increased inhibitor dose is only slightly improved from the scan with the 50 ppm inhibitor dose. The E_{corr} is slightly higher (50 mV) but the hysteresis loop is nearly identical to the previous scan at the lower inhibitor dose. The weight loss corrosion rate was actually greater on the electrode with the higher inhibitor dose. This may be due to the slight change to the brine composition for the tests performed at the higher dosage level. Pitting was still observed on the electrodes at each inhibitor dose.

The ZRA scan on the cell with the increase in dose from 50 ppm to 200 ppm (refer to Figure 5) exhibited an almost immediate drop in the current. The current was 0.6 milliamps initially, half of the initial current of 1.2 milliamps for the 50 ppm dose. At five hours elapsed the ZRA scan on the 200 ppm dosed cell already showed a reduction in potential to 0.16 milliamps, a dramatic difference from the uninhibited cell which had been 1.5 milliamps at the same elapsed time.

While the electrochemical monitoring of the current flow between the galvanic couple showed that the higher dose had a significant effect on the anodic member of the pair it was essential to evaluate the gravimetric results to determine the actual corrosion rate of each member of the galvanic couple (refer to Table 3). In each phase of the ZRA testing (uninhibited, 50 ppm inhibited and 200 ppm inhibited), the corrosion resistant alloy showed no visual damage and a weight loss corrosion rate of 0.0 to 0.1 mpy (0 to 25.4 μm/year) The high strength steel exhibited an uninhibited corrosion rate of 88.9 mpy (2.29 mm/year) and etching over the entire surface. The high strength steel electrode inhibited with 50 ppm of corrosion inhibitor exhibited etching, crevice corrosion and pitted patches and bands. The weight loss corrosion rate at 50 ppm was 50.1 mpy (1.27 μm/year) far from an acceptable level of protection. In the last phase of testing the 200 ppm dose significantly improved, with a weight loss corrosion rate of 8.5 mpy (0.216 mm/year). Etching and crevice corrosion was also observed as well.

CONCLUSIONS

The electrochemical testing of this galvanic couple yielded very useful information. In the potentiostatic scan the high strength steel did not perform well under any of the test conditions. Even the addition of 200 ppm inhibitor only decreased the corrosion rate to 15 mpy (0.381 mm/year). However, the potentiodynamic scan, as well as visual inspection showed that the higher dose did not prevent pitting of the specimen. The corrosion rate on the corrosion resistant alloy was successfully reduced by a relatively low dose of corrosion inhibitor. The alloy performed similarly at both concentrations of inhibitor, 50 and 200 ppm, however some pitting was still observed as a result of the CPP scan. The pitting was not mitigated by the higher doe of corrosion inhibitor.

By examining the galvanic current in the ZRA scan it was evident that the 200 ppm dose was the most effective in lowering the corrosion rate of the high strength steel, which was the anodic member of the couple. However, it was necessary to closely examine the gravimetric and visual results as well in order to determine the actual corrosion rate of each species. The increased dosage did dramatically lower the corrosion rate from 88.9 mpy (2.29 mm/year), uninhibited to 8.5 mpy (0.216 mm/year) in the 200 ppm inhibited solution. This level of protection was still not effective enough to prevent etching or crevice corrosion which could have serious implications were this galvanic couple to be implemented in a practical situation.

This experiment was successful in demonstrating how electrochemical monitoring in a laboratory environment can provide a wealth of information for use in the selection and pairing of alloys for real-life applications. The dose and type of corrosion inhibitor applied in this experiment was not effective in lowering the corrosion rate to an acceptable level, or reducing the localized damage of the anodic member of the couple. Additional testing with different doses or types of inhibitors utilizing the electrochemical tests outlined here may have been successful in reducing the corrosion rate of the anodic member of this galvanic couple.

REFERENCES

1. Barbara A. Shaw, Gerald Frankel, Rudy Buchheit, and Howard Pickering, Short Course on Corrosion Fundamentals and Experimental Methods (Penn State University Corrosion Center, 2005)

2. Joe H. Payer and Neil G. Thompson, DC Electrochemical Test Methods (Houston, Texas: NACE International Book Publications, 1998), p. 11, 42 – 47.

3. N. Rothwell and M. Tullmin, Machine and Systems Condition Monitoring Series: The Corrosion Monitoring Handbook, First Edition (Oxford, UK: Coxmoor Publishing Company, 2000), p.27, 62

TABLE 1
EXPERIMENTAL PARAMETERS

Test	Reference Electrode	Working Electrode	Counter Electrode	Test Period	Measurement Intervals
Potentiostatic Scan	Hastelloy 276-C	Test Alloy	Hastelloy 276-C	96 Hours	30 Minutes
Potentiodynamic Scan	Hastelloy 276-C	Test Alloy	Hastelloy 276-C	30-60 Minutes	Continuous
ZRA Scan	Hastelloy 276-C	Test Alloy # 1	Test Alloy # 2	168 Hours	30 Minutes

