Prediction and Prevention: The development of test methods to predict and corrosion inhibitors to prevent localized corrosion in extreme environments

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Abstract

As the world's demand for oil continues to increase, the need to explore and produce oil in more challenging local environments also increases. Some of these challenges require production in offshore environments under extreme conditions that are often highly corrosive. Many of these are offshore in deep and ultra-deep water and often the conditions have high levels of CO_2, salinity and organic acids. These types of conditions often lead to extremely high corrosion rates with the main failure mechanism being localized corrosion, which is a ubiquitous problem within the oil and gas industry. Although it is a common problem within the industry, there is a limited understanding of how to predict and prevent the occurrence of localized corrosion. The focus of this work is primarily on developing standard laboratory methods that effectively screen corrosion inhibitors for these extreme conditions. The primary goal is to determine which corrosion inhibitors are more effective at preventing localized corrosion. This work employs use of white light interferometry to objectively quantify the presence of localized corrosion and the effectiveness of corrosion inhibitors at mitigating localized corrosion. With these techniques, corrosion inhibitors were developed and screened for their ability to mitigate localized corrosion.

Key words: pitting, white light interferometer, pit dimension, localized corrosion, pitting corrosion rate

Introduction

The world population has nearly doubled in the past 40 years, and the demand for oil and gas has shown a similar increase. In 1956 US oil production was predicted to peak in 1970, and shortly following 1970 US oil production began to decline.[1] This presents the need to produce oil in environments that are much more extreme, such as deep water, high temperature, high pressures, high percentages of CO_2, high salinity and high organic acid content. These conditions are conducive to pitting corrosion and a corrosion mitigation program to mitigate localized corrosion under these extreme conditions is a must. While the delivery of a chemical to these types of environments is a challenge in and of itself, treating at depths of near 1000 meters below sea level is also no mundane task. Figure 1 shows field examples of failures caused by CO_2 corrosion.

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The CO_2 content in these types of environments can be greater 10% with brines with total dissolved solid (TDS) values near 150,000 ppm. The presence of percent levels of organic acids can also contribute to pit formation and lead to corrosion failures. With the increasing need to produce oil and gas under these conditions, there needs to be a method available to screen these chemicals to treat corrosion in these environments.

As a point of reference, the annual cost of corrosion in the US was estimated in 2002 to be \$276 billion, where \$7 billion was spent annually on pipeline maintenance.[2] Most often pitting corrosion is the primary contributor to failures in the oilfield, but corrosion inhibitors have traditionally been chosen based on their ability to mitigate general corrosion. Often there are significant differences between general corrosion rates and pitting corrosion rates in a given system, [3]and a fundamental understanding of these differences is required in order to have an optimal corrosion mitigation program. Pitting corrosion rates can be up to 100 times higher than general corrosion rates. In order to assess these differences, it is crucial to produce and mitigate these pits in laboratory tests. [4]

Product Development and Evaluation

The development of products has been fed by synthesis of developmental corrosion inhibitor actives, which have been formulated into field ready products that can be applied in these environments to treat corrosion. This work was conducted to evaluate the products that were developed. Ultimately, the goal is to evaluate inhibitors by comparing their ability to mitigate localized corrosion.

Figure 2 shows the three stage process for the development of corrosion inhibitors, where Phase I primarily evaluates the corrosion inhibitors' stabilities under these extreme conditions. If the corrosion inhibitor is not stable at the conditions in a low shear test it is not likely to perform under the more aggressive shear conditions. The second phase of this evaluation is to evaluate the corrosion inhibitors under conditions that match the field as closely as possible and the final phase evaluates their ability to inhibit pitting. Three products were originally chosen for evaluation. Product A is a best in class onshore product that has been successfully used in a system that is 14% CO_2. Product B is a best in class offshore product that has been used in a high temperature and high pressure environment (HPHT) with a TDS greater than 130,000 ppm. Product C is an experimental product that was developed specifically to treat HPHT systems.

