

# Evaluation of a Novel Top-of-the-Line Corrosion (TLC) Mitigation Method in a Large-Scale Flow Loop

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## ABSTRACT

*Innovative top-of-the-line corrosion (TLC) inhibition techniques are being investigated as an alternative to batch treatment. A novel idea consists of injecting the corrosion inhibitor within a foam matrix. Previously, a “proof of concept” validation of the novel TLC mitigation method was successfully conducted in a small-scale laboratory setup. The findings in this paper present the next step in the study before field trial: validation of the method and characterization of the foam properties in realistic, large-scale flowing systems. The foam containing the inhibitor was injected into the flow loop, forming a dense plug, which was pushed forward by the gas. The foam-generation method carried considerable importance for foam stability, as well as inhibition persistency. Foam created under stagnant conditions retarded the corrosion rate up to 97%, however the inhibition effect was not persistent. When the foam containing 20,000 ppm<sub>v</sub> of corrosion inhibitor, TOFA/DETA imidazoline, was created in flowing conditions, the corrosion inhibition efficiency was calculated to be higher than 90%, and the inhibition effect lasted up to 50 h. The novel TLC mitigation method showed promising results in a large-scale flow loop, and applications in oil and gas field environments should be considered.*

**KEY WORDS:** carbon dioxide, carbon steel, corrosion inhibitor, flow effects

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## INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) top-of-the-line corrosion (TLC) occurs in wet gas flow where a significant temperature gradient between the outside environment and the inner pipeline surface leads to high condensation rates. A thin film of condensed water forms on the sides and upper section of internal pipe walls, and the presence of various corrosive species, such as CO<sub>2</sub> and acetic acid (CH<sub>3</sub>COOH, abbreviated hereafter as HAC) causes a severe corrosion problem.<sup>1-7</sup> TLC occurs typically in wet gas pipelines and only in stratified or stratified-wavy flow regimes. In annular and slug flow, TLC is not an issue, as the water chemistry is rather uniform around the pipe circumference, as well as the availability of any corrosion inhibitor.<sup>8-10</sup>

The paramount problem of TLC is the large uncertainty associated with the use of traditional corrosion mitigation techniques. Corrosion inhibition is one of the most commonly used methods for corrosion control in carbon steel equipment for oil and gas production; however, conventional mitigation methods can fall short in protecting the top of the line, since conditions do not allow the inhibitor to reach the top sections of the wall.<sup>11-12</sup> Gravity effects, low flow rates, and stratified flow make the transfer of the corrosion inhibitor to the top of the pipe difficult. The most common method used in the case of TLC is batch treatment, but this results in regular decreases in production rates and consequently in revenue. Different physical and operational criteria of the pipeline, as well as the availability of special equipment (e.g., the presence of pig launchers and receivers) must be

considered prior to applying this inhibition treatment. New inhibitor delivery methods are being investigated as an alternative to conventional batch treatment.<sup>13-14</sup> A novel idea consists of injecting the corrosion inhibitor within a foam matrix and delivering the corrosion inhibitor to locations where condensation occurs. This method could theoretically be implemented without affecting the production conditions within a given pipeline. A “proof of concept” validation of the novel TLC mitigation method was successfully conducted in a small-scale laboratory setup.<sup>15</sup>

In order to raise confidence that the previously obtained results can be applied in the field, the novel TLC mitigation method had to be evaluated under simulated field conditions. A multiphase flow system was incorporated in the experimental study in order to evaluate the novel TLC method under more realistic conditions. Large-scale flow loop studies are better suited for the simulation of corrosive environments and flow conditions (realistic gas temperature, gas flow rate, CO<sub>2</sub> partial pressure, and condensation rate) encountered in the field.<sup>13,16-17</sup>

Foam has been used for various purposes in the oil and gas industry: in improved oil recovery methods, as a tool for the removal of liquid loading from wells, and in drilling as a tool for hole cleaning in case of underbalanced horizontal wells. The hydrodynamics of foam are especially challenging because the foam has a complex structure with metastable characteristics caused by the large interfacial area. For example, foam stability and strength are affected by many parameters (liquid-phase properties, surfactant type, surfactant concentration, foam generator, pipe diameter, etc.).<sup>18-19</sup>

In this study, two injection techniques were considered. The foam was injected into the flow loop piping, forming a dense plug, which was pushed forward by the gas. This method was designed to uniformly deliver the inhibitor to the inner pipe wall. It should have consequently led to the formation of strong chemical bonds that would allow the product to remain on the pipe wall for long periods of time between treatments.<sup>11</sup>

The objective of the work described in this paper was to test the applicability of this novel TLC mitigation method in a large-scale flow loop. Hydrodynamic tests in the flow loop were performed in order to investigate the foam stability as a function of gas velocity, as well as the effect of different foaming-agent concentrations on the consistency and strength of the foam. The corrosion rate was monitored under condensing conditions using electrical resistance (ER) measurements.

## EXPERIMENTAL PROCEDURE

### *Experimental Flow Loop*

All experiments have been performed in a wet-gas corrosion flow loop specially designed to study the

effect of operating parameters on the corrosion of carbon steel under condensing conditions. The flow loop is made of AISI 316 (UNS S31600) (stainless steel), 25 m long, horizontally leveled, with 4 in (10.1 cm) inner diameter (ID). A schematic of the loop is presented in Figure 1.

The mixture of CO<sub>2</sub> and water vapor was circulated through the loop. The tank was filled with 150 gal (570 dm<sup>3</sup>) of distilled (DI) water. HAc was added to the DI water in the tank to reach the concentration of 0.02 mol dm<sup>-3</sup>. The loop was thermally insulated from the ambient air in order to reduce the dissipation of heat into space. Heat was added to the system using resistance-heaters, which were immersed in the tank. Wet-gas flow condensation on the internal pipe wall was achieved by cooling the test section using copper tubing coiled around the outside of the pipe. The condensation rate was controlled by adjusting the cooling liquid (tap water) flow rate through the coils.