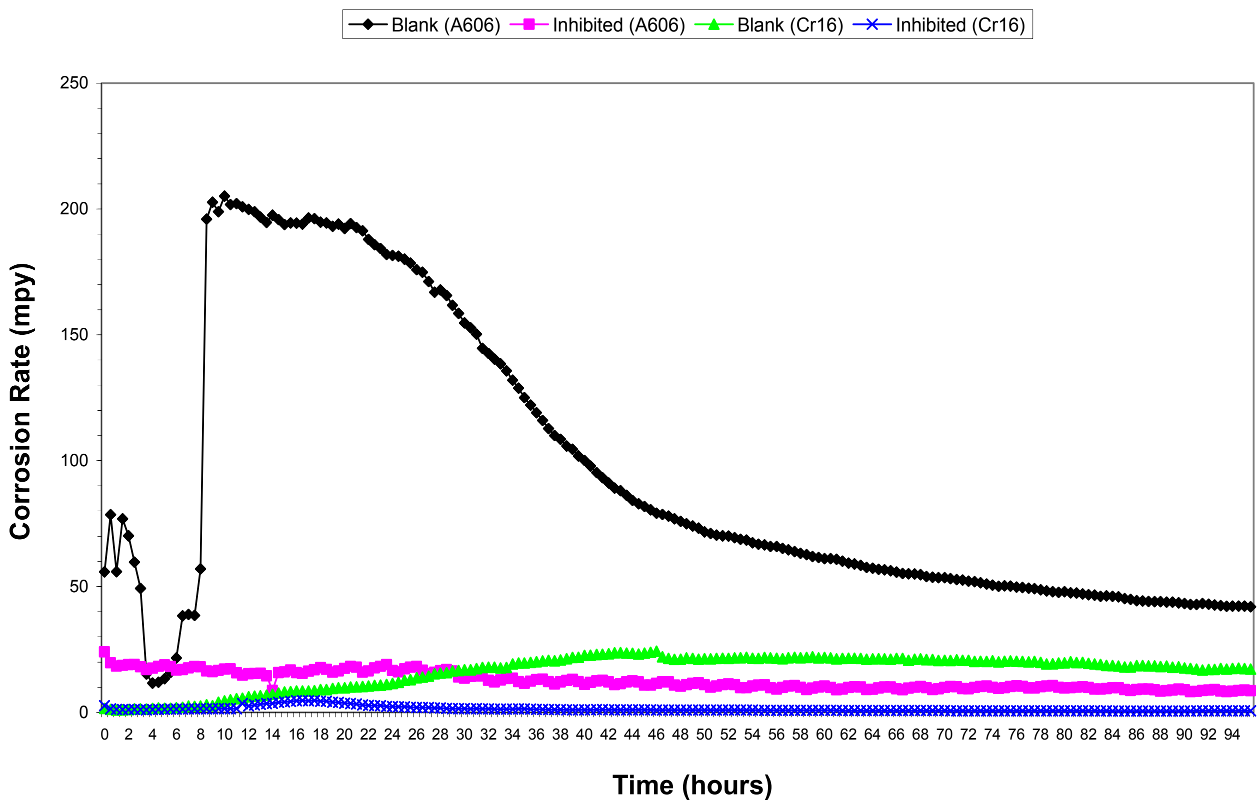


FIGURE 1 – LPR Data, Uninhibited and 50 ppm Inhibited Cells

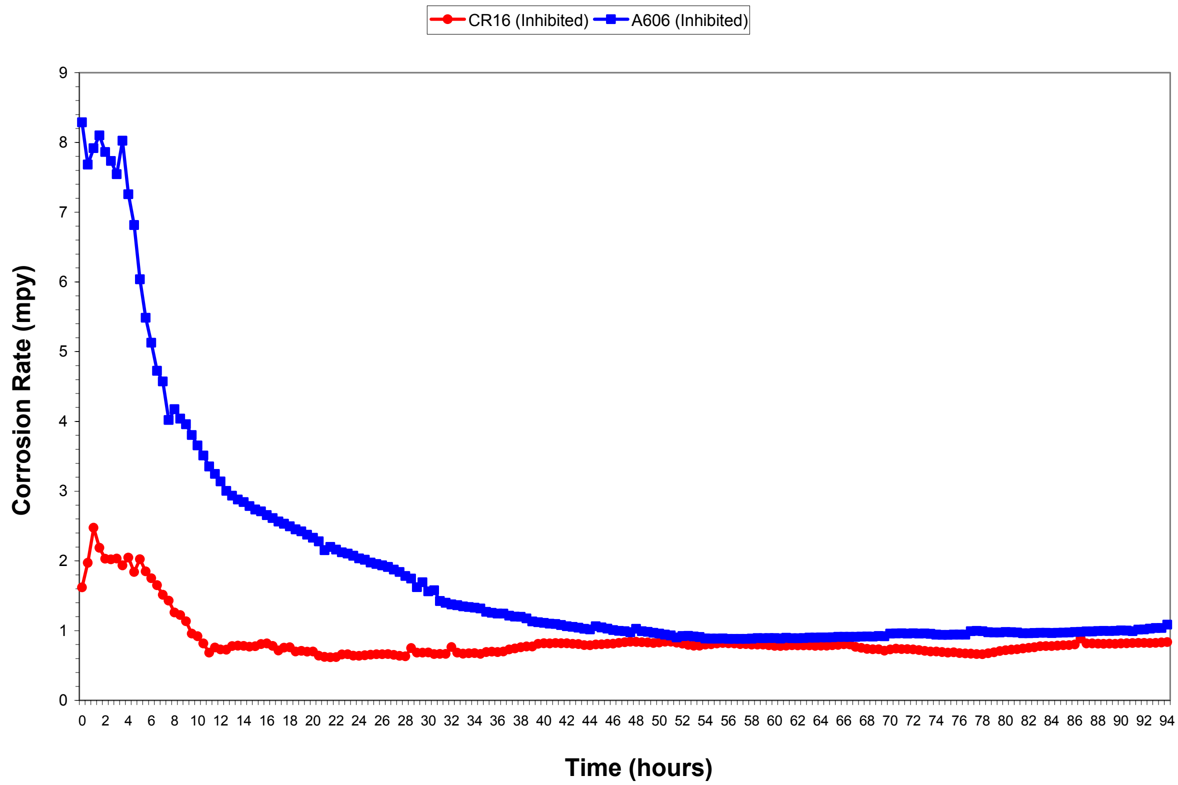


FIGURE 2 – LPR Data, 200 ppm Inhibited Cells

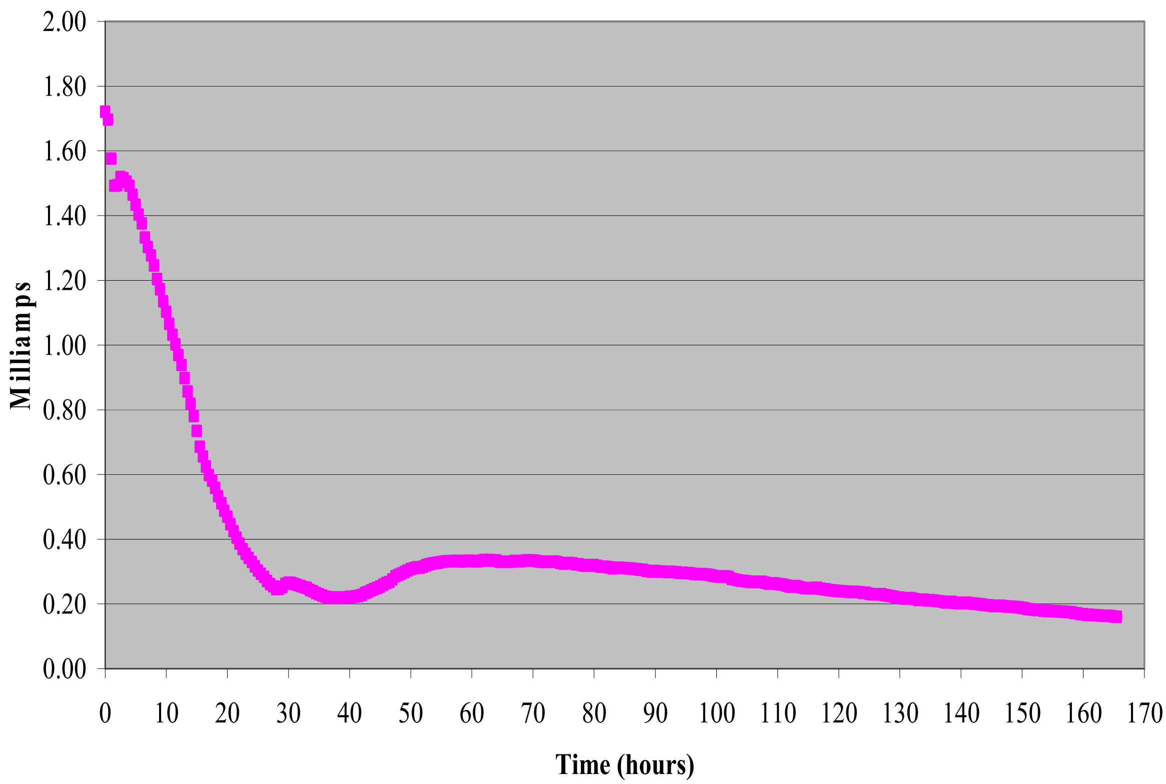


FIGURE 3 – ZRA Data, Galvanic Current, Uninhibited

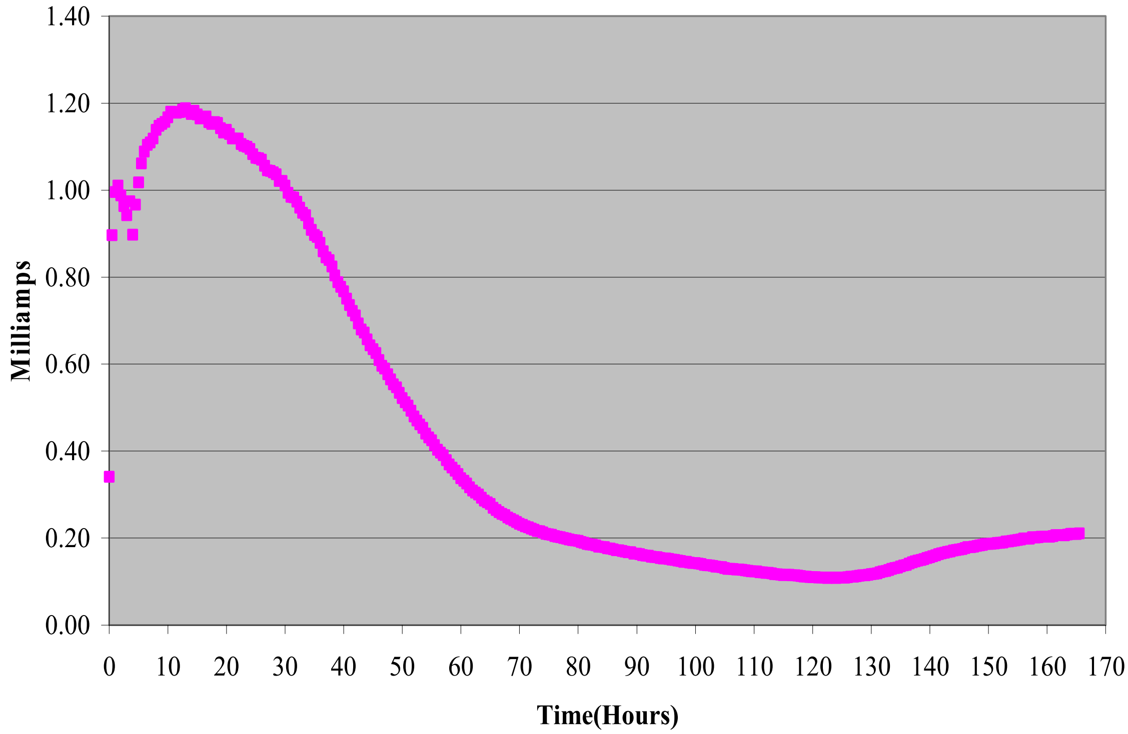


FIGURE 4 – ZRA Data, Galvanic Current, 50 ppm Inhibited

