INTERCORR2016_269

Copyright 2016. ABRACO Work presented during INTERCORR 2016, in Búzios/RJ in the month of May 2016. Information and opinions contained herein are the exclusive responsibility of the authors.

> **Study of Corrosion Inhibitor Selection for Amazon Pipelines** Lyongjin Lee^a, Jiwon Jung^b, Suyeon Lee^c, and Cheolho Kang^d

Abstract

The selection of corrosion inhibitor for oil and gas pipelines is very important for the prevention of internal pipeline corrosion. Typically, a corrosion inhibitor pre-screening tests using laboratory equipment (e.g. bench-top, autoclaves and flow loops) are carried out for the selection of the best corrosion inhibitor and concentration. The corrosion inhibitor performance (or effectiveness) can be changed depending on many parameters such as temperature, pressure, flow rates, inhibitor type, chloride concentration, CO2, O2, H2S, and so on. It is important for corrosion and corrosion inhibitor tests in laboratory that tests adequately represent field conditions. For the inhibitor selection, the comparison study between autoclave and flow loop is not well-known. This paper will address the comparison results between autoclave and flow loop.

For the inhibitor selection of Amazon pipelines, three commercial corrosion inhibitors for 30% water cut were tested using autoclaves and 30m long HTHP flow loop. Each corrosion inhibitor results obtained from autoclaves and flow loop will be compared. The results showed that for both autoclave and flow loop tests, inhibitor U showed the best performance. However, at the same conditions, the flow loop tests required higher inhibitor concentration in comparison with autoclave tests to achieve the target corrosion rate (less than 0.1 mm/yr).

Key words: corrosion inhibitor, autoclave, flow loop, inhibitor selection

Introduction

Carbon steel and low alloy steels are extensively used in the oil and gas industry as they are excellent and cheap materials. However, these alloys offer very poor resistance to corrosion and this costs the industry millions of dollars in replacement and repairs and loss in production. Here, the selection of corrosion inhibitor is very important since each corrosion inhibitor shows a totally different performance depending on many parameters such as flow rates, water cut, water chemistry, turbulent intensity, pressure, temperature, and so on.

^a PHD, Chemical Engineer - Vice President, Unicoh Specialty Chemicals

^b Microbiologist - Vice President, DYCE Global

^c BS, Industrial Engineer – Sr. Researcher, Unicoh Specialty Chemicals

^d MS, Chemical Engineer - Sr. Vice President, DYCE USA

Laboratory testing for the right choice of the corrosion inhibitor has become a critical step. There are many testing methods for corrosion inhibitor selection test such as bubble test, jet impingement test, autoclave, and flow loop. Bubble test is being used for corrosion inhibitor pre-screening tests. After the bubble test, autoclave and/or flow loop are used for the final inhibitor selection. An autoclave is good to simulate oil field chemistry with shear stress. The main disadvantage of autoclave cannot simulate real flowing conditions including flow pattern. A flow loop can simulate real pipeline flowing conditions including flow pattern. The main disadvantages of the flow loop are that the fabrication of flow loop requires much higher cost than autoclaves and material cost (e.g. oil, brine, gas) for flow loop testing is higher than autoclaves. Also, loop operators must have good backgrounds (e.g. multiphase flow, monitoring and corrosion) to obtain good testing results. *Even though the comparison results between autoclave test and flow loop test are very important, it is very difficult to find a comparison paper*.

Recently, an innovative flow loop was designed and fabricated for the study of corrosion, hydrate, drag reducing agents (DRAs), materials, and inhibitors. In addition, this flow loop is fully equipped with explosion probe. Therefore, any flammability materials (e.g. crude oil, CH4) can be used for tests.

This paper presents the study of corrosion inhibitor selection using commercial corrosion inhibitors for Petrobras onshore production pipeline located in Amazon forest, Brazil. The comparison results between autoclave and flow loop are also described in this paper.

Methodology

Carbon steel weight-loss corrosion coupon (API 5LX65) with a rectangular block of size 30x50x1 mm was used in this experiment. A hole of diameter 4 mm was made on the top position in order to attach the rotating shaft. 316L SS autoclave with 2L volume was used for the experiments. The autoclave is equipped with magnetic drive for stir and automatic temperature control system. The schematic diagram of the apparatus used in this experimental study is shown in Figure 1.