The initial screening tool mentioned for determining the *in situ* thermal stability of chemical as it relates to performance is the HPHT wheelbox test. The conditions for this test were developed to simulate very aggressive conditions, which are high in organic acid content and total dissolved solids. The conditions for this 3 day test can be seen in Table 1, where the CO_2 content is 75% and the temperature is 204°C. The synthetic oil used is LVT-200 and uses a 150,000 ppm chloride brine. The bicarbonate was 1/5th of the acetic acid content to prevent buffering of the acetic acid. The inhibitors in the test are typically dosed at 10, 25, 50 and 100 ppm. To evaluate the performance of the inhibitors, weight loss methods were employed using 1018 carbon steel coupons. Upon cleaning and weighing the coupons, they were inspected for pitting although in this low shear environment pitting is not expected.

Figure 4 shows the results from the Phase I testing, which indicates that Product B and Product C were superior to Product A. As the dosages get higher the performance of Product A does not exceed 80% protection, so it was eliminated from further testing. This work also indicates that under these conditions, Product C is statistically equivalent to Product B at 10 ppm and statistically superior to Product B at 25, 50 and 100 ppm.

In Phase II the corrosion inhibitors are evaluated under shear conditions. To evaluate the inhibitors under these conditions, two methods are employed: the flow loop and the rotating cage autoclave. A schematic of the flow loop and a photograph of the rotating cage can be seen in Figure 5 and Figure 7, respectively. Each test can deliver shear stresses of up to 1000 Pa. In both tests Product B and Product C were tested as Product A had been eliminated due to its inferior performance in Phase I.

For the flow loop the maximum temperature for a test is 95ºC and the maximum total pressure is 7 bar. The flow loop is equipped with linear polarization resistance probes, which allow *in situ* corrosion rate measurements. The probes are positioned in three regions to represent various flow regimes: the dead leg, elbow and the flow through. The flow through region is high shear, the elbow is low shear with high turbulence and the dead leg has no shear.

The conditions for the flow loop testing can be seen in Table 2, where the acid gas was 100% CO_2 and the total pressure was 4 bar. The temperature was 93°C and the test was conducted in 100% brine with no oil present. The brine consisted of 150,000 ppm chloride with the same ratio of acetic acid: bicarbonate ratio of 5:1. The test was run for three days and corrosion measurements were made using LPR techniques.

Figure 6 shows a graphical representation of the flow loop results plotted as percent protection for clarity, but the corrosion rates are not shown. The average baseline corrosion rates for the dead leg, elbow and flow through regions were 74 mpy, 1288 mpy and 5745 mpy, respectively. As can be seen the reduction for each region was dramatic. The flow through region showed the greatest percent protection bringing the percent protection greater than 99% for both products.

Figure 7 shows the coupon assembly for the rotating cage autoclave test. In this test, the coupons were placed on a Teflon assembly, which holds the coupons in place while the head is spun inside an autoclave. Following the test, the coupons were removed, cleaned and weighed. From the weight loss, the corrosion rates were calculated on four coupons per test. The results were compared to that of an uninhibited blank for comparison.

For the autoclave testing, the conditions were similar to the flow loop testing. The total pressure is 27.6 bar with 75% CO_2 and nitrogen as the inert gas. The temperature was at a maximum of 176°C. The oil used in the test was LVT-200 and the brine was 150,000 ppm chloride. The acetic acid content was 2500 ppm and bicarbonate was 500 ppm. The test was run for 3 days and corrosion measurements were made at the end of the test.

Table 4 shows the results from the rotating cage autoclave testing which tested Product B and Product C. The uninhibited corrosion rate for this test was 212.8 ± 5.8 mpy and the corrosion rate for Product B dosed at 100 ppm was 7.7± 0.8 mpy. The corrosion rate when Product C was dosed at 100 ppm was 7.2 ± 0.5 mpy. Because the average corrosion rate for Product B was lower than Product C, it was eliminated and Product C was chosen for pitting evaluation.