The temperature was controlled by a proportional integrator differential (PID) regulator. Monitoring of the liquid phase temperature was performed in the tank as well as between the inlet and the outlet of the heat exchangers. Thermocouples were installed at the test section in order to monitor the temperature of the gas phase. The pressure in the tank was also controlled and monitored. A positive-displacement, progressive-cavity pump and gas blower were used to move the liquid and the gas phase, respectively. A gas flow meter installed in line was used to monitor the gas velocity.

The experiments were set up by injecting CO<sub>2</sub> into the loop at a specific pressure. The liquid phase was then heated by electrical resistance heaters to approximately 80°C. The temperature of the circulating wet-gas phase measured at the test section was approximately 60°C. Deoxygenation was performed by depressurizing the system several times until the concentration of oxygen was less than 50 ppb in a water sample taken from the tank, as measured using a colorimetric test kit.

The pH of the system did not vary significantly and was between pH 3.5 and pH 4 at operating pressure. Testing was conducted using a superficial liquid velocity below 0.01 ms<sup>-1</sup> and a superficial gas velocity up to 5 ms<sup>-1</sup>. The ER measurements are based on exposing a specimen to the corrosive environment and measuring the increasing resistance as the specimen corrodes. The ER probe used can measure metal loss very accurately at a sensitivity of up to 0.01 μm. The ER flush-element corrosion probes were introduced under pressure into the test section so that the front face of the element was flush with the inner pipe wall. The ER probe sensing element, which was mounted in epoxy, is made of carbon steel (UNS K03005) with a thickness of 10 mils (0.25 mm). The usable working life of the sensing element is 5 mils (0.125 mm), one-half of its total thickness. The ER probes take

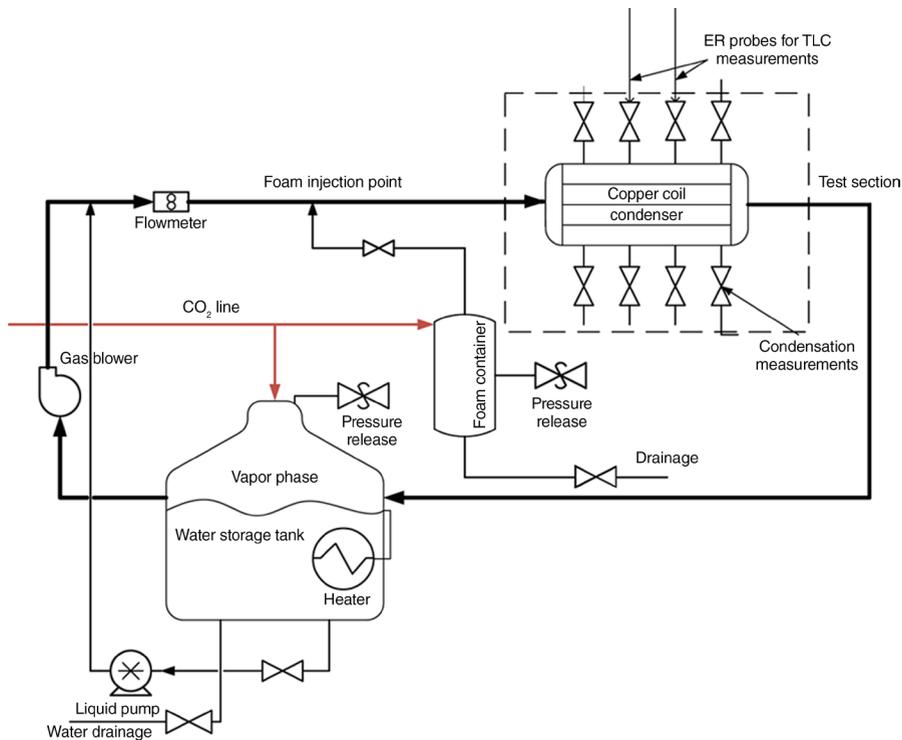


FIGURE 1. Schematic of the TLC flow loop.

readings of the metal thickness loss every 5 min. A borescope was installed in order to perform continuous visualization of the flow inside the pipe and for the recording of videos. The experimental conditions are summarized in Table 1.

### Foam Matrix Optimization

Foam was created by using two different generation methods in the flow loop. The foam stability and consistency were estimated by recording videos of the foam flow through the pipe with a borescope connected to a digital camera. Different concentrations of the foaming agent were tested in the range of 5 vol% to 40 vol% in the DI water.

**Foam Injection Under Stagnant Conditions** — The foam was created pneumatically by sparging CO<sub>2</sub> gas through a separate container containing a foaming agent. The foam quickly filled the container and the overflow was directed to the flow loop through a 1 in (2.54 cm) ID connector. The CO<sub>2</sub> bubbling was performed for 2.5 min, creating a plug of foam inside the pipe. The foam injection was performed under stagnant conditions (the gas phase was not circulated at that time). After the CO<sub>2</sub> injection was stopped, the gas blower and the liquid pump were restarted and the plug was pushed down the pipe. The borescope was inserted into the upper part of the pipe in order to visualize the distribution of the foam in the whole cross-section of the pipe.

**Foam Plug Created in Flowing Conditions** — The foaming agent was injected directly into the middle

TABLE 1  
Experimental Conditions in the Flow Loop

| Parameters                                    | Conditions                                |
|---|---|
| Test solution                                 | 0.02 mol dm <sup>-3</sup> HAc in DI water |
| Test gas                                      | CO <sub>2</sub>                           |
| Temperature in the liquid phase, °C           | 80  |
| Temperature in the vapor phase, °C            | 60  |
| pH  | 3.5 to 4                                  |
| Pressure in the system, bar                   | 1.1 bar                                   |
| Superficial gas velocity, ms <sup>-1</sup>    | 0.5 to 5                                  |
| Superficial liquid velocity, ms <sup>-1</sup> | <0.01                                     |

of the flow stream via a 0.25 in (0.64 cm) ID tubing and a nozzle. The injection system was tested in a transparent flow loop before being implemented in the high-pressure stainless steel system (Figure 2). The foam-generating apparatus was composed of a stainless steel tank containing a foaming agent pressurized at 30 psi.