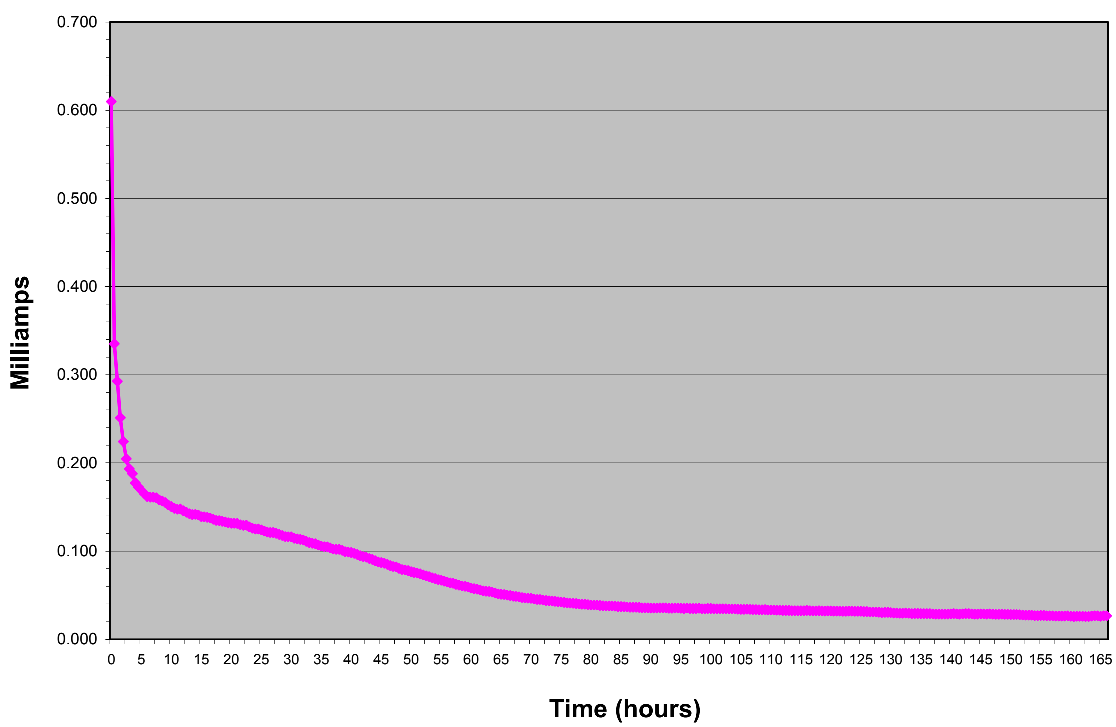


FIGURE 5 – ZRA Data, Galvanic Current, 200 ppm Inhibited

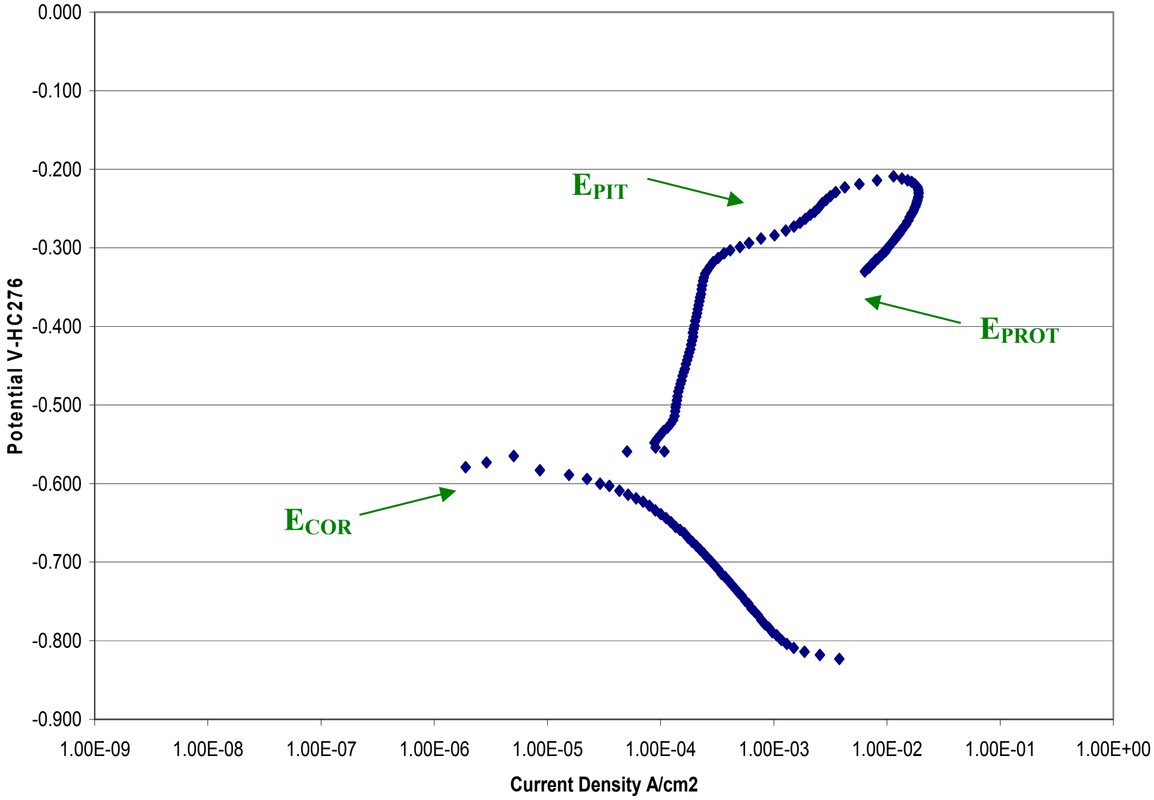


FIGURE 6– CPP Scan, HS-80, 50 ppm Inhibited

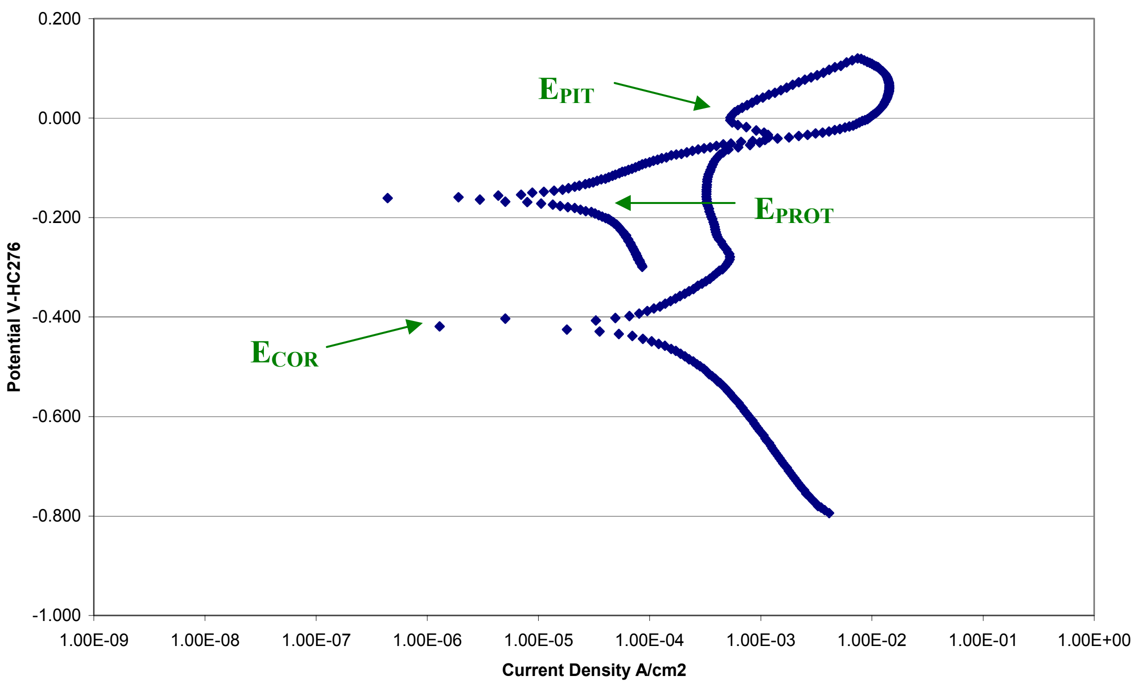


FIGURE 7– CPP Scan, Corrosion Resistant Alloy Cr-16, Uninhibited

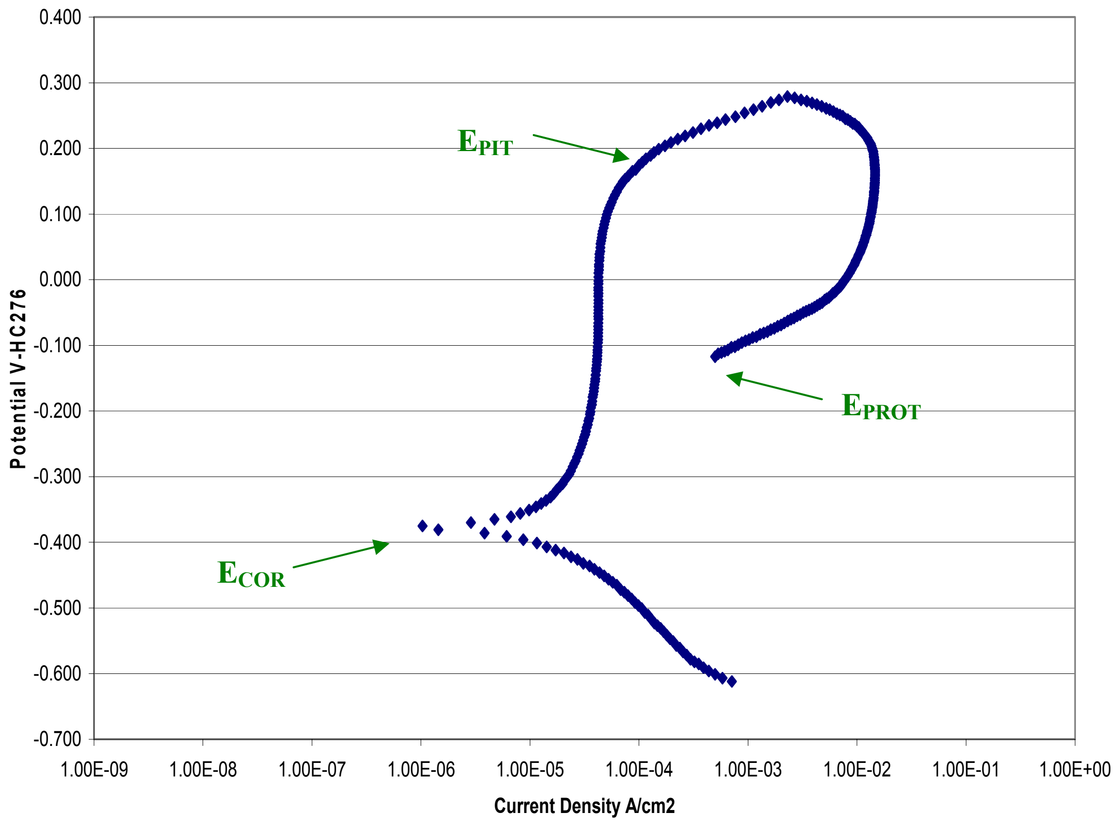


