

A Novel Method to Mitigate the Top of the Line Corrosion in Wet Gas Pipelines by Corrosion Inhibitor within a Foam Matrix

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ABSTRACT

Top of the Line Corrosion (TLC) has been a serious issue for the Oil & Gas industry. Conventional inhibition techniques are expensive and often do not seem to provide enough protection to the steel surface at the top of the pipe.

A novel idea is to inject the corrosion inhibitor within a foam matrix. The foam slug is first formed at an injection port and carried along the pipe by the gas phase. This process ensures homogeneous delivery of the inhibitor to the pipe wall along pipe sections suffering from TLC. This paper presents more comprehensive study performed in an innovative glass cell setup which consisted of a foaming cell and a corrosion cell in order to simulate intermittent contact between the foam and the steel surface.

Corrosion measurements were performed using electrochemical techniques (EIS, LPR, potentiodynamic sweep) and electrical resistance (ER) measurements, in order to determine the inhibitive performance of investigated inhibitor talloil diethylenetriamine imidazoline (TOFA/DETA imidazoline) within a foam matrix (sodium C14-16 olefin sulfonate).

Key words: TLC, carbon steel, foam, inhibitor, electrochemical measurements, electrical resistance measurements

INTRODUCTION

Top of the Line Corrosion (TLC) can occur in wet gas pipelines where the difference between high inlet temperatures and the cold environment can easily result in water vapor condensation on the cooler surface of the pipe wall at the top of the line.¹⁻⁴ Corrosion appears inside the pipe due to the condensation of water containing dissolved corrosive gases such as CO₂, CH₃COOH, or other short chain acids.⁵ Acetic acid or other organic acids which can be present in the gas will dissolve in the water and thereby lower the pH of the condensed water phase and increase the amount of iron which can be dissolved in the condensing water.^{6,7}

Organic corrosion inhibitors are used as a standard method for corrosion control in the oil and gas industry. They inhibit corrosion by forming an adsorbed organic compound film on the steel surface. Conventional inhibitors are often not very volatile and consequently not useful for TLC prevention as there is no easy way to ensure that they can be transported to the top of the line.¹⁻⁴ Any non standard method developed to physically transport an inhibitor must guarantee that it reaches all parts of the pipeline potentially suffering from TLC.

Several methods have been proposed as vehicles for corrosion inhibitors in order to provide uniform and sufficient distribution of corrosion inhibitor.^{8,9} The method described here consists of injecting the corrosion inhibitor within a foam matrix. Injected inhibitor liquids are carried with the foam slug along the line with the gas flow. The foam carrier provides homogeneous delivery of the inhibitor through the pipe which then forms a protective film all over the internal pipeline surface.¹⁰

This paper focuses on a new laboratory study performed in an innovative glass cell setup which consisted of a foaming cell and a corrosion cell simulating intermittent foam contact with the pipe wall.

Experimental study performed here includes:

- Investigating of inhibitor efficiency in liquid phase
- Confirming that the inhibitor can be carried in the foam matrix and provide sufficient inhibition to the top of the line.

EXPERIMENTAL PROCEDURE

Electrochemical study of corrosion inhibitor efficiency in the aqueous phase

The objective was to investigate basic inhibition properties of the conventional inhibitor talloil diethylenetriamine imidazoline (TOFA/DETA imidazoline). Experiments were conducted using a conventional three-electrode cell arrangement (Figure 1). The rotating cylinder test specimens (5.4 cm² exposed area), machined from API 5L X65 pipeline steel were used as working electrode (WE). A concentric platinum wire was used as counter electrode (CE) and an Ag/AgCl reference electrode (RE) was connected externally *via* a Luggin capillary tube. The test specimens were sequentially polished using 240, 320, 400 and 600 grit silicon carbide paper, rinsed with isopropanol and dried with hot air. Experiments were conducted at atmospheric pressure, at room temperature and 70°C, under stagnant conditions. Test solution was 3 % wt. aqueous NaCl. The solutions were deoxygenated by purging CO₂ gas for 1 hour before the start of the experiment. A positive pressure of CO₂ was maintained in the cell during