The liquid foaming agent was delivered at a specified pressure and spread on a thin, porous mesh installed between two pipe flanges inside the flow loop.

A foam plug was created and pushed forward by the gas as soon as the mesh was sufficiently soaked with foaming agent.

**Corrosion Inhibitor and Foam Solution Composition** — A synthetic detergent, sodium C14-16 olefin sulfonate, with different concentrations of corrosion inhibitor added, was used to create metastable foam in the flow loop. Sodium C14-16 olefin sulfonate is

a high-foaming anionic surfactant with a molecular weight of  $324 \text{ gmol}^{-1}$ ; it is water soluble, and is commercially available as 40 vol% aqueous solution, with density and viscosity measured at  $25^\circ\text{C}$  of  $880 \text{ kgm}^{-3}$  and  $500 \text{ mPa}$ , respectively. It consists of a mixture of long-chain sulfonate salts prepared by sulfonation of C14-16 alpha olefins.

A commercial inhibitor with a known formulation based on tall oil, diethylenetriamine imidazoline (TOFA/DETA imidazoline) was tested in the present study. TOFA/DETA imidazoline is prepared by reacting tall oil fatty acid (TOFA), a mixture of oleic and linoleic acids, with an equimolar amount of diethylene triamine (DETA).<sup>20</sup> TOFA/DETA imidazoline is a water-dispersible corrosion inhibitor with imidazoline content min 72 vol% and total amine concentration up to  $5.20 \text{ meqg}^{-1}$ . Molecular weight of TOFA/DETA imidazoline is  $359 \text{ gmol}^{-1}$ , while its density and viscosity, measured at  $25^\circ\text{C}$ , are  $980 \text{ kgm}^{-3}$  and  $200 \text{ mPa}$ , respectively. In our experiments, 10 vol% aqueous foaming agent was used with corrosion inhibitor at a concentration range of from 1,000 ppm<sub>v</sub> to 20,000 ppm<sub>v</sub>. The full composition of the foam matrix is summarized in Table 2.

### Corrosion Measurements in the Flow Loop

The corrosion rate data were acquired by using ER measurements. The ER probes were introduced into the flow loop as soon as the system had reached steady state (temperature, pressure, and flow velocities). The sensing elements of the ER probes were pretreated with 78 wt%  $\text{H}_2\text{SO}_4$  for 30 s, rinsed with DI water for 10 s, polished with emery paper grit 600, and rinsed with DI water again. The ER probe was then flush mounted on the top pipe wall of the flow-loop test section so that the sensing element was directly exposed to the corrosive environment (Figure 3). The exposure time was between 30 h and 60 h.

## RESULTS AND DISCUSSION

### Foam Matrix Optimization

The objective of this part of the work was to optimize the conditions for foam formation. The range of hydrodynamic conditions where the foam matrix is stable was methodically investigated before corrosion measurements were performed. Many parameters that affect the foam stability (surfactant type, C14-16 sodium olefin concentration, foam generator, pipe diameter, etc.) as well as the operating conditions in the flow loop (gas temperature, gas flow rate,  $\text{CO}_2$  partial pressure, etc.) were extensively varied.

**Effect of Foaming Agent Formulations on Foam Stability** — The foaming agent and corrosion inhibitor were previously tested for compatibility and foam stability purposes in a small-scale setup, and the effects of different corrosion inhibitor concentrations on foaminess and foam stability were evaluated. Different

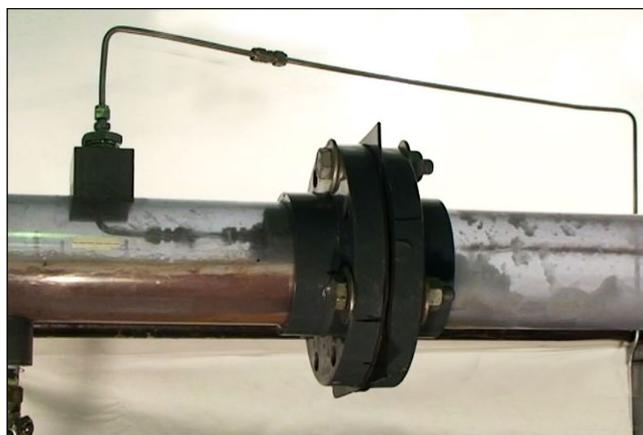


FIGURE 2. Experimental setup used for injection of foam.

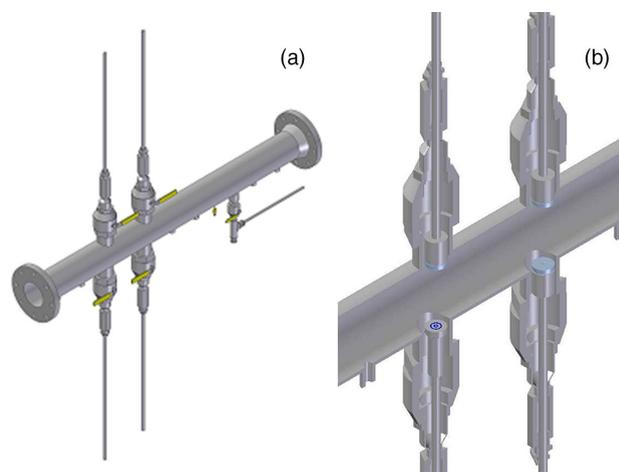


FIGURE 3. Electrical resistance probe setup at the test section: (a) full view, (b) cross-sectional view.

