

## **Dual Functional Corrosion Inhibitor Design and Testing for Top-of-Line and Bottom-of-Line Corrosions**

Larry Chen  
Clariant Oil Services  
2730 Technology Forest Drive  
The Woodlands, Texas 77381  
The United States of America

Nihal Obeyesekere  
Clariant Oil Services  
2730 Technology Forest Drive  
The Woodlands, Texas 77381  
The United States of America

Jonathan Wylde  
Clariant Oil Services  
2730 Technology Forest Drive  
The Woodlands, Texas 77381  
The United States of America

Michael Sim  
Clariant Oil Services  
No.79-80 Hicom Sector B  
Jalan Taluk Agung 27/93A, 40000 Shah Alam  
Malaysia

### **ABSTRACT**

Bottom-of-Line (BOL) corrosion inhibitor design and production has been a successful story and a mature technology in oil and gas industry. However, preventing Top-of-Line (TOL) corrosion with inhibitors is very challenging, and even more challenging when pursuing dual functional corrosion inhibitors that serve for both BOL and TOL at the same time. Designing a dual functional corrosion inhibitor for both BOL and TOL is a difficult and challenging task, with several hurdles to overcome in this endeavor. Some of the difficult issues are: calculate the treating weight between the top of line and bottom of line, how to make the combined products perform effectively for both top and bottom of lines, how to make the low and high volatile molecules for mitigating BOL and TOL corrosion to be compatible and homogenous in a single blend.

More than 60 active components were used to develop more than 30 formulated products. These products were screened using a TOL rig, RCE and RCA methods to pare down the products. These were then subjected to various physical properties such as flash point, viscosity requirements, emulsion and foaming tendencies as well as thermal stability issues. Finally, two products were selected that satisfied all desired chemical characteristics and performance.

One BOL and TOL combined product denoted as TB-3 was developed for treating both BOL and TOL applications. TB-3 is a water-soluble product that exhibited excellent thermal stability

up to 110°C and demonstrated high efficacy in corrosion inhibition for both BOL and TOL applications under sweet or sour conditions with or without the presence of organic acids.

Key words: Top-of-Line Corrosion, Bottom-of-Line Corrosion, dual functional corrosion inhibitor, corrosion inhibitor, sour gas corrosion, CO<sub>2</sub> corrosion, organic acids.

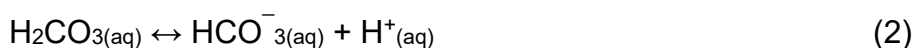
## INTRODUCTION

TOL corrosion is reported to occur in large diameter wet gas pipeline in stratified flow conditions due to low fluid velocities<sup>1</sup>. With increasing distance from the inlet, the wet gas pipeline becomes cooler as it loses heat to the environment. Such cooling causes water, hydrocarbon, and other high vapor pressure species to condense on the pipe wall. The upper part of the pipe will constantly be supplied with freshly condensed water while the less corrosive water saturated with corrosion products will be drained along the pipe wall to the bottom of the line. The presence of acidic components in the gas phase, such as CO<sub>2</sub> and H<sub>2</sub>S, promotes corrosivity in gas transportation and production pipelines. The condensation of water can occur at the top of the pipeline due to the temperature difference of the top and bottom sections of the flow line. This condensed water can be corrosive when the acid gases and low molecular weight organic acids become dissolved in it. The condensed water and CO<sub>2</sub> undergo a hydration reaction to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>, eq 1). The dissociation of carbonic acid leads to hydrogen and bicarbonate ions (eq 2). H<sub>2</sub>S will dissolve in condensed water to produce hydrogen and bisulfide ions (eq 4) and further dissociation would yield another hydrogen ion and a sulfide ion (eq 5)<sup>2</sup>. These ionic species are in equilibria. Although normal oil field brine carries various ionic species such as bicarbonates to control pH, the condensed water does not carry salt. Therefore, without pH controlling salts, these soluble acid gases and volatile organic acids dissolved in condensed water can be corrosive with low pH, as shown in the following reactions:

As CO<sub>2</sub> gas dissolves in water, aqueous CO<sub>2(aq)</sub> is hydrated to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>):



The H<sub>2</sub>CO<sub>3</sub> dissociates to release a H<sup>+</sup> and a bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) in solution:



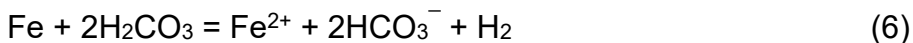
The HCO<sub>3</sub><sup>-</sup> also dissociates to release another H<sup>+</sup> and a carbonate ion (CO<sub>3</sub><sup>2-</sup>)



After H<sub>2</sub>S dissolves in water, it dissociates to bisulfide (HS<sup>-</sup>) and sulfide (S<sup>2-</sup>) species in a series of dissociation relations in solution:



As the corrosion process takes place the pH and alkalinity in the condensed water will increase, as described in these simplified reactions:



Both reactions (6) and (7) give two moles alkalinity ( $2\text{HCO}_3^-$  or  $2\text{HS}^-$ ) for each mole iron corroded, and consequently the pH will increase, and the bicarbonate / bisulfide concentration will increase. As the concentration of dissolved iron ( $\text{Fe}^{2+}$ ) increase during corrosion reactions, solid corrosion products like  $\text{FeCO}_3$  and  $\text{FeS}$  may form, depending on the solubility and kinetics at the present conditions. Usually,  $\text{FeCO}_3$  precipitation is kinetically slow, particularly at low temperatures, and it requires high supersaturation before precipitation occurs<sup>3</sup>. If a film of dense protective corrosion product forms on the steel surface it may reduce or potentially stop the corrosion process. Previous TOL experiments have shown that even with very low levels of  $\text{H}_2\text{S}$  compared to  $\text{CO}_2$ , iron sulfide is the dominating corrosion product at low temperatures<sup>4</sup>, most likely due to the slow kinetics of iron carbonate formation.

It is generally accepted that top of line corrosion is limited by the solubility of corrosion products in the condensing water, at least unless the condensation rates are exceptionally high<sup>5,6</sup>. If organic acids are present in the gas phase they will condense together with water and make it even more acidic and consequently increase the solubility of iron<sup>7</sup>.



In typical multiphase pipelines, the inlet temperatures are high ( $30^\circ\text{C} - 90^\circ\text{C}$ ), and apart from acetic acid, formation water also contains other volatile organic acids. For most of its lifetime a pipeline is operating under stratified gas-liquid flow conditions where condensate (HC) and water is flowing in the bottom of the line (BOL). The gas phase is in thermodynamic equilibrium with the condensate and water in the BOL, and volatile condensate and water condense out at the TOL. The combination of high fluid temperature, environmental temperature and organic acids (usually acids such as acetic acid, formic acid, propanoic acid, 1-butanoic acid, malonic acid, oxalic acid etc.) in the gas phase implies that TOL-corrosion will take place in multiphase pipelines, unless countermeasures are taken. Therefore, the corrosion mechanism is the corrosion of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and organic acid.

The water chemistry at the TOL will be composed of only species which are found in the gas phase. Therefore, the main corrosive species of TOL corrosion are acid gas components and volatile organic acids. This condition is valid when the flow regime is stratified, and bottom-of-line water cannot reach the top of the line section. Literature<sup>8,9</sup> indicates that the organic acid concentration in the TOL condensed fluid is approximately equal to the BOL concentration at low condensation rates. High condensation rates reduce the TOL organic acid concentration to approximately three quarters of the BOL organic acid concentrations<sup>10</sup>.

TOL is particularly problematic because it is difficult to ensure continuous inhibition. In general, we can distinguish three distinct corrosion regimes in a wet gas pipeline based on the locations: bottom of the line corrosion, sidewall corrosion and at top of the line corrosion<sup>11</sup>. The corrosive environment and conditions are considerably different at each of these locations. At the bottom of the line, the liquid is accumulated, the degradation is uniform, and the corrosion rate can be mitigated with the use of inhibitors. On the sidewalls and the top of the pipe, corrosion inhibitors are usually applied by several techniques including batch treatment using a traditional or spray pig and continuous injection<sup>12,13</sup>. In addition, neutralizers can be applied to the pipelines to raise the system pH between 6.5 and 7.5<sup>14</sup>. This technique is also known as pH stabilization which

promotes the formation of iron carbonate scale on the pipe wall reducing the corrosion rate. Inhibitors typically used in pH stabilization processes include mercaptobenzothiazole, methyldiethanolamine (MDEA) and cyclohexylamine<sup>15</sup>.

