Paper No.
11238

NACE INTERNATIONAL CORROSION 2011 CONFERENCE & EXPO

Integrity of Corrosion Inhibitor Films in Multiphase Flow

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ABSTRACT

The integrity of corrosion inhibitor films was challenged in a large scale multiphase flow loop using slug flow. Two different kinds of water-soluble corrosion inhibitors were tested at two different concentrations. A slug flow regime was used because of the high wall shear stress that can be generated. Results show that mechanical forces in this multiphase flow regime as described by the high levels of turbulence and wall shear stress did not have a detrimental effect on the performance of the corrosion inhibitors used in this study. However, the formation of foam appeared as a likely cause of corrosion inhibitor's lack of performance in multiphase flow environments.

Key words: corrosion inhibitors, multiphase, slug flow, shear stress

INTRODUCTION

The effect of flow on CO_2 corrosion can be described via wall shear stress and/or mass transfer, parameters that play an important role governing interactions between the steel surface and the liquid phase [1]. Both of these variables may be responsible for increasing corrosion in aggressive environments [2]. As a general rule, corrosion rate increases with flow velocity as it enhances the turbulent mass transfer of corrosive species from the bulk solution to the steel surface. Likewise it is commonly thought that high wall shear stress can lead to surface film removal by purely mechanical or combined chemo-mechanical means.

Pipeline transmission of oil frequently occurs under multiphase flow conditions that combine the oil, water, gas, and any entrained solid particles such as sand. Therefore, in order to reflect those field conditions, studies of flow effects on inhibitor film performance should not be conducted only in single phase flow systems. Multiphase flow systems need to be incorporated in order to evaluate inhibitor film performance more realistically.

Depending on gas and liquid flow velocities as well as water cut, multiphase flow can form many different regimes/patterns[1-11]. Multiphase flow patterns are complex due to the immiscibility of the phases and due to gravitational forces, causing an asymmetric phase distributions and phase separation. One of the most common and most turbulent flow regime is slug flow [2, 4, 7]. Many researchers have attempted to measure shear stress in horizontal pipelines in a slug flow pattern [8, 9]. In 2006, Schmitt reported that the critical wall shear stress in a horizontal pipe could reach a value of 260 Pa [6]. Nesic reported similar values and argued that shear stress may be up to two orders of magnitude larger in the section of maximum turbulence (front of the slug) [10] than elsewhere in the flow. It has also been argued that his high shear stress could be reduced with the addition of inhibitors into the system due to drag reduction properties [5].

If the steel surface is covered with a protective corrosion inhibitor film, the flow velocity apparently does not play any significant role if the system is under single phase flow [7]. According to Gulbrandsen and Grana[7], the viscous sub-layer in a turbulent flow with a flow velocity of 20 m/s is of the order of micrometers while the inhibitor film is of the order of nanometers. Consequently, the viscous sub-layer leaves the corrosion inhibitor film unperturbed. Nevertheless, there are conflicting reports in the literature which suggest that flow velocity is responsible for corrosion inhibitor failure [8, 9, 12-13] while other work did not find any effect on film integrity due to flow velocity [7,10,14,15]. Instead, these authors reported that loss of inhibitor protectiveness could be due to contaminants, poor partitioning between oil and water, or parasitic consumption of inhibitors.

One of the key goals of the work presented below was to shed more light on this issue, by investigating if slug flow can affect the performance of typical corrosion inhibitors.

EXPERIMENTAL PROCEDURE

All experiments were conducted at pH 5 and 25ºC. The tested inhibitor concentrations corresponded to 20 and 50 ppm. The effect of a moving slug was evaluated in a 10 cm ID, “Hilly-Terrain System” flow loop (Figure 1) holding 300 gallons of water. This complex flow system exhibits a variety of flow regimes seen in horizontal, inclined, and vertical flows. The gas/liquid mixture first flows over a horizontal distance of 6-m before reaching the crossing section. There the fluids turn through a 90^o degree bend (nine-diameter radius) to flow upward through a 2-m riser, turn again and go through the horizontal crossing section, turn once more and go through the downcomer, and finally make another turn and go forward through a 4-m horizontal discharge section into a separation tank. Current testing was conducted with a superficial liquid velocity of 1 m/s and different superficial gas velocities of (1, 3, 6 and 10 m/s).