TABLE 2  
Foam Matrix Composition

| Parameters                                | Conditions                     |
|---|--------------------------------|
| Corrosion inhibitor                       | TOFA/DETA imidazoline          |
| Inhibitor concentration, ppm <sub>v</sub> | 1,000; 10,000; 20,000          |
| Foaming agent                             | Sodium C14-16 olefin sulfonate |
| Foaming agent concentration               | 10 vol%                        |

cationic and anionic foaming agents (aqueous solution of alkyl polyglycosides based on a natural fatty alcohol C8-10, N-decyl-N-dimethylamine oxide, dodecylaminodipropionate, sodium C14-16 olefin sulfonate, dodecylbenzene sulfonic acid, dentritic polymer) were first tested for stability. The foam volume was recorded as a function of time for the tested foaming agents in the presence and absence of corrosion inhibitors. A successful foaming agent produced stable, persistent foam with a high volume. An anionic foaming agent, C14-16 sodium olefin sulfonate, was found to be very stable in foam tests and the most resistant to the defoaming action of corrosion inhibitors. It was

shown that sodium C14-16 olefin sulfonate displayed good foaming tendency before and after the addition of corrosion inhibitor.<sup>14</sup> Consequently, this foaming agent, sodium C14-16 olefin sulfonate, was identified as a promising candidate for our future study.

*Effect of Foaming Agent Concentration on Foam Stability* — Different concentrations of C14-16 sodium olefin sulfonate were then tested in the range of 5 vol% to 40 vol%. It was impossible to form a plug of foam of good consistency using a solution containing 40 vol% of foaming agent. It seems that a high concentration of foaming agent affects the stability of the foam plug, making it collapse rapidly and disappear. It has been reported that foamability declines at extremely high concentrations of surfactant in the aqueous solution.<sup>21</sup> At a concentration of 10 vol% of foaming agent, a stable plug of foam was formed inside the flow loop.

*Effect of Superficial Gas Velocity on Foam Stability* — The tests were performed in different setups (the low pressure, low temperature transparent PVC flow loop and TLC flow loop made of stainless steel). The effect of the superficial gas velocity on the foam plug consistency was also tested. The foam flow through the flow loop, from the injection point to the test section, was recorded at different superficial gas velocities in the range of  $0.5 \text{ ms}^{-1}$  to  $5 \text{ ms}^{-1}$ , while the superficial liquid velocity was held constant. The foam stability was determined qualitatively and by measuring the foam collapse time after injection. At low superficial gas velocity ( $<3 \text{ ms}^{-1}$ ), the foam was observed to be compact and stable, while at a higher gas velocity ( $>3 \text{ ms}^{-1}$ ), the foam decomposed easily and failed to fully cover the internal pipeline surface.

*Effect of Foam Generation Method on Foam Stability* — The way the foam was generated carried considerable importance for the foam stability as well. Two different methods were used to create the foam. The advantages of foam formation under stagnant conditions were its simplicity and the establishment of relatively stable and dense foam. Upon variation of different parameters under stagnant conditions pressure of 3 psi (0.2 bar) and 10 vol% of sodium C14-16 olefin sulfonate foaming agent solution were selected for the corrosion measurements. At these conditions, the internal pipeline surface was fully covered with foam. The main drawback was procedural: the gas blower had to be stopped in order to successfully inject and form a consistent plug of foam in the pipe, which would not be practical in the field.

The most satisfying results were acquired when the foam was created in flowing conditions. The foaming agent (sodium C14-16 olefin sulfonate) was injected under pressure directly into the middle of the flow stream via a 0.25 in (0.64 cm) ID tubing and a nozzle. This was a less disruptive method for foam injection because there was no need to stop the gas flow inside the loop. We assessed the foam stability visu-

ally and by measuring the foam collapse time after the injection of the foaming agent into the flow loop. The conclusions drawn from comparisons of foams generated under stagnant and flowing conditions are summarized in Table 3.

As can be seen in Table 3, under stagnant conditions, injection of the foaming agent was performed for 150 s by sparging  $\text{CO}_2$  gas through a separate container containing a foaming agent. Under flowing conditions, the foaming agent was injected directly into the middle of the flow stream for about 30 s in order to attain the necessary contact time between the foam and the ER probe. The contact time between the ER probe and the foam matrix, under stagnant conditions, was measured to be around 15 s. Under flowing conditions, the contact time was approximately 2 min, and about 10 min later, the foam film completely disappeared. The pipeline became free of foam for the remainder of the experiment. Under flowing conditions, a sufficiently long retention time of the foam matrix coating on the metal surface enabled the establishment of a viable corrosion inhibitor film. At these conditions, the foam was observed to be compact and stable, and the foam density and consistency seemed satisfactory.

## Corrosion Measurements

*Inhibitive Properties of the Foam Matrix Injected Under Stagnant Conditions without Corrosion Inhibitor Added* — In these experiments, the foam was created pneumatically by sparging  $\text{CO}_2$  through the foaming agent in a container outside the flow loop. The foam was then injected into the flow loop at a superficial gas velocity of  $1.4 \text{ ms}^{-1}$ . The contact time between the ER probe and the foam matrix was in this case around 15 s, and the foam film completely disappeared shortly afterward. The time dependence of metal thickness loss for mild steel exposed at the top of the line to a wet  $\text{CO}_2$  gas before and after it was contacted by the foam plug (without any corrosion inhibitor) is shown in Figure 4.