Phase III testing evaluates the inhibitor's ability to prevent pitting and Product C was promoted for pit testing in this phase. Similar to Phase II, flow loop testing was used except the conditions are such to maximize pitting corrosion in a shorter period of time. The primary goal is to select corrosion inhibitors that are as effective at inhibiting pitting corrosion as they are at inhibiting general corrosion. The first step in this project is to establish screening methods for pitting corrosion under sweet conditions. In the flow loop a flat coupon is inserted that could be used for surface analysis. Figure 8 shows the probe that was used for initial flow loop pitting tests. This flat probe can be used for surface analysis to examine pitting as well as for electrochemical measurements. For this study only the surface analysis method has been presented.

The test conditions can be seen in Table 5. The total pressure for this test was 6 bar and the CO_2 content was 100%. The shear stress was 5 Pa and the brine:oil ratio was 100:0. The metallurgy used was 1018 carbon steel and the test was run for 7 days. The brine used was 10,000 ppm chloride with 5000 ppm acetic acid. In contrast to the previous testing, the brine contained no bicarbonate to buffer the acetic acid. A blank test was performed in order to establish a baseline to compare pitting and general corrosion protection. Product C was then tested under the same conditions at both 20 and 150 ppm.

The results from the Phase III testing can be seen in Table 6 and Table 7 and Figure 9, Figure 10 and Figure 11. General corrosion rates were calculated by weight loss and the coupon was then examined under a white-light interferometer to count the number of pits over the scanned region to determine the maximum pit depth. Table 6 shows the effectiveness of Product C at mitigating general corrosion under the tested conditions. From previous results it was known that the product is very effective at mitigating general corrosion and these results were also validated by this test method where 95% protection was seen at 20 ppm and 99% protection at 150 ppm.

The pitting corrosion analysis shows that the product is also effective at mitigating pitting corrosion. For this analysis the white-light interferometer parameters were set to scan any pit with a depth greater than one mil and at width of at least two mils. To classify a "localized pit", however, a criteria needs to be set to determine whether the pitting depth is significantly different from the general corrosion rate. For this analysis a pit ratio was calculated by taking the pitting corrosion rate calculated from the max pit depth and exposure time divided by the general corrosion rate. A criterion was set that this pit ratio has to be greater than 3 in order to classify the pit as a "localized pit" and differentiate from general corrosion.

Table 7 shows the results of the pitting corrosion rate analysis. The measured data includes the pit density (number of pits per scanned area), max pit depth, and the pit ratio. For the blank coupon a large number of pits was observed, which met the cut-off criteria of 1 mil depth and 2 mil width. When the pit ratio was calculated, however, it was 0.5, which is less than the criterion set of 3. This means that these pits cannot be classified as "localized pits". The coupon from the 20 ppm test, however, does show the presence of "localized pits" as the pit ratio is 9.9. At a dosage of 150 ppm no pits were observed. The images from the white-light interferometer are shown in Figure 9, Figure 10 and Figure 11.

From this analysis it can be seen that Product C is effective at mitigating pitting corrosion when it has been adequately dosed. At low treat rates, however, Product C did not mitigate the maximum pit depth as the maximum pit depth for the blank was similar. Due to the lowering of the general corrosion rate but the persistence of the maximum pit depth this attributed to the formation of a "localized pit" with a pit ratio greater than 3. Rather it appears that the inhibitor is not as effective at mitigating the maximum pit rate at 20 ppm and this makes this pit more discernable amongst the general corrosion occurring on the rest of the coupon. This can be seen in Figure 9 and Figure 10. Figure 9 shows that there are observable small pits on the surface but this is simply the manifestation of general corrosion. When the general corrosion rate is lowered then observable "localized pits" can be seen while other areas of the coupon are protected. Figure 11 shows that with adequate dosages these pits can be mitigated.