Table 1: Experimental Test Matrix

Material	X-65 Carbon steel
Test solution	1 wt% NaCl
Temperature	25 ˚C
pH	5.0
Inhibitor ("quat")	P1 (proprietary formulation) K2 (alkylbenzyldimethylammonium chloride)
Time exposure	24 hours
Superficial gas velocity	1, 3, 6, 10 m/s
Superficial liquid velocity	1 m/s
Measurements techniques	Linear polarization resistance – LPR Weight loss – WL

Three measurement points were used in the first zone – the horizontal section of the Hilly Terrain System. They were typically experiencing a stratified or slug flow regime and were used for weight loss (WL) samples. The second zone in the Hilly Terrain System was in the upward facing bend that turns the flow from horizontal to vertical. This section of the loop saw very turbulent slug/churn flow. Here, there are two test ports on the outer radius of the bend: one was used for electrochemical measurements (LPR) and the other for WL. The next zone had test ports on the inner radius of the downward facing bend. Only WL coupons were used in this section.

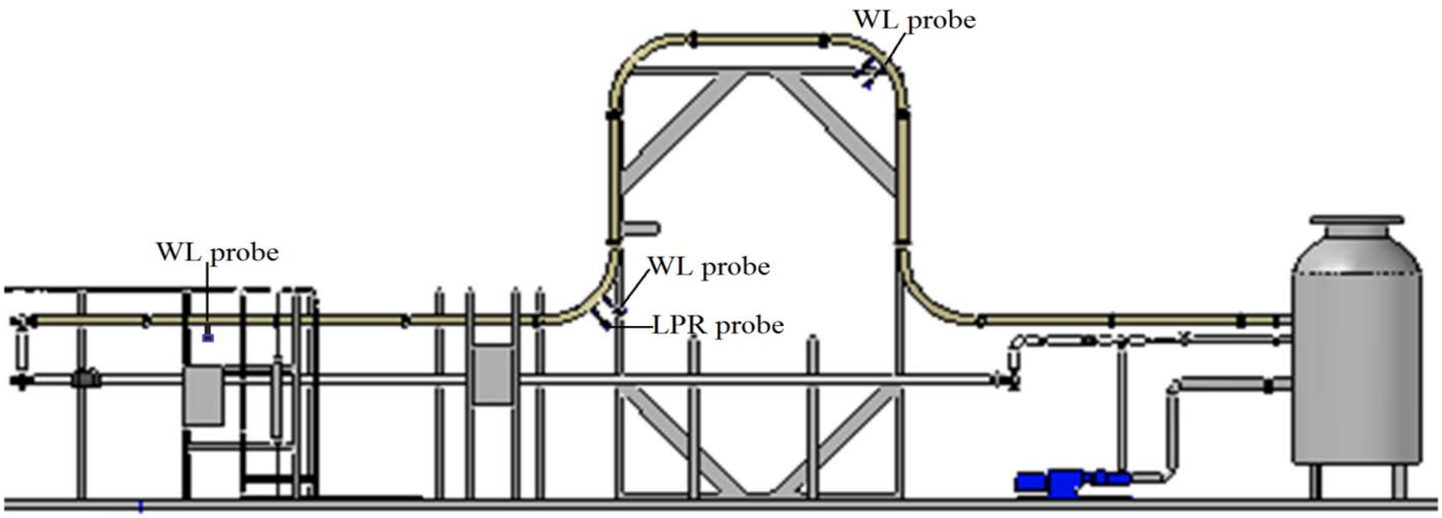


Figure 1: Hilly Terrain System – a transparent multiphase flow loop with corrosion measurement capability.