FIGURE 8– CPP Scan, Corrosion Resistant Alloy Cr-16, 50 ppm Inhibited

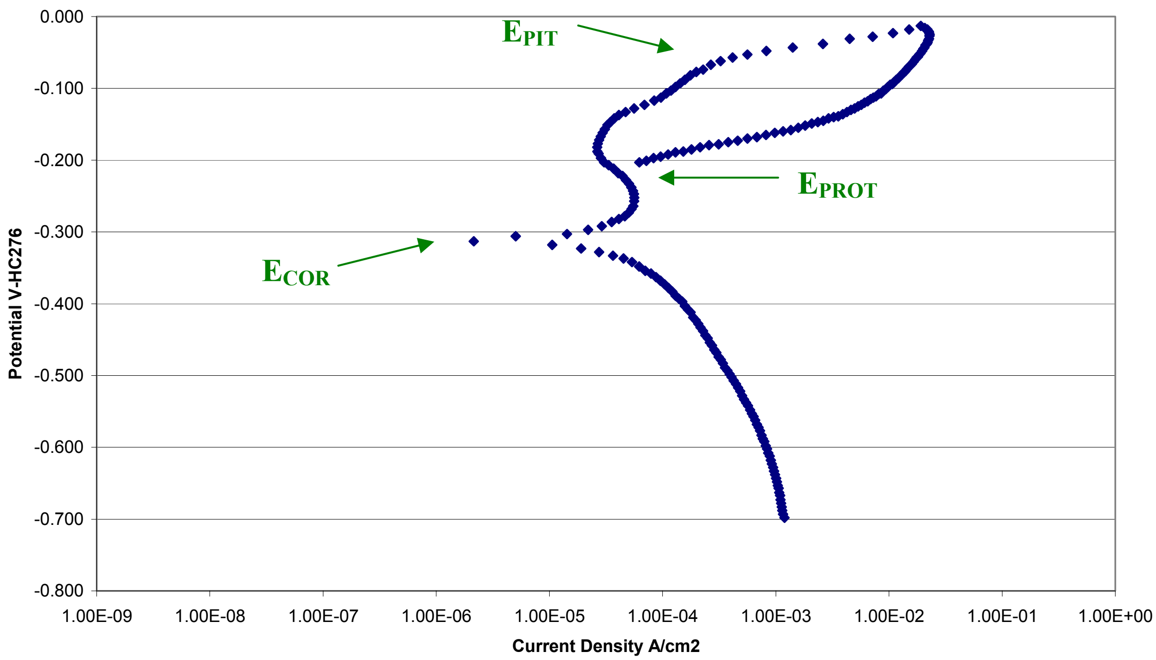


FIGURE 9– CPP Scan, High Strength Steel HS-80, 200 ppm Inhibited

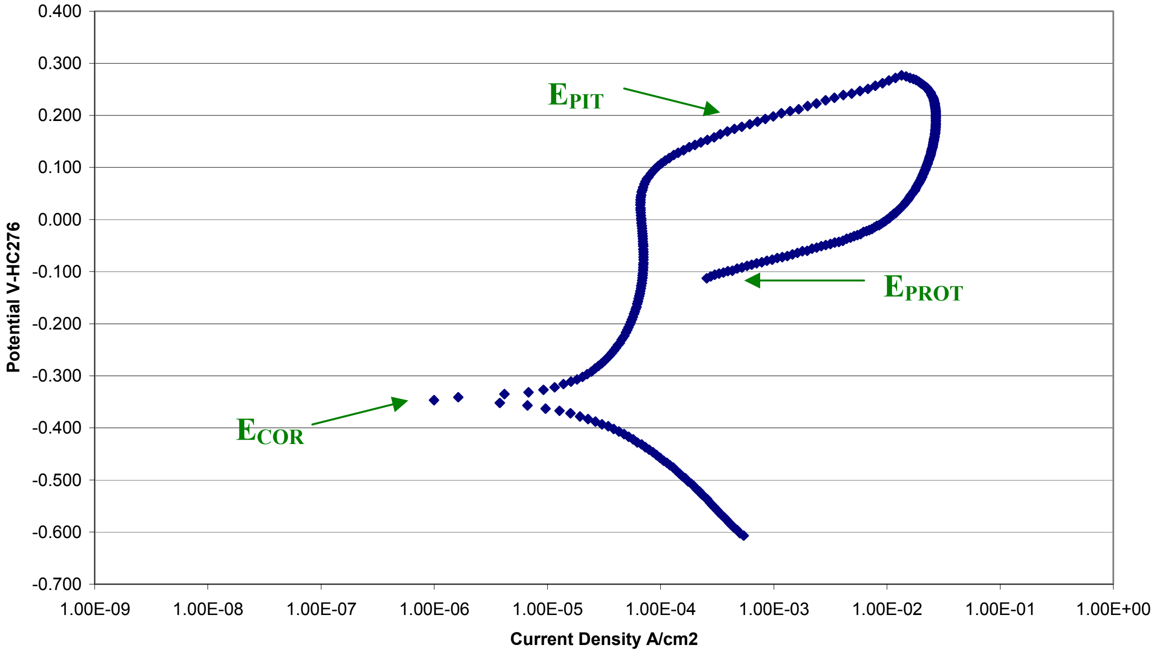


FIGURE 10– CPP Scan, Corrosion Resistant Alloy Cr16, 200 ppm Inhibited

TABLE 2 – GRAVIMETRIC AND VISUAL DATA FROM LPR/CPP SCANS