An experimental project was initiated to formulate corrosion inhibitors for treating top of line corrosion under conditions typical for pipelines containing majorly CO<sub>2</sub>, with traces of H<sub>2</sub>S and considerable amounts of acetic acid (~500 mg/l) in the gas phase (acetate is initially in the water).

## EXPERIMENTAL

### Inhibitor Development

More than thirty new products were formulated and tested during this study. These products were blended with suitable solvent packages, an assortment of traditional pipeline corrosion inhibitors, standard and novel volatile amine compounds. The volatile corrosion inhibitor (VCI) / non-volatile corrosion inhibitor (BCI) ratios in these experimental blends were variedly formulated for optimizing the effectiveness in treating both TOL and BOL corrosions, and in accordance with the field operating conditions as well. This paper summarizes the test results on the most effective dual functional corrosion inhibitors developed for TOL and BOL corrosion, which will be subsequently deployed in the field.

### Corrosion Inhibitor Evaluation

Several lab test methodologies were utilized to evaluate corrosion inhibitor performance. Since the system conditions within a pipeline differ between the top and the bottom, the testing regime was designed to assess inhibitor performance under either bottom or top-of-line conditions or evaluated both at the same time.

- The Rotating Cylinder Electrode (RCE) test was used as an initial screening tool to evaluate inhibitor efficacy under bottom-of-line conditions.
- The TOL test cell was used to evaluate the inhibitor efficacy under top-of-line corrosion.
- The High-Pressure Rotating Cylinder Electrode (HP-RCE) weld test was used to evaluate the inhibitor efficacy on the weld metal sections under bottom-of-line conditions.
- Finally, the high-pressure autoclave was used to determine corrosion inhibitor performance under both top and bottom line conditions.

### Rotating Cylinder Electrode Test

Corrosion inhibitors were tested using RCE test method for initial selection. Linear polarization resistance (LPR) measurements were made with an electrochemical measurement system. The working electrode was made of an UNS K03014 carbon steel (CS) cylinder with a surface area of 3.16 cm<sup>2</sup>. A UNS N10276 electrode was used as a pseudo-reference, and a titanium rod was used as the counter electrode. The corrosion inhibitors were added at 15 ppm based on the brine volume after the baseline corrosion rate was monitored and observed to be stable. The experimental setup for the RCE tests is shown in Figure 1 and test conditions are shown below.

- Temperature            80°C (194°F)
- Gas Composition       100% CO<sub>2</sub> for Sweet RCE testing, 76%mol CO<sub>2</sub> + 100ppm H<sub>2</sub>S + N<sub>2</sub> for sour RCE testing
- Pressure                Ambient

- Brine Composition 1,000 mg/L NaCl brine
- Dose Rates 15ppm with respect to the total fluids
- Test Duration 17 hours
- Rotation Speed 6.4 Pa



Figure 1. Experimental setup for the RCE tests

### TOL Corrosion Test

TOL test device as shown in Figure 2 is used for testing a corrosion inhibitor performance in a simulated TOL environment. A 2L of glass kettle contains 700 ml testing fluid that sits on the heating stirrer. The coupon holder holds a metal coupon and contains a coolant fluid (50/50 MEG and water) that cools coupon backside to control the condensation rate ( $\sim 0.20$  to  $0.30 \text{ ml/m}^2/\text{s}$ ), the cooling temperature was set at desired temperature ( $10^\circ\text{C}$  -  $40^\circ\text{C}$ ) to achieve a constant condensation rate. The bulk brine solution and the vapor phase in the glass kettle were well maintained at  $80^\circ\text{C}$  for this study, while a magnet bar was stirring at 200 rpm throughout the testing. General corrosion rate was calculated by weight loss measurement. Testing fluid was pre-deaerated and transferred into the TOL testing cell. Vapor space was purged by applying a slightly positive pressure of  $\text{CO}_2$ , and then apply a required gas mixture for the testing. Bottom line corrosion rate could also be monitored by a 3-electrode LPR probe. However, since the corrosion inhibitors were tested by RCE method from the initial screening, the LPR data was not recorded during TOL testing.