In addition to the flow loop testing, a glass cell (Figure 3) was connected to the flow loop using the same liquid, so that inhibitor efficiency could be directly compared between the two experimental systems. The rotating cylinder electrode (RCE) made of 1018 carbon steel was used as the working electrode, a concentric platinum wire was used as the counter electrode, and the silver-silver chloride reference electrode was connected externally *via* a Luggin capillary tube.

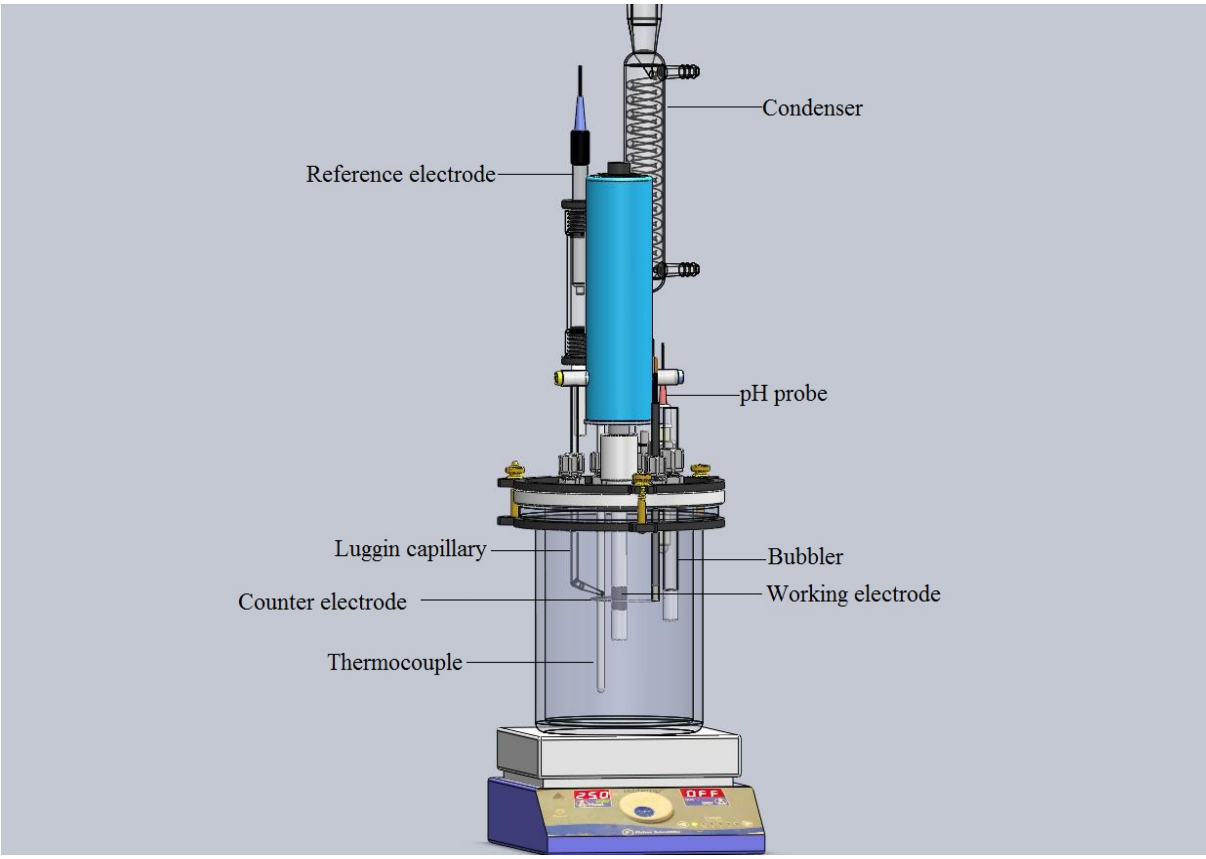


Figure 2: A rotating cylinder 3-electrode electrochemical glass cell testing apparatus

Two quaternary ammonium chloride (quat) based inhibitors were tested in the present study. A proprietary formulation inhibitor (labeled P1) and a commercial inhibitor with a known formulation (labeled K2) were evaluated in the Hilly-Terrain System multiphase flow loop, as described below. The inhibitor K2 has 49~ 52% of active component that is an alkylbenzyldimethylammonium chloride, shown in Figure 3.