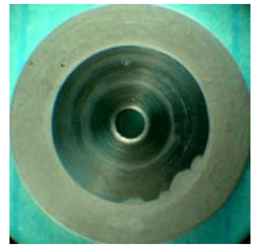
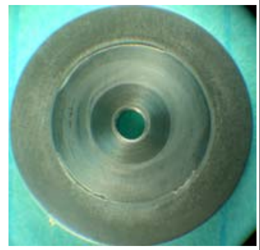
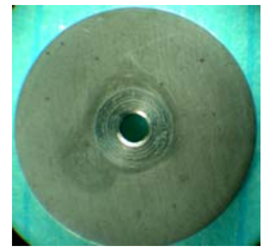
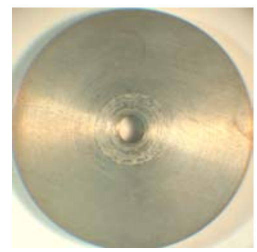
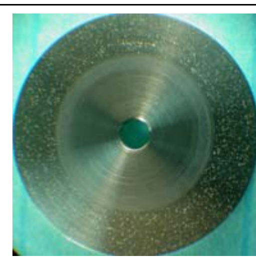
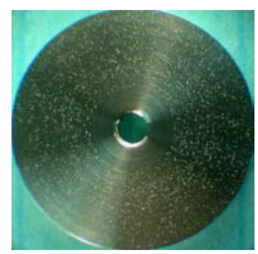
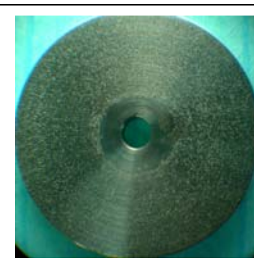
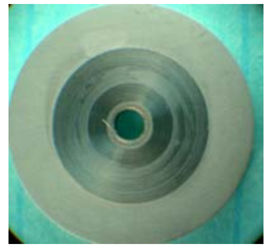
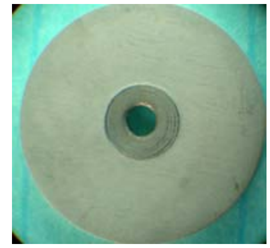