Conclusions

With the increasing world demand for oil and decreasing worldwide reserves the need to treat corrosion in HPHT conditions requires a process for evaluating corrosion inhibitors that effectively mitigate pitting corrosion. While most corrosion inhibitors adequately protect systems that have more typical conditions the laboratory evaluation of corrosion inhibitors to prevent pitting remains largely unexplored. With the development of the three phase process for evaluation of corrosion inhibitors, the possibility of successful treatment of HPHT corrosion in these more challenging systems is much more likely. This process outlines the three stages that address three facets of corrosion inhibitor performance, which include *in situ* stability, high shear and evaluating for the prevention of pitting corrosion. With this process the consideration of pitting corrosion as a parameter in inhibitor selection allows a much more informed decision to be made. When the correct chemistry is applied at the correct location at an adequate dosage the life of these assets can be significantly prolonged even in these challenging environments.

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Figures

Figure 1: Field Examples of Pitting Corrosion

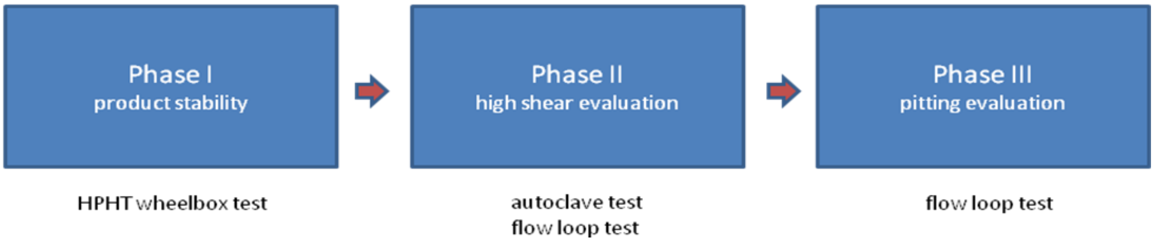

Figure 2: Development stages for CI evaluation

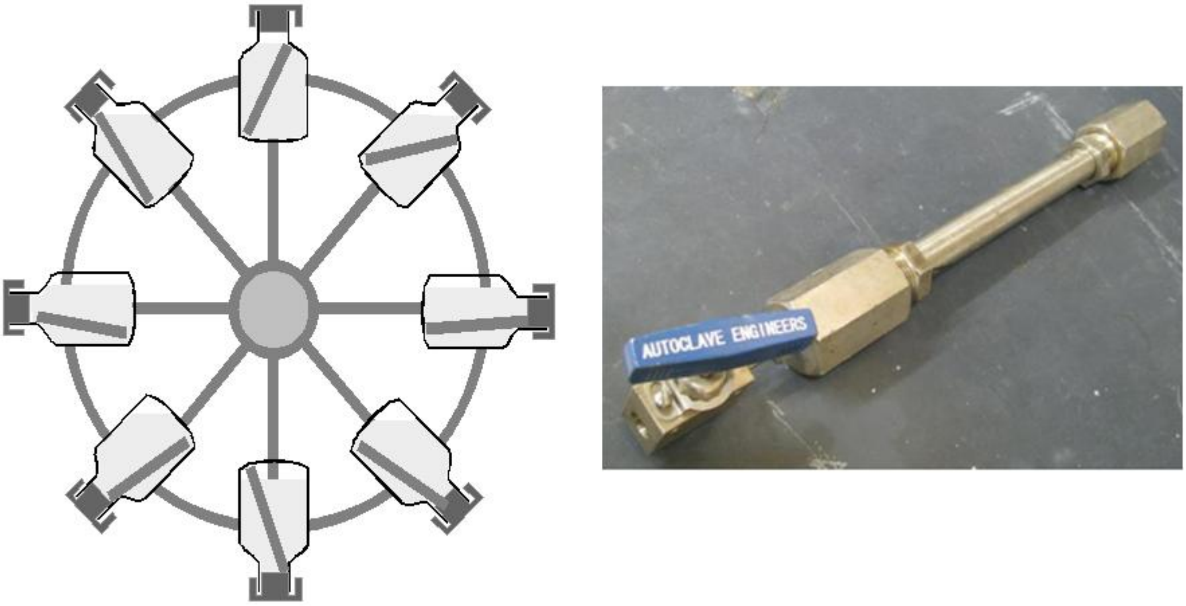

Figure 3: HPHT wheelbox test

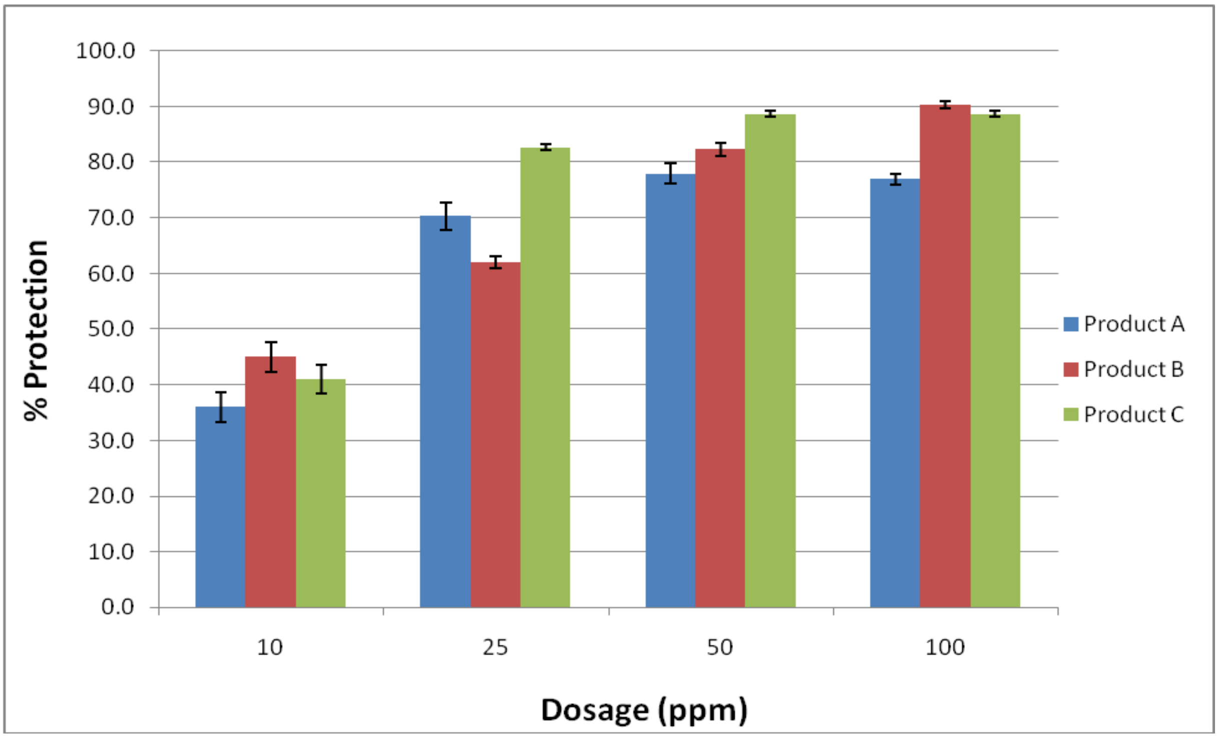

Figure 4: Phase I HPHT wheelbox results

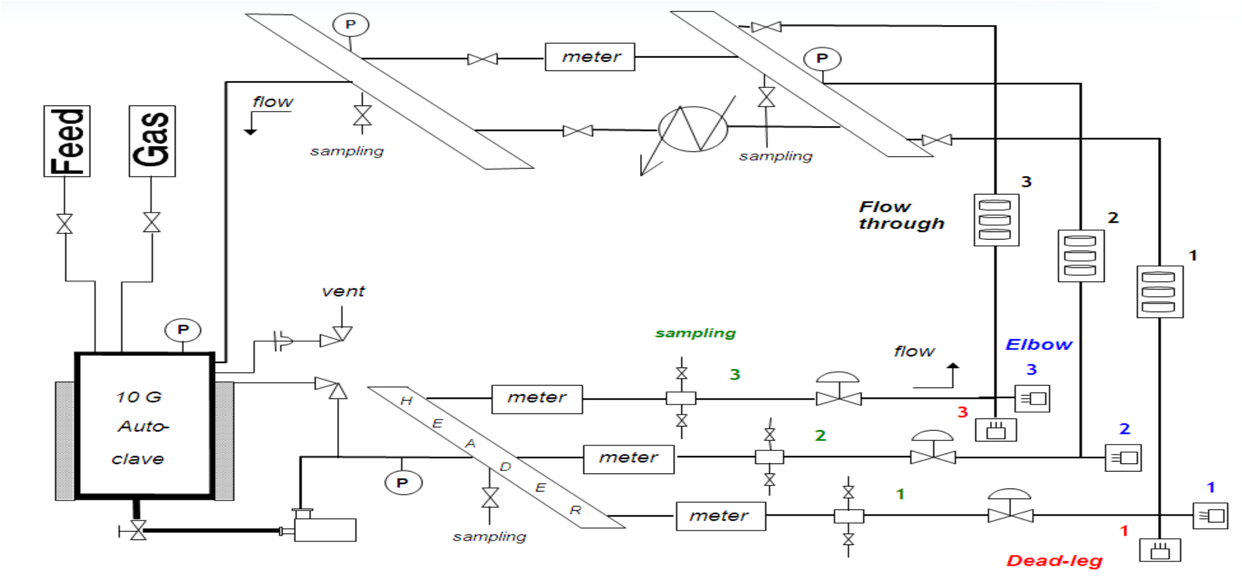

Figure 5: Schematic representation of the flow loop

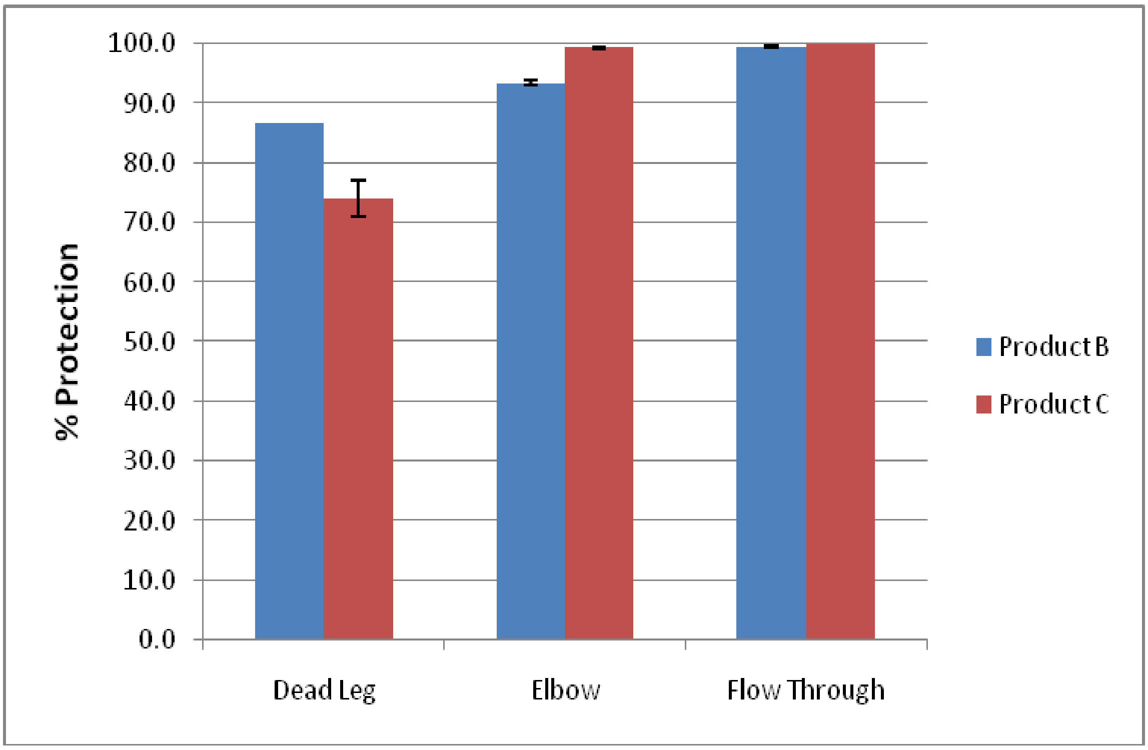

Figure 6: Graph of flow loop results plotting percent protection for each region of the product comparing the performance of Product B and Product C