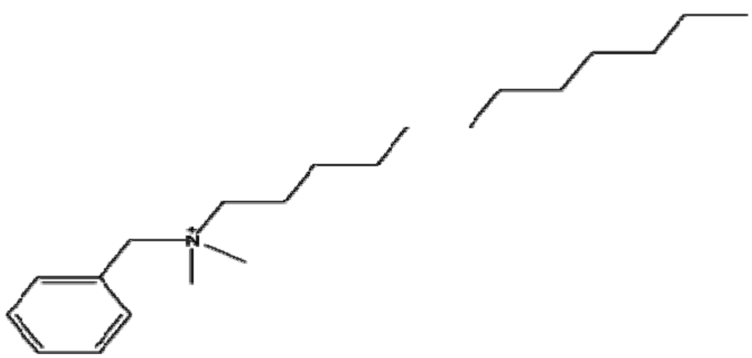
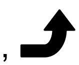
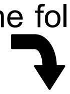


Figure 3: Inhibitor K2, alkylbenzyldimethylammonium chloride

RESULTS

Hilly terrain flow visualization

The flow regime in the horizontal section of the Hilly Terrain Flow Loop varied from stratified flow at the lowest gas velocities to slug flow at higher velocities. For example, with a fixed V_{sl} = 1 m/s and V_{sg} = 1 m/s slugging occurred at a frequency of 7 slugs/minute. The slug frequency increases when the V_{sg} increases, giving a slug frequency of 10 slugs/minute for V_{sg}= 3 m/s, and 15 slugs/minute for V_{sg}= 6 m/s and annular flow for V_{sg}= 10 m/s. The second zone is the bottom bend of the loop that predominantly showed continuous turbulent slug/churn flow behavior with occasionally slug "blow-through". As the gas velocity increased, the continuous slugging intensity became higher. The third zone, at the top bend, had the least turbulent flow in the system. The slugs formed prior to this bend impacted the outer wall and then drained to the bottom of the bend.

Each zone is denoted in the following figures by:  (for the horizontal section),  (for the upward turning bend), and  (for the downward turning bend).

Corrosion measurements

Figure 4 shows an example of the effect that multiphase flow has on corrosion rate when the system has no inhibitor (called "Baseline"). Each time that the superficial gas velocity (V_{sg}) was increased the corrosion rate increased,

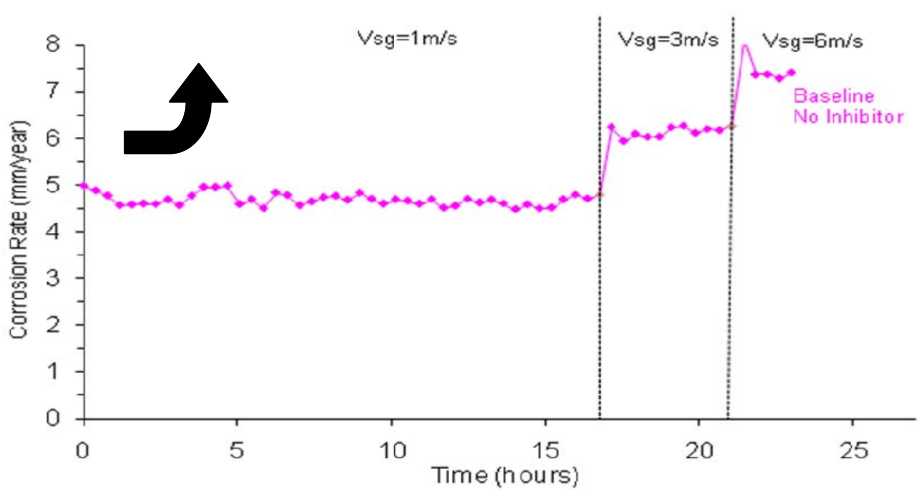


Figure 4: Baseline corrosion rate from LPR (no inhibitor present). Superficial gas velocity changed from 1 m/s to 3m/s and from 3m/s to 6m/s. (pH 5, 25ºC, pCO_2=1 bar, liquid velocity 1m/s).