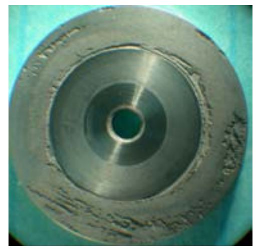
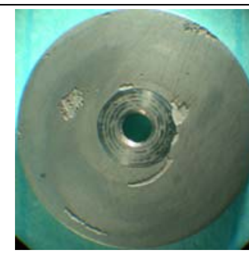
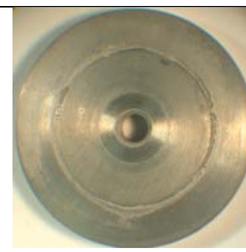
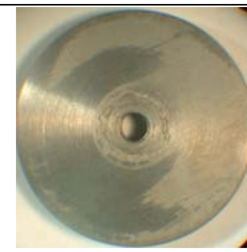
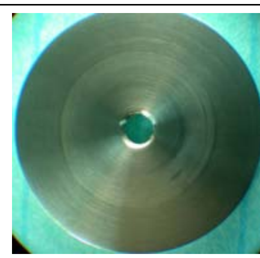
Alloy	Inhibitor Conc. (ppm)	Test	Weight Loss (mg)	Corrosion Rate (mpy, mm/year)	Visual	Electrode Top	Electrode Bottom
HS-80	0	LPR /CPP	94.2	66.3 (1.62)	Etched		