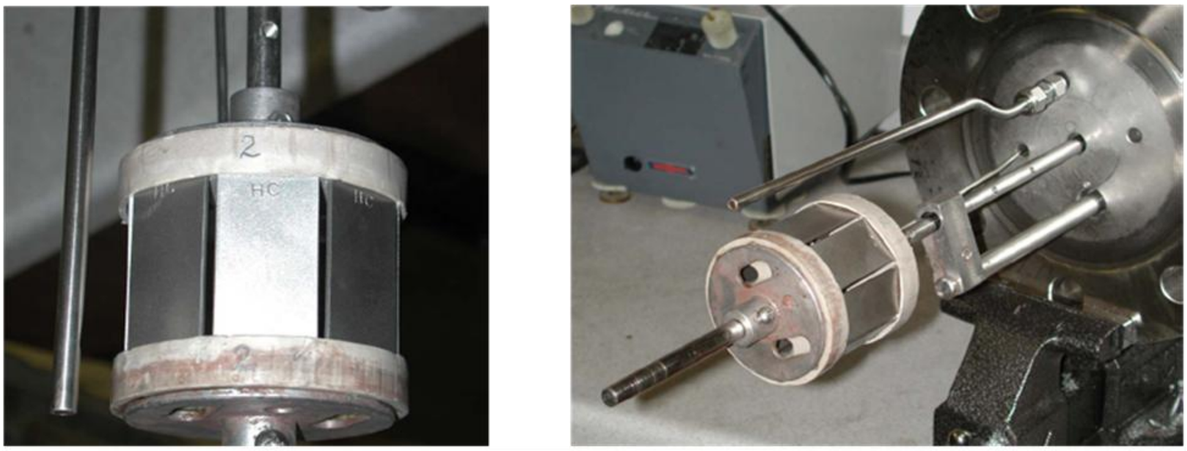

Figure 7: Rotating cage autoclave coupon assembly

Figure 8: Localized corrosion probe used for flow loop testing

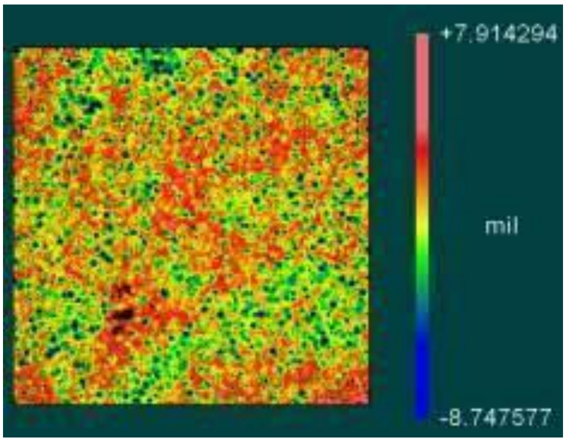

Figure 9: Surface analysis of blank (uninhibited) coupon

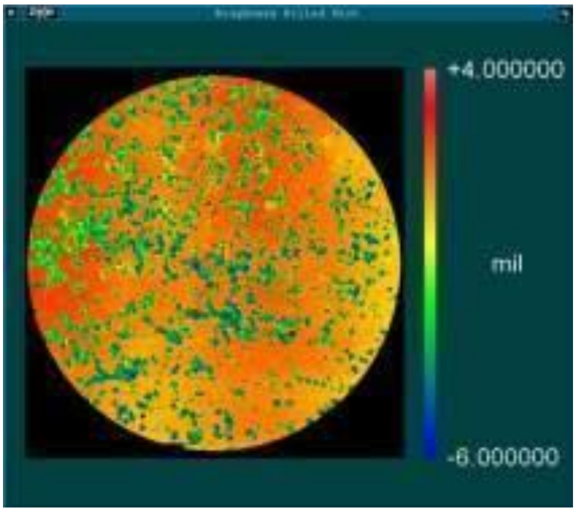

Figure 10: Surface analysis of coupon dosed at 20 ppm Product C

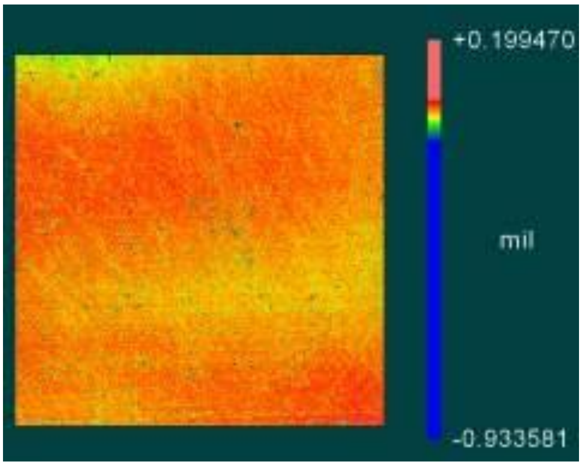

Figure 11: Surface analysis of coupon dosed at 150 ppm Product C

Tables

Total Pressure (bar)	69
pCO2 (bar)	52
pN2 (bar)	17
Temperature (ºC)	204
Brine/Oil Ratio	90/10
Oil Type	LVT-200
Metal	C1018
Duration (days)	3
Brine (ppm)	
Chloride	150000
Bicarbonate	500
Acetic Acid	2500

Table 1: Test conditions for HPHT wheelbox testing

Total Pressure (bar)	4
pCO2 (bar)	4
pN2 (bar)	0
Temperature (ºC)	93
Brine/Oil Ratio	100
Oil Type	None
Metal	C1018
Duration (days)	3
Brine (ppm)	
Chloride	150000
Bicarbonate	500
Acetic Acid	2500

Table 2: Test conditions of flow loop test

Total Pressure (bar)	27.6
pCO2 (bar)	20.7
pN2 (bar)	6.9
Temperature (ºC)	176