Figure 5 shows the Baseline corrosion rate (no inhibitor) from WL at the three different locations in the Hilly Terrain System. Note that the flow induced corrosion is highest on the lower bend where the turbulence is also at a maximum. At the top bend, where the turbulence is at a minimum, flow induced corrosion is the lowest.

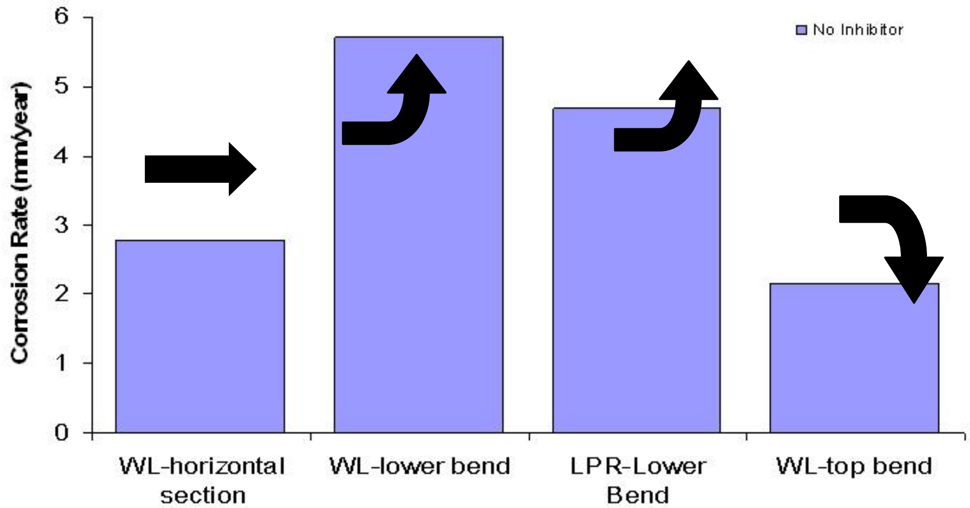


Figure 5: Baseline corrosion rates, no inhibitor present, from weight loss measurements for three different locations in the Hilly terrain system (pH 5, 25ºC, pCO_2=1 bar, superficial gas velocity was 1m/s, superficial liquid velocity was 1m/s).

Figure 6 shows the relative performance obtained with 20 ppm and 50 ppm of inhibitor P1, measured by LPR. When the system has a concentration of 20 ppm, this inhibitor does not show adequate protection, with an efficiency of 40%. However, the performance of inhibitor P1 is largely unaffected by the increase in V_{sg}. There is a small increase in the corrosion rate with V_{sg} increase, however the efficiency of the inhibitor is not affected much. The same effect is seen with 50 ppm of P1, where the efficiency for the 50 ppm concentration of inhibitor is around 85%, before and after the flow rate was increased.