The ASTM G1695 standard for corrosion was applied to the present study in order to calculate corrosion rate values from the obtained ER probe data. The corrosion rate was calculated, over time, by the method of least squares, giving the trend line that minimizes the sum of the squared vertical deviations of the metal-thickness-loss data from the regression line. The method of linear regression is the most common statistical method of calculating the corrosion rate as the slope of the best straight line through a set of metal-thickness-loss data points.<sup>22</sup> Consequently, we have used linear regression to fit metal-thickness-loss data to a linear relationship, and to determine the value of the corrosion rate. All of the measurements were repeated at least twice, and then the representative measurement was reported herein. We have also calculated the arithmetic mean and the standard deviation of the presented data according to suggestions

TABLE 3

Comparison of Foams Generated Under Stagnant and Flowing Conditions

| Parameters   | Foam Created in Stagnant Conditions | Foam Created in Flowing Conditions |
|--|-------------------------------------|------------------------------------|
| C14-16 sodium olefin sulfonate concentration, vol% | 10                                  | 10                                 |
| Superficial gas velocity, $\text{ms}^{-1}$         | 1.4                                 | 3                                  |
| Superficial liquid velocity, $\text{ms}^{-1}$      | <0.01                               | <0.01                              |
| Foam generation                                    | In a separate container             | In the flow loop                   |
| Foam injection time, s                             | 150                                 | 30                                 |
| Foam generation pressure, psi                      | 3                                   | 30                                 |
| Foam collapse time, min                            | 1                                   | 10                                 |
| Foam contact time with ER probe, s                 | 15                                  | 120                                |

stated in ASTM G1695. Standard deviation of  $\pm 10\%$  indicates that the data can be considered statistically significant. The same standard deviation was obtained for the different concentrations of inhibitor used. The calculated TLC rate (CR) was around  $0.1 \text{ mm y}^{-1}$  at the beginning of the experiment. As can be seen in Figure 4, an increase in the corrosion rate to  $0.35 \text{ mm y}^{-1}$  occurred when HAc was injected into the system at a concentration of  $0.02 \text{ mol dm}^{-3}$ . This is most likely due to the presence of undissociated HAc in the condensed water on the steel surface. HAc is volatile, so it can be transported in the gas phase and condense with the water on the walls of the pipe. HAc decreases the pH of the solution, increases the overall cathodic current, and enhances the metal dissolution. This influence of HAc on the corrosion rate in TLC has been previously reported in the literature.<sup>3,10</sup> The corrosion rate was steady for another 25 h when the ER probe was contacted by the plug of foam. The corrosion rate decreased by approximately a factor of two ( $0.15 \text{ mm y}^{-1}$ ), showing that the foaming agent alone has some retarding effect on the TLC rate, most likely by interfering with condensation. With further exposure of the ER probe to the corrosive wet-gas environment, a gradual increase in the corrosion rate was detected. After 4 h, the baseline corrosion rate of  $0.3 \text{ mm y}^{-1}$  was again established in the system, presumably due to the foam breaking up.

**Inhibitive Properties of TOFA/DETA Imidazoline Corrosion Inhibitor** — The molecular structure of TOFA/DETA imidazoline is depicted in Figure 5, where it can be seen that the inhibitor molecule consists of three different substructures: a nitrogen-containing five-member ring, a pendant side chain with a hydrophilic active functional group (ethylamino pendent group) attached to N1, and a long C-17 hydrophobic chain (R) attached to the C2 atom. Nitrogen-based organic surfactants, such as imidazoline and its derivatives, have been used successfully as inhibitors in combating oilfield  $\text{CO}_2$  corrosion. They are water dispersible, and their solubility can be modified by neutralization with different organic acids. These organic compounds inhibit the corrosion of mild steel by adsorption on the metal-solution interface. The proposed mechanisms suggest that the adsorbed in-

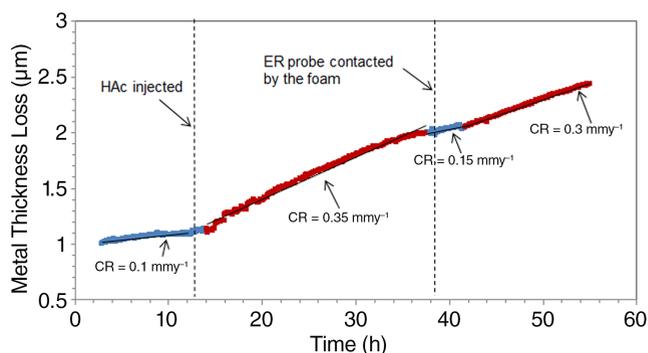


FIGURE 4. The time dependence of metal thickness loss for mild steel set in vapor phase after being contacted by the foam plug without the corrosion inhibitor.

hibitor molecules may change the anodic or cathodic reaction rates or displace the water molecules on the surface with the hydrophilic heads, thereby creating a barrier that prevents the active ions in the corrosion reactions from getting to the surface. The physical/chemical adsorption of the inhibitor at the metal surface is influenced by various factors, including the electron density and p-character of donor atoms, types of functional groups, steric effect, and the charge on the surface.

TOFA/DETA imidazoline compound can be adsorbed on the mild steel surface by electrostatic interaction between the negative charge on the metal surface (as a result of the specific adsorption of  $\text{Cl}^-$  ions) and the positive charge on the imidazoline ring. Donor-acceptor surface complex can be established by the interaction of the p-system of the aromatic ring in TOFA/DETA imidazoline and a vacant d-orbital of metal. The inhibitor molecules can also adsorb on the steel surface by the formation of Fe-N coordination bonds.