Figure 1. Autoclave System

All the experiments were conducted using the same apparatus. After the test, the corrosion product on the coupon surface was removed using ultrasonic cleaning

machine with the solution of HCL liquid with acid inhibitor. After the corrosion coupon was cleaned, the corrosion coupon was rinsed using sodium bicarbonate solution in order to neutralize the acid. Then the moisture was immediately removed using dry air. The corrosion coupon was weighed by weight 0.1mg unit.

The experiments were carried out in a flow loop system as shown in Figure 2. The flow loop consisted of a 30 m long, high pressure and high temperature system. The entire flow loop system was manufactured from ANSI 316L stainless steel. The system is equipped with a heater and chiller to automatically maintain a desire temperature during the test.



Figure 2. Flow loop photo

The concentration of iron was maintained below 10 mg/L since the corrosion rate is greatly affected in the presence of iron in the system. When iron concentration occurred from corrosion of carbon steel weight-loss coupon increases in the solution, the pH increases. This leads the decrease of corrosion rate. For the prevention of iron concentration on corrosion, the flow loop tank volume of 0.11 m³ (30 gallons) was adopted. A sampling tube is connected to one of the ports in the test section which is used for the determination of oxygen and iron concentrations. The pH of the system is also monitored during the test.

Preparation and handling process for coupons were carried out based on NACE Standard RP 0775-2005. The corrosion rate was calculated as follows:

$$Corrosion Rate (mpy) = \frac{2.227 X 10^4 X W}{A X T X D}$$

where,

W	= mass loss in grams (g)
А	= initial exposed are of coupon in square inches (in^2)
Т	= exposure time in days (d)
D	= density of coupon metal in grams per cubic centimeter (g/cm^3)

Table 1 shows the test conditions for the experiments. The Amazon pipeline pressure is 6.8 MPa (986 psi). The pipeline diameter and pipeline length are 0.25 m (10 inches) and 35 km. The pipeline contains O2, which is approximately 0.1 mg/L (100 ppb).

Parameter	Condition
CO ₂ Pressure, MPa	0.14
Temperature, ^o C	35
Chloride, %	210,000
Autoclave: Shear Stress, Pa	10.5 & 21.4
Flow Loop: Liquid Velocity, m/s	1.0, 2.0 and 3.0
Corrosion Inhibitors	A, B & U

Table 1:	Test	Conditions
----------	------	------------

Results and discussion

The comparison tests for three candidate corrosion inhibitors were performed using autoclave with magnetic drive and flow loop. Figure 3 shows the comparison of corrosion inhibitors in 30% water cut using autoclaves. The baseline corrosion rate increased from 080 mm/yr to 0.99 mm/yr with an increase of shear stress from 10.5 Pa to 21.4 Pa. It can be seen that the corrosion rate decreased dramatically with an addition of inhibitors with 20 mg/L. Corrosion inhibitor A presented higher than 0.45 mm/yr for both shear rates. Inhibitors B and U showed much better performance than inhibitor A. A little higher corrosion rates than target corrosion rate were obtained with 30 mg/L of corrosion inhibitor B. Corrosion inhibitor U showed the best performance. The target corrosion rate (0.1 mm/yr) was achieved with only 20 mg/L of inhibitor B.

Comparison photos of weight-loss coupons after each corrosion inhibitor test (before cleaning) are shown in Figures 4 and 5. For corrosion inhibitor A, corrosion product film covers coupon surface. In case of corrosion inhibitor B, a little corrosion product can be seen. Corrosion inhibitor C showed very clean coupon surface.



Figure 3. Comparison of Corrosion Inhibitors, 70% Oil/30% Water, Autoclave Results



BaselineInhibitor AInhibitor BInhibitor UFigure 4. Surface Photos of Weight-Loss Coupons Before Cleaning
Autoclave Test Results, Shear Stress = 10.5 Pa



BaselineInhibitor AInhibitor BInhibitor UFigure 5. Surface Photos of Weight-Loss Coupons Before Cleaning
Autoclave Test Results, Shear Stress = 21.4 Pa

Figure 6 shows the baseline corrosion rates at the liquid velocities of 1.0, 2.0 and 3.0 m/s. It can be seen that the corrosion rate increased with an increase of liquid velocity from 1.0 m/s to 2.0 m/s. This is due to the fact that the turbulent intensity increases with an increase of the liquid velocity, which leads the increase of shear stress. However, the baseline corrosion rate decreased when liquid velocity further increased to 3 m/s. This is due to the fact that more oil contacts around the pipe wall. Here, the flow pattern can be dispersed flow.