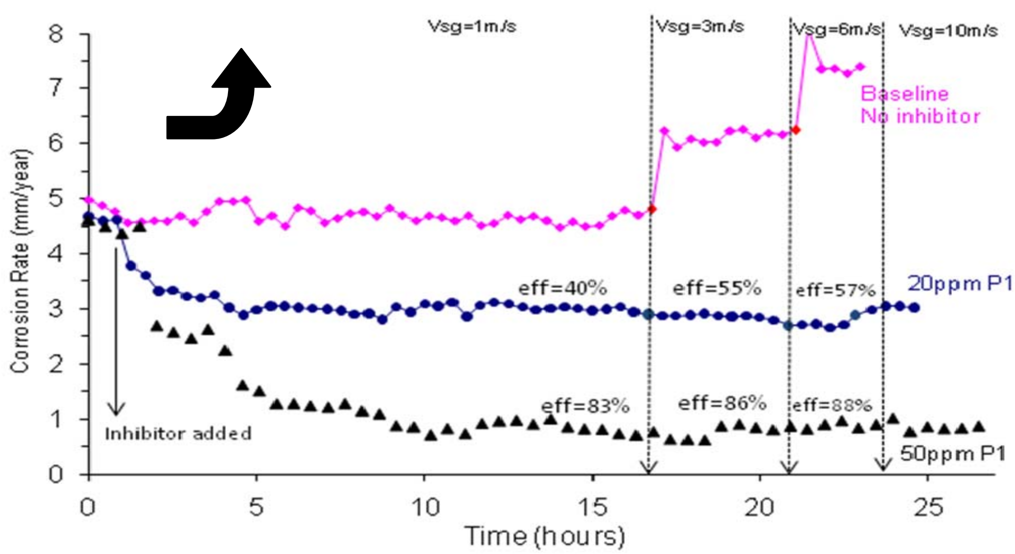


Figure 6: Corrosion rate from LPR with 20 and 50 ppm of inhibitor P1. Superficial gas velocity was: 1 m/s, 3m/s, 6m/s, 10 m/s (pH 5, 25ºC, pCO_2=1 bar, superficial liquid velocity was 1m/s).

Figure 7 shows the performance of a quaternary ammonium inhibitor K2. The 20 ppm gave an efficiency of 63%, and this efficiency did not appreciably change when V_{sg} was increased to 3m/s or to 6m/s. When the 50 ppm of K2 was added, the inhibitor efficiency stayed around 80%. The increases in the inhibited corrosion rate seen with an increase in V_{sg} were attributed to the higher baseline un-inhibited corrosion rate which made it harder for the inhibitor to achieve the same low inhibited corrosion rate.

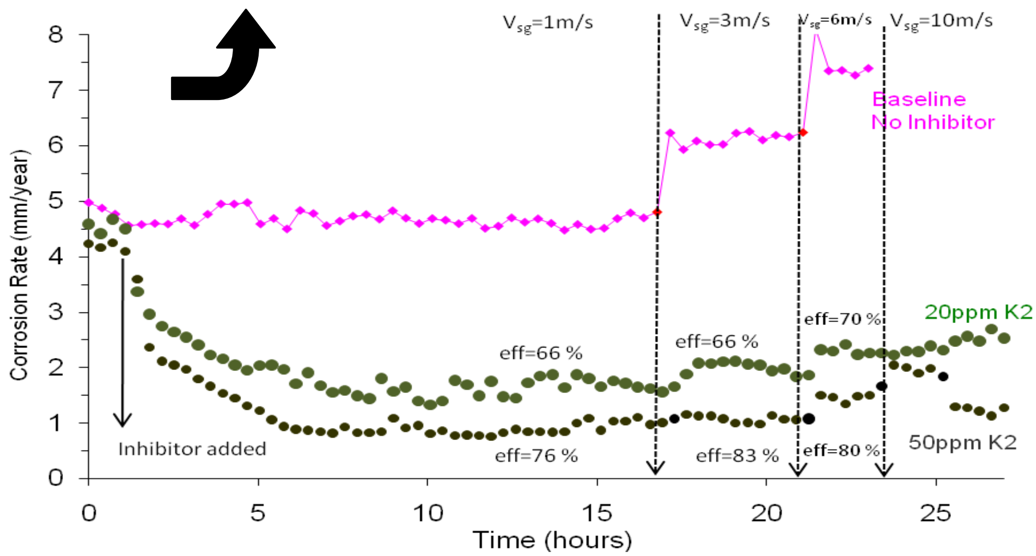


Figure 7: Corrosion rate from LPR with 20 and 50 ppm of inhibitor K2. Superficial gas velocity was: 1 m/s, 3m/s, 6m/s, and 10 m/s (pH 5, 25ºC, pCO_2=1 bar, superficial liquid velocity was 1m/s).