As a cationic surfactant with a positively charged hydrophilic head and a hydrophobic tail, TOFA/DETA imidazoline affects the surface tension by accumulating at the solution/air interface. The surface tension decreases as the corrosion inhibitor concentration increases, until the critical micelle concentration (CMC) is attained. The CMC is a property of a surfactant's nature and the concentration, temperature,

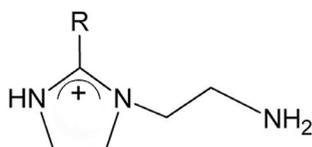


FIGURE 5. Molecular structure of TOFA/DETA imidazoline.

pH, pressure and ionic strength of the solution.<sup>23-24</sup> Jevremović, et al., investigated inhibitor efficiency for mild steel corrosion in 3 wt% aqueous NaCl solution saturated with CO<sub>2</sub> at different temperatures in a small laboratory setup (electrochemical glass cell), using electrochemical and weight-loss measurements; the surface morphology of mild steel was studied by atomic force microscopy (AFM).<sup>15</sup> The mechanism and kinetics of TOFA/DETA imidazoline adsorption and the influence of temperature and inhibitor concentration on the adsorption process were followed with a quartz crystal microbalance (QCM). They found that the addition of the TOFA/DETA imidazoline inhibitor to chloride solution significantly reduced the corrosion rate, while the inhibition efficiency was calculated to be around 95%. The inhibition efficiency was observed to slightly increase with increase in pH, but also decrease with a rise in temperature, indicating an acceleration of the corrosion rate.<sup>15</sup> QCM measurements confirmed that TOFA/DETA imidazoline forms self-assembled monolayers, and that adsorption kinetics of this self-assembled system can be described by Langmuir adsorption isotherm. TOFA/DETA imidazoline has been found to have a CMC value of 65 ppm<sub>v</sub> in 3 wt% aqueous NaCl solution saturated with CO<sub>2</sub> at 20°C, pH 5.<sup>15,25</sup> The CMC decreases with increasing salt concentrations and ionic strength, while the micellar size increases. Based on these results, TOFA/DETA imidazoline was judged to display good inhibiting properties, making it a good candidate for further TLC study.

*Inhibitive Properties of the Foam Matrix with TOFA/DETA Imidazoline Corrosion Inhibitor Injected Under Stagnant Conditions* — Corrosion inhibitor efficiency is a function of many factors: fluid composition, flow regime, temperature, and partial pressure of CO<sub>2</sub>. The inhibition efficiency (IE, %) can be calculated from the corrosion rate according to Equation (1):

$$IE, \% = \frac{CR_0 - CR_{inh}}{CR_0} \times 100 \quad (1)$$

where CR<sub>0</sub> and CR<sub>inh</sub> are the corrosion rate values without and with inhibitor, respectively.

The performance of the corrosion inhibitor carried within the foam matrix was observed with different concentrations of corrosion inhibitor. The time dependence of metal thickness loss (measured by ER) for mild steel exposed at the top of the line in wet CO<sub>2</sub> gas flow was monitored before and after it was

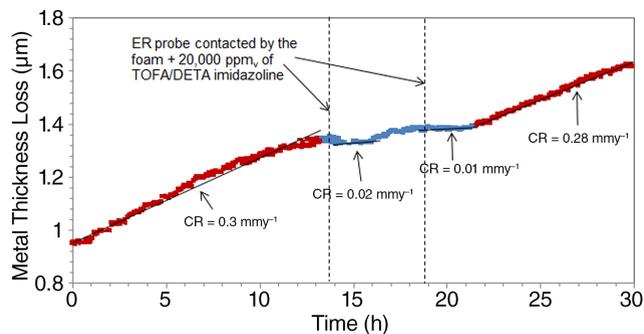
contacted by a foam plug containing lower concentrations of inhibitor. The baseline corrosion rate was measured to be around 0.35 mm y<sup>-1</sup>. When a plug of foam containing 1,000 ppm<sub>v</sub> of TOFA/DETA imidazoline was pushed through the flow loop, the resulting corrosion rate decreased by a factor of two, and the calculated inhibition efficiency was around 58%. The corrosion rate remained the same during the following 15 h (data not shown). Compared to the results obtained with the pure foam matrix without the corrosion inhibitor, the corrosion rate did not decrease to very low values.

On the other hand, experiments conducted in a small-scale laboratory setup with 1,000 ppm<sub>v</sub> of TOFA/DETA imidazoline injected into the foam matrix caused a significant decrease in the corrosion rate, and the calculated inhibition efficiency was above 90%.<sup>15</sup> This seems to indicate that the performance of the inhibitor was somehow affected by the flow conditions.

Results show that a foam matrix with TOFA/DETA imidazoline concentrations of up to 1,000 ppm<sub>v</sub> cannot efficiently inhibit TLC in the flow loop conditions. It can be concluded that higher concentrations of inhibitor in the foam matrix are needed to reduce TLC sufficiently. In this experiment, the concentration of the inhibitor in the foam matrix was increased. The time dependence of metal thickness loss (measured by ER) for mild steel exposed at the top of the line in wet CO<sub>2</sub> gas flow, before and after it was contacted by a foam plug containing 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline, is shown in Figure 6.

As can be seen in Figure 6, the baseline corrosion rate was again around 0.3 mm y<sup>-1</sup>. When the concentration of TOFA/DETA imidazoline in the foam matrix was increased to 20,000 ppm<sub>v</sub>, the corrosion rate after the treatment approached very low values (0.01 mm y<sup>-1</sup>), with the corrosion inhibition efficiency around 97%. The metal thickness loss was steady for bare steel and practically stopped when the ER probe was contacted by the plug of foam containing 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline. The inhibition effect lasted for approximately 3 h. After 3 h the corrosion rate gradually increased to 0.3 mm y<sup>-1</sup>. It can be deduced that the plug of foam containing 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline retarded the corrosion rate, but it seems that the applied inhibitor film was not persistent enough and was removed by the condensation of water. It appears that the plug of foam should be re-applied more frequently.