### TOL Test Conditions:

- Pressure: Ambient
- Temperature:  $80^\circ\text{C}$  for Bulk Vapor and  $40^\circ\text{C}$  for Coupon
- Gas Composition:  $6.5 \text{ mol}\% \text{ CO}_2 + \text{N}_2$  balanced for sweet testing  
 $100 \text{ ppm H}_2\text{S} + 6.5 \text{ mol}\% \text{ CO}_2$  and balanced with  $\text{N}_2$  for sour testing
- Brine: 1,000 mg/L NaCl synthetic Brine + 500ppm acetic acid

- CI Dose Rate: 300 ppm with respect to the total fluids
- Test Duration: 7 Days

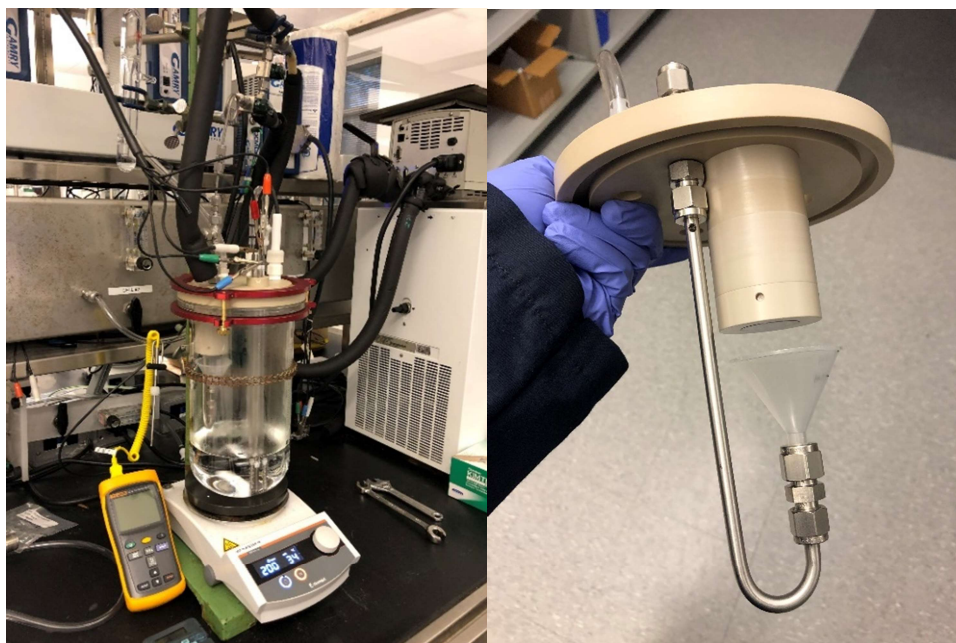


Figure 2: TOL Test Setup (left), Coupon holder and coolant liquid chamber (right)

### High Pressure Rotating Cylinder Electrode Test (Weld Test)

The scope of the project required the corrosion inhibitor performance evaluation in protecting pipeline weld sections from galvanic corrosion, also known as dissimilar-metal corrosion in which one metal corrodes preferentially when in electrical contact with a different type of metal, and both metals are immersed in an electrolyte such as condensed water in a pipeline. The weld test was conducted using high pressure rotating cylinder electrode (HP-RCE) equipment shown in Figure 3. After 3,200 ml deaerated synthetic brine was introduced into the autoclave, the vessel was sealed and heated to the testing temperature (110°C). After the testing temperature reached, 8 bar CO<sub>2</sub> was charged into the system. Turned the test controller on and started to run a baseline period for 34 hours and then inject 300 ppm of corrosion inhibitor respect to the total fluid. Continue to run the CI inhibited period for 56 hours.

The suitable weld electrodes were constructed from a cross section of pipeline. The weld metal sample was sectioned to make 2x5-electrodes assemblies, comprising of two parent metal electrodes (Parent 1 and Parent 2), two heat affected zone electrodes (HAZ 1 and HAZ 2) and a weld electrode (Weld). The electrodes were mounted in resin to form a 5-electrode assembly, a diagram of a 5-electrode weldment is shown in Figures 4 and 5. The testing conditions are shown below:

- Temperature 110°C
- Gas Composition CO<sub>2</sub> and N<sub>2</sub>
- Total Pressure 157 bar (2,277 psi = 6.5 mol CO<sub>2</sub> in N<sub>2</sub>)
- Fluid Composition 1,000 ppm NaCl brine
- Dose Rate 300 ppm with respect to brine
- Test Duration >3 day