One thing that was common for both inhibitors is that the inhibition efficiency obtained did not change much with the change in the multiphase flow intensity and flow regime, even if there was a slight increase in the corrosion rate due to the different un-inhibited Baseline condition. What was more pronounced however, were the corrosion rates as well as the efficiency of inhibition, measured in the multiphase flow loop which were not as favorable as those measured with the same inhibitors at the same concentrations in independent glass cell experiments. This seemed to indicate that the inhibitor performance was somehow impaired under multiphase pipe flow conditions. However, when the glass cell experiments were conducted in parallel with the flow loop, by taking the electrolyte directly from the flow loop into the glass cell, the efficiency of inhibition in the glass cell was also very poor, equivalent to that seen with much less inhibitor when tested in independent glass cell experiments (see Figure 8). This indicated that a significant fraction of the inhibitor which was added into the multiphase flow loop system was not present in the water and was not protecting the steel sample adequately.

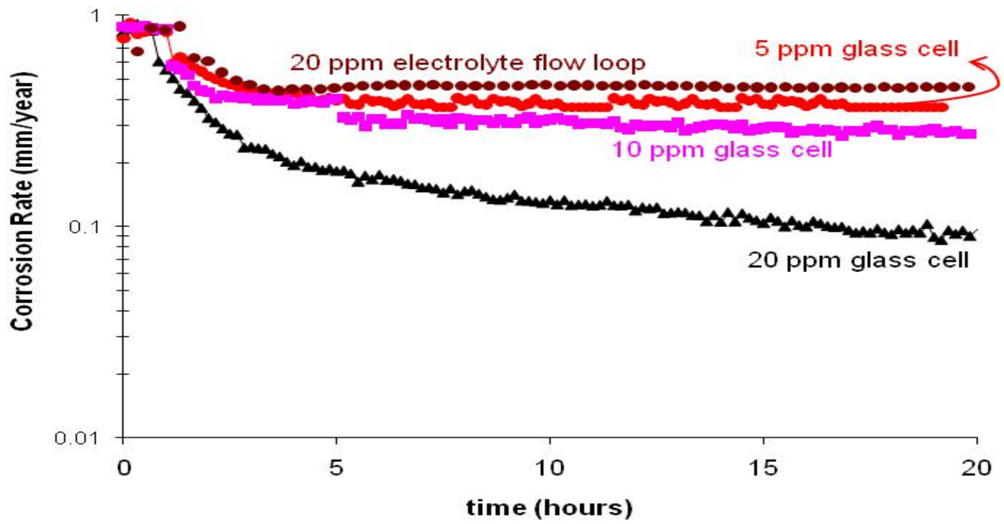


Figure 8: Comparison of corrosion rates from three different concentrations of corrosion inhibitor P1 with electrolyte withdrawn from the flow loop (initial concentration 20 ppm). Experiments were conducted in a glass cell (pH 5.0, 25 ºC, pCO_2=1 bar, 1000 rpm).

After investigating various possible causes, it was concluded that most of the "missing" inhibitor was lost due to foam formation as a result of the inhibitor's affinity for accumulating at the liquid/gas interface. Visual evidence of foam formation is shown in Figure 9.

Figure 9: Formation of foam in the Hilly-Terrain system when the flow loop has 20ppm of inhibitor P1.

CONCLUSION

Two different quat based corrosion inhibitors (a commercial and a known formulation) were tested in a multiphase flow loop, and it was found that:

- The performance of both inhibitors was significantly poorer in multiphase slug/churn flow when compared to nominally identical single-phase flow tests conducted in a glass cell using a rotating cylinder;

- The lack of inhibitor performance in slug flow was caused by the loss of corrosion inhibitor to the gas/liquid interface (producing foam) and not due to some extreme hydrodynamic forces;
- The increase in flow velocity and the intensity of slugging and churning had very little effect on the corrosion inhibitor performance tested at three different flow geometries.