*Inhibitive Properties of the Foam Matrix with TOFA/DETA Imidazoline Corrosion Inhibitor Injected Under Flowing Conditions* — In these experiments, the foaming agent was injected directly into the middle of the flow stream through a nozzle and sprayed onto a fine mesh with uninterrupted gas flow. The method of foam creation in flowing conditions provided a retention time of approximately 2 min for the foam matrix coating on the metal surface. The time dependence of



**FIGURE 6.** The time dependence of metal thickness loss for mild steel set in vapor phase after being contacted by the foam plug containing 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline.

metal thickness loss for mild steel exposed to a vapor phase after the ER probe was contacted by the foam plug containing 10,000 ppm<sub>v</sub> of TOFA/DETA imidazoline is shown in Figure 7. Testing was conducted with a superficial gas velocity of 3 ms<sup>-1</sup>; therefore, the baseline corrosion rate in the vapor phase, measured over an exposure time of 65 h, was 0.55 mm y<sup>-1</sup>. A higher baseline corrosion rate indicates that the increase in gas velocity causes an increase in the corrosion rate at the top of the pipe. High gas velocity has a direct effect on the condensation rate that in turn affects the corrosion rate.<sup>26-27</sup>

A plug of foam containing 10,000 ppm<sub>v</sub> of TOFA/DETA imidazoline was created at the injection port, and the resulting corrosion rate decreased by a factor of 2.00 to 0.26 mm y<sup>-1</sup>. The calculated inhibition efficiency was around 53% and remained effective for another 50 h. The procedure was then repeated once again with 10,000 ppm<sub>v</sub> of TOFA/DETA imidazoline, and the corrosion rate decreased even further to a value of 0.07 mm y<sup>-1</sup> (Figure 7). It was found that a concentration of 10,000 ppm<sub>v</sub> of TOFA/DETA imidazoline or higher is required to reduce corrosion rates to approximately 90% inhibition efficiency in the vapor phase.

As can be seen in Figure 7, the foam matrix with TOFA/DETA imidazoline corrosion inhibitor injected in flowing conditions exhibited more than an order of magnitude (up to 60% increase) higher inhibition persistency compared to injection under stagnant conditions. These results can be explained by the more stable foam, which provided longer contact time between the ER probe and the foam matrix. It can be concluded that TOFA/DETA imidazoline carried by the foam matrix forms a thin film on the surface of the ER probe that stops access of the corrosive species to the metal. Hence, the results show that the foam matrix can be used to effectively distribute inhibitor liquids to the top of the pipe.

The time dependence of metal thickness loss for mild steel exposed to a vapor phase after the ER probe was contacted by the foam plug containing 1,000 ppm<sub>v</sub> and 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline,

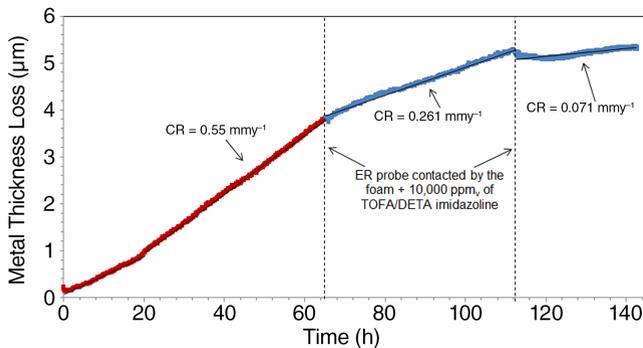
respectively, is shown in Figure 8. The baseline corrosion rate in the vapor phase, measured over an exposure time of 25 h, was 0.79 mm y<sup>-1</sup>. A plug of foam containing 1,000 ppm<sub>v</sub> of TOFA/DETA imidazoline was created at the injection port, and the corrosion rate remained almost unchanged (0.72 mm y<sup>-1</sup>). After 55 h of testing, a foam plug containing 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline was created, and the resulting decrease in corrosion was much more pronounced (CR around 0.30 mm y<sup>-1</sup> and 63% inhibition efficiency). As can be seen in Figure 8, this corrosion reduction lasted about 45 h, after which the corrosion rate increased gradually back to 0.55 mm y<sup>-1</sup>.

It can be observed that one injection of a foam plug containing 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline (Figure 8) provides 63% inhibition efficiency, while successive injections of foam plugs containing 10,000 ppm<sub>v</sub> of TOFA/DETA imidazoline inhibitor solution (Figure 7) provide increased corrosion protection. As can be seen in Figure 7, the second foam injection was carried out approximately 40 h after the first injection, and approximately 90% inhibition efficiency was achieved; this was probably due to a better-oriented and more completely developed inhibitor film on the metal surface. It seems that successive foam plug injections increase inhibitor placement and provide better corrosion protection.

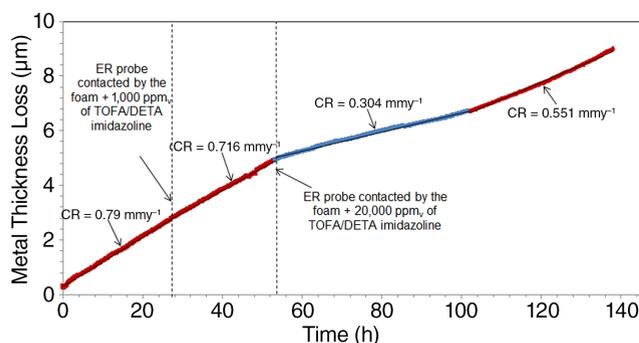
At this point of research, our results indicate that a slug of foam with TOFA/DETA imidazoline corrosion inhibitor must be re-applied every 40 h to 50 h in order to ensure the ongoing effectiveness of the novel TLC mitigation method.

## CONCLUSIONS

- ❖ A novel TLC mitigation method was evaluated under simulated field conditions in a large-scale multi-phase flow loop. The use of a flow loop enabled realistic simulations of the corrosive environments as well as the flow conditions typically encountered in the field.
- ❖ The foam in this study was created pneumatically by sparging CO<sub>2</sub> through the foaming agent in stagnant and flowing conditions. It was observed that foam characteristics were dependent on the pressure of the CO<sub>2</sub> used for foam formation and on the concentration of the foaming agent.
- ❖ After the ER probe placed at the top of the line was contacted by a plug of foam without a corrosion inhibitor, the corrosion rate decreased by a factor of two for a short period of time. This shows that the foaming agent alone had retarding effects on the TLC rate, probably by interfering with the condensation process.
- ❖ The TLC rate of mild steel, as measured by an ER probe, was effectively reduced by periodic treatment with foam created in stagnant conditions and containing 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline corrosion inhibitor. The corrosion rate after the treatment approached very low values (0.01 mm y<sup>-1</sup>), compared



**FIGURE 7.** The time dependence of metal thickness loss for mild steel set in vapor phase after being contacted by the foam plug containing 10,000 ppm<sub>v</sub> of TOFA/DETA imidazoline.