Brine/Oil Ratio	90:10
Oil Type	LVT-200
Shear Stress (Pa)	100
Metal	C1018
Duration (days)	3
Brine (ppm)	
Chloride	150000
Bicarbonate	500
Acetic Acid	2500

Table 3: Testing conditions for HPHT autoclave testing

	Corrosion Rate (mpy)	% Protection
Blank	212.8 ± 5.8	0
Product B	7.7 ± 0.8	96%
Product C	7.2 ± 0.5	97%

Table 4: Rotating cage autoclave results

Total Pressure (bar)	6
pCO2 (bar)	6
pN2 (bar)	0
Temperature (ºC)	50
Shear Stress (Pa)	5
Brine/Oil Ratio	100:0
Oil Type	None
Metal	C1018
Duration (days)	7
Inhibitor Concentration (ppm)	0, 20, 150
Brine (ppm)	
Chloride	10000
Bicarbonate	0
Acetic Acid	5000

Table 5: Conditions for Pitting Flow Loop Test

		Weight Loss	
Inhibitor	Dosage (ppm)	General Corrosion Rate	Percent Protection
Blank	N/A	1106 +/- 27	N/A
Product C	20	51 +/- 31	95.4
Product C	150	2.9 +/- 0.5	99.7

Table 6: General corrosion rate results

		Pitting Data		
Inhibitor	Dosage (ppm)	Max Pit Depth (mil)	Pit Density (pits/in^2)	Pit Ratio
Blank	N/A	8.67	13884	0.5
Product C	20	7.39	2026	9.9
Product C	150	0	0	0

Table 7: Pitting corrosion rate results