Figure 6. Baseline Corrosion Rates, 70% Oil/30% Water Flow Loop Test Results

The liquid velocities of 1.0, 2.0 and 3.0 m/s correspond to shear stress of approximately 3.1Pa, 10.5 Pa and 21.4 Pa, respectively. At the liquid velocities of 1.0, 2.0 and 3.0 m/s, the corrosion rates were 0.95, 1.08 and 0.45 mm/yr, respectively. The pH was monitored during the test. The pH values for all baseline tests and all corrosion inhibitors without and with corrosion inhibitors were approximately 4.5 (+/- 0.1).

The corrosion coupon surface after the baseline tests was seen in Figure 7. At liquid velocities of 1.0 and 2.0 m/s, the color of corrosion coupons turned out black (Iron carbonate corrosion product). It can be seen that the corrosion coupon at a liquid velocity of 3.0 m/s, the coupon surface showed that corrosion product film became weaker.



Figure 7. Surface Photos of Weight-Loss Coupons After Baseline Test (Before Cleaning) Flow Loop Test Results

The performance of corrosion inhibitor B for 30% water cut is shown in Figure 8. At all liquid velocities with 20 mg/L of corrosion inhibitor B, the corrosion rates reduced dramatically, but higher than 0.2 mm/yr. Further increase of inhibitor concentration to 40 ppm slightly decrease the corrosion rates. However, the corrosion rates at all liquid velocities were slightly higher than the target corrosion rate. At superficial liquid velocities of 1.0, 2.0 and 3.0 m/s, the corrosion rates were 0.11 mm/yr, 0.12 mm/yr and 0.12 mm/yr, respectively. Following effectiveness was 88.4%, 88.6% and 73.5%, respectively. To achieve the target corrosion rate showed slightly lower than the target corrosion rate.



Figure 8. Performance of Corrosion Inhibitor B Flow Loop Test Results

Figure 9 shows an equivalent plot of corrosion inhibitor U. It can be seen that the corrosion rates were decreased dramatically with an addition of corrosion inhibitor U of 20 mg/L. At all liquid velocities, the corrosion rates were lower than 0.16 mm/yr. When additional corrosion inhibitor of 10 mg/L (total 30 mg/L) was injected, the target corrosion rate was achieved at all liquid velocities. Here, at liquid velocities of 1.0, 2.0 and 3.0 m/s, the corrosion rates were 0.08 mm/yr, 0.08 mm/yr and 0.09 mm/yr, respectively. The following effectiveness showed 91%, 91.9% and 79%, respectively. When the total dosage of 40 mg/L, the effectiveness was higher, which were 95.3%, 95.6% and 87.3%, respectively.



Flow Loop Test Results

Figure 10 presents the surface photos of weight-loss coupons after 40 mg/L corrosion inhibitor B testing (before cleaning). Figure 11 shows an equivalent plot of 30 mg/L corrosion inhibitor U. It can be seen from both Figures that inhibitor U showed clearer coupon surface.



Figure 10. Surface Photos of Weight-Loss Coupons After Inhibitor B Test (Before Cleaning), Flow Loop Test Results, 40 mg/L

It can be seen from Figures 3, 8 and 9 that for both corrosion inhibitors of B and U, the flow loop required higher inhibitor concentration to reduce corrosion rate. For example, the corrosion rates for autoclave test with 30 ppm at shear rates of 10.5 Pa, and 21.4 Pa were 0.11 mm/yr and 0.13 mm/yr, while the corrosion rates for flow loop test at the same conditions showed higher corrosion rates (0.16 mm/yr for both shear rates). For autoclave tests with corrosion inhibitor U, the target corrosion rate was achieved with 20 mg/L. However, for flow loop tests, 10 more

mg/L of corrosion inhibitor concentration (total 30 mg/L inhibitor concentration) was required to achieve the target corrosion rate.