**FIGURE 8.** The time dependence of metal thickness loss for mild steel set in vapor phase after being contacted by the foam plug containing 1,000 ppm<sub>v</sub> and 20,000 ppm<sub>v</sub> of TOFA/DETA imidazoline.

to the baseline corrosion rate ( $0.3 \text{ mm y}^{-1}$ ), with the corrosion inhibition efficiency around 97%. The effect was not persistent, however, and the inhibition effect lasted between 3 h and 15 h.

❖ The method of foam creation in flowing conditions represented a significant improvement in the experimental procedure (as a non-disruptive method), foam stability, and contact time between the ER probe and the foam matrix, and made the experiments representative of a realistic field scenario.

❖ It was found that both injection methods showed similar trends in terms of corrosion-inhibition measurement. However, the injection under flowing conditions led to a corrosion-inhibition persistency that was more than an order of magnitude longer than that of the injection under stagnant conditions.

❖ Successive injections of foam plugs containing 10,000 ppm<sub>v</sub> of TOFA/DETA imidazoline led to approximately 90% inhibition efficiency, and the inhibition effect lasted up to 50 h.

❖ The results indicate that a slug of foam with TOFA/DETA imidazoline corrosion inhibitor must be re-applied every 40 h to 50 h in order to ensure the most effective level of TLC prevention.

❖ The foam matrix is a promising method for delivering a corrosion inhibitor that can control the TLC rate in wet CO<sub>2</sub> gas flow. However, it is important to continue examining different foam generators and the wide range of foam formulations in order to produce stable, long-lasting foam and consequently extend the contact time between the corrosion inhibitor and the metal surface.

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## REFERENCES

1. M. Singer, S. Nešić, Y. Gunaltun, *Corrosion* 63 (2007): p. 1051-1062.
2. F. Vitse, S. Nešić, Y. Gunaltun, D. Larrey de Torreben, P. Duchet-Suchaux, *Corrosion* 59 (2003): p. 1075-1084.
3. M. Singer, A. Camacho, B. Brown, S. Nešić, *Corrosion* 67 (2011): p. 085003-1.
4. S. Nešić, *Corros. Sci.* 49 (2007): p. 4308-4338.
5. D. Hinkson, Z. Zhang, M. Singer, S. Nešić, *Corrosion* 66 (2010): p. 045002-045002-8.
6. M. Singer, J. Al-Khamis, S. Nešić, *Corrosion* 69 (2013): p. 624-638.
7. S.D. Zhu, A.Q. Fu, J. Miao, Z.F. Yin, G.S. Zhou, J.F. Wei, *Corros. Sci.* 53 (2011): p. 3156-3165.
8. U. Lotz, L. van Bodegom, C. Ouwehand, *Corrosion* 47 (1991): p. 635-644.
9. M. Singer, D. Hinkson, Z. Zhang, H. Wang, S. Nešić, *Corrosion* 69 (2013): p. 719-735.
10. W. Akers, M. Turner, *Aiche J.* 8 (1962): p. 587-589.
11. I. Jevremović, A. Debeljković, M. Singer, M. Achour, V. Mišković-Stanković, S. Nešić, *J. Serb. Chem. Soc.* 77, 8 (2012): p. 1047-1061.
12. G. Schmitt, *Mater. Corros.* 52 (2001): p. 329-343.
13. C. Kirkbride, *Industrial & Engineering Chemistry* 25 (1933): p. 1324-1331.
14. M. Achour, D. Blumer, T. Baugh, C. Lane, Ph. Humble, J. Waters, J. Wilcher, R. Hudgins, "A Novel Method to Mitigate Top of the Line Corrosion in Wet Gas Pipelines: Part I—Proof of Concept," CORROSION/2010, paper no. 11332 (Houston, TX: NACE International, 2010).
15. I. Jevremović, M. Singer, M. Achour, D. Blumer, T. Baugh, V. Mišković-Stanković, S. Nešić, *Corrosion* 69 (2013): p. 186-192.
16. S. Nešić, L. Lunde, *Corrosion* 50 (1994): p. 717-727.
17. S. Papavinasam, R.W. Revie, M. Attard, A. Demoz, K. Michaelian, *Corrosion* 59 (2003): p. 1096-1111.
18. N.S. Deshpande, M. Barigou, *Chem. Eng. Sci.* 55 (2000): p. 4297-4309.
19. M.I. Briceno, D.D. Joseph, *Int. J. Multiphas. Flow* 29 (2003): p. 1817-1831.
20. US Patent, US7005087 B2, "Composition and Method for Preventing Fouling in (Meth) Acrylic Acid Processes."
21. P.R. Garrett, *The Science of Defoaming: Theory, Experiment and Applications*. Vol. 155. CRC Press, 2013.
22. ASTM G16-95 (2004), "Standard Guide for Applying Statistics to Analysis of Corrosion Data" (West Conshohocken, PA: ASTM International, 2004).
23. F. Schreiber, *Prog. Surf. Sci.* 65 (2000): p. 151-25.
24. V. Jovancevic, S. Ramachandran, P. Prince, *Corrosion* 55, 5 (1999): p. 449-455.
25. I. Jevremović, M. Singer, S. Nešić, V. Mišković-Stanković, *Corros. Sci.* 77 (2013): p. 265-272.
26. Y.H. Sun, T. Hong, C. Bosch, *Corrosion* 59 (2003): p. 733-740.
27. L. Pan, T. Hanratty, *Int. J. Multiphas. Flow* 28 (2002): p. 385-408.