ACKNOWLEDGEMENTS

Helpful discussions with Yao Xiong and Dr. David Young have contributed to the evolution of this research project, as well as the preparation of this paper. Sponsoring companies of the Corrosion Center Joint Industry Project supported the work in this project: Baker Petrolite, BG Group, BP, Champion Technologies, Chevron, Clariant Oil Services, ConocoPhillips, Encana, ENI S.p.A., ExxonMobil, WGIM, NALCO Energy Services, Occidental Petroleum Co., Petrobras, PETRONAS, PTT, Saudi Aramco, Teikoku Oil, and Total.

REFERENCES

1. D. Efird, “Jet Impingement Testing for Flow Accelerated Corrosion” CORROSION/2000, paper no. 52 (Houston, TX: NACE, 2000)
2. D. Efird, “Disturbed Flow and Flow Accelerated Corrosion in Oil and Gas Production” Journal of Energy Resources Technology, 120 (1998): p. 72-77.
3. A. Petersen D. Klenerman, W. Hedges, L. Harris “Effect of Cavitation on Carbon Dioxide Corrosion and the Development of a Test for Evaluating Inhibitors” Corrosion, 58, 3 (2002): p. 216-224
4. A. Petersen D. Klenerman, W. Hedges “Evaluation of the Effect of Carbon Dioxide Corrosion Inhibitors on Cavitation Damage Caused during the Ultrasonic Test” Corrosion, 60, 2 (2004): p. 187-194
5. B. Heeg, T. Moros, D. Klenerman, “Persistency of Corrosion Inhibitor Films on C-Steel under Multiphase Flow Conditions. Part I: the Jet Cylinder Arrangement” Corrosion Science, 40,8 (1998): p. 1303-1311
6. G. Schmitt, C. Bosch, M. Muller, G. Siegmund, “A Probabilistic Model for Flow Induced Localized Corrosion” CORROSION/2000 paper no. 49 (Houston, TX: NACE, 2000)
7. E. Gulbrandsen, A. Grana, “Testing of Carbon Dioxide Corrosion Inhibitor Performance at High Flow Velocities in Jet Impingement Geometry. Effects of Mass Transfer and Flow Forces” Corrosion, 63, 11 (2007): p. 1009-1020.
8. L. Maley, P. Jepson, “Wall Shear Stress and Differential Pressure in Large-Diameter Horizontal Multiphase Pipelines” Journal of Energy Resources Technology, 122 (2000): p. 193-197.
9. R. Hausler, G. Scmitt, “Hydrodynamic and Flow Effects on Corrosion Inhibition” CORROSION/04 paper no. 4402 (Houston, TX: NACE, 2004)
10. S. Nesic, G. Solvi, S. Skjerve, “Comparison of Rotating Cylinder and Loop Methods for Testing CO2 Corrosion Inhibitors” British Corrosion Journal, 32, 4 (1997): p.269-276.

11. G. Hewitt, N. Hall-Taylor, Annular Two-Phase Flow, Pergamon Press, (Great Britain, 1970), chapter 1.

12. G. Schmitt, C. Bosch, P. Plagemann, K. Moeller, “Local Wall Shear Stress Gradients in the Slug Flow Regime – Effect of Hydrocarbon and Corrosion” CORROSION/02 paper no. 02244 (Houston, TX: NACE, 2002).

13. C. Menendez, S. Weghorn, Y. Ahn, A. Jenkins, W. Mok “Electrochemical Evaluations of High Shear Corrosion Inhibitors Using Jet Impingement” CORROSION/05 paper no. 5331 (Houston, TX: NACE, 2005)

14. J. Kvarekval, E. Gulbrandsen, “High Temperature and High Flow Velocity Test for CO2 Corrosion inhibitor” CORROSION/01 paper no. 1025 (Houston, TX: NACE, 2001)

15. A. Jenkins, W. Mok, C. Gamble, S. Keenan, “Development of Green Corrosion Inhibitors for High Shear Applications” CORROSION/04 paper no. 4370 (Houston, TX: NACE, 2004).