VL = 1.0 m/s

VL = 3.0 m/s

Figure 11. Surface Photos of Weight-Loss Coupons After Inhibitor U Test (Before Cleaning), Flow Loop Test Results, 30 mg/L

Tables 2 and 3 show the comparison of corrosion inhibitors for the flow loop tests. It can be seen from both Tables that effectiveness of corrosion inhibitor U was higher than that of corrosion inhibitor B. 30 mg/L of corrosion inhibitor U was required to achieve the target corrosion rate (0.1 mm/yr) in all liquid velocities. However, it is seen from Table 3 that the corrosion rates with 40 mg/L of corrosion inhibitor B showed higher than the target corrosion rate.

V _L m/s	Baseline mm/yr (mils/yr)	Inhibitor B mm/yr (mils/yr)	Effect. %	Inhibitor U mm/yr (mils/yr)	Effect. %
1	0.95 (37.9)	0.14 (5.6)	85.2	0.08 (3.4)	91.0
2	1.08 (43.1)	0.16 (6.3)	85.4	0.08 (3.5)	91.9
3	0.45 (18.1)	0.16 (6.4)	64.6	0.09 (3.8)	79.0

Table 2. Comparison of Corrosion Inhibitors with 30 mg/L

Table 3. Comparison of Corrosion Inhibitors with 40 mg/L

V _L m/s	Baseline mm/yr	Inhibitor B mm/yr (mils/yr)	Effect. %	Inhibitor U mm/yr (mils/yr)	Effect. %
1	0.95 (37.9)	0.11 (4.4)	88.4	0.05 (1.8)	95.3
2	1.08 (43.1)	0.12 (4.9)	88.6	0.05 (1.9)	95.6
3	0.45 (18.1)	0.12 (4.8)	73.5	0.06 (2.3)	87.3

Conclusions

The comparison study of three commercial corrosion inhibitors (A, B and U) for Petrobras' Amazon pipelines was carried out at 30% water cut. The comparison data between autoclave tests and flow loop tests is very limited. In this paper, the comparison results for autoclave and flow loop is also presented.

The baseline corrosion rate for autoclave tests increased from 0.80 mm/yr to 0.99 mm/yr with an increase of shear stress from 10.5 Pa to 21.4 Pa. However, the baseline corrosion rate for flow loop tests decreased when liquid velocity increased from 2 m/s (shear stress of 10.5 Pa) to 3 m/s (shear stress of 21.4 Pa). This is due to the fact that more oil contacts around the pipe wall.

Autoclave and flow loop results showed a different corrosion inhibitor performance. For both corrosion inhibitors of B and U, the flow loop required higher inhibitor concentration to achieve the target corrosion rate.

For autoclave tests, corrosion inhibitor A showed the worst performance. Inhibitor U presented the best performance, which achieved the target corrosion rate with only 20 mg/L of inhibitor concentration.

For flow loop tests, inhibitor U showed much better performance than inhibitor B. 30 mg/L of inhibitor U required to achieve the target corrosion rate (0.1 mm/yr) in all liquid velocities. However, the corrosion rates with 40 mg/L of corrosion inhibitor B showed higher than the target corrosion rate.

References

(1) Kang. C., Rhodes, J., and Magalhaes, A., "Corrosion Inhibitors in Deep Offshore Catenary Risers," NACE MP, 2014.

(2) Kang, C., Magalhaes, A. A. O. and Silva, J., , "Study of the Inhibitor Selection at Low Water Cut in Closed to Deep Offshore Wellhead Flow Lines" NACE International Conference and Exhibition, 2012.

(3) Ferreira, P. A., Magalhaes, A. A. O. and Kang, C., "Effect of Flow on Corrosion in Catenary Risers Risers and Its Corrosion Inhibitor Performance," Rio pipeline Conference and Exposition, paper # IBP1259-09, Rio de Janeiro, Brazil, Oct. 2009.

(4) Kang. C., Ferreira, P. A., Silva, J., and Magalhaes, A. A. O., "Corrosion Control in Severe Slugging SCR Risers," Offshore Africa Conference and Exhibition, paper # 55, January 2009.

(5) Sintoorahat, P., Wairatpanich, A., Chimam, S., Mongkholkhajornsilp, D., and Kang, C., "Performance of Corrosion Inhibitors at High CO2 Pressures in Wet Gas Pipeline," International Pipeline Conference (IPC 2008), paper # IPC08-64114, Calgary, Canada, Sep. 2008.

(6) Pacheco, J. L., Ibrahim, F. C., Franco, R. J., "Testing Requirements of Corrosion Inhibitor Qualification for Pipeline Applications," NACE International Conference and Exhibition, 2010.