HS-80	50	LPR /CPP	21.2	14.9 (0.365)	Etched, Crevice Corrosion		
HS-80	200	LPR /CPP	4.6	4.7 (0.115)	Etched, Crevice Corrosion		
CR16	0	LPR /CPP	13.4	9.4 (0.230)	Pitted		
CR16	50	LPR /CPP	7.5	5.3 (0.130)	Pitted		
CR16	200	LPR /CPP	7.1	7.3 (0.179)	Dull Etch		

TABLE 3 – GRAVIMETRIC AND VISUAL DATA FROM ZRA SCANS

Alloy	**Inhibitor Conc. (ppm)**	**Test**	**Weight Loss (mg)**	**Corrosion Rate (mpy, mm/year)**	**Visual**	**Electrode Top**	**Electrode Bottom**
HS-80	0	ZRA	218.5	88.9 (2.18)	Etched		
HS-80	50	ZRA	123.2	50.1 (1.23)	Etched, Crevice Corrosion, Pitted Patches and Bands		
HS-80	200	ZRA	14.6	8.5 (0.208)	Etched, Crevice Corrosion		
CR16	0	ZRA	0.0	0 (0.0)	No damage		
CR16	50	ZRA	0.2	0.1 (0.0)	No damage		
CR16	200	ZRA	0.1	0.1 (0.0)	No damage