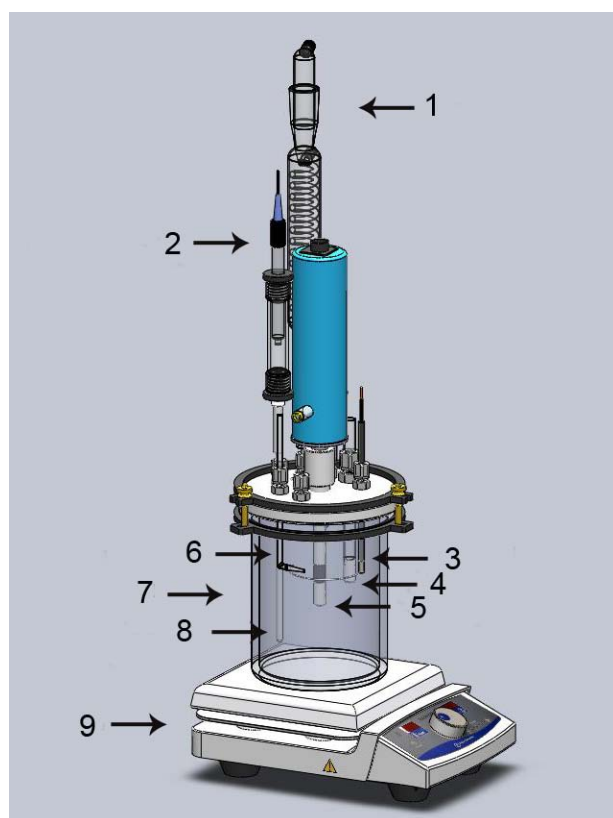
the experiments minimizing the possibility of air ingress. The pH was continuously measured and adjusted to pH5 with NaHCO_3 and HCl . The basic inhibition properties of the inhibitor on the CO_2 corrosion were investigated by injecting 70 ppm in the solution after the bare steel corrosion tests had been conducted. The experimental conditions are summarized in Table 1.

Electrochemical impedance spectroscopy (EIS), potentiodynamic sweep (PDS) and linear polarization resistance (LPR) measurements were performed after 30 minutes of open circuit potential (OCP) measurements.

The electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range of 10 kHz to 10 mHz using a 10 mV amplitude of sinusoidal variation around the open circuit potential.

The potentiodynamic sweep (PDS) measurements were carried out from a cathodic potential of -0.25 V to an anodic potential of +0.25 V with respect to the corrosion potential, at a scan rate of 1 mV/s.

The linear polarization resistance (LPR) measurements were carried out from a cathodic potential of -5 mV to an anodic potential of +5 mV with respect to the corrosion potential at a scan rate of 0.125 mV/s.



1. Condenser
2. Reference Electrode (Ag/AgCl)
3. Platinum Counter Electrode
4. Bubbler
5. Working Electrode
6. Luggin Capillary
7. Glass Cell
8. Temperature Probe
9. Hot Plate

Figure 1: Three-electrode glass cell setup
(Image courtesy Institute for Corrosion and Multiphase Technology, Athens OH)

Table 1
Experimental conditions for electrochemical measurements.

| Parameters | Conditions |
|---|----------------------------|
| Total pressure (bar) | 1 |
| CO ₂ partial pressure (bar) | 0.96 and 0.69 |
| Liquid temperature (3 % wt. aqueous NaCl) | Room temperature and 70 °C |
| Corrosion inhibitor | TOFA/DETA imidazoline |
| Inhibitor concentration (ppm) | 0 and 70 |
| pH | 5 |
| Measurements | OCP, LPR, EIS, PDS |

Corrosion inhibitor performance in an aqueous phase investigated using the ER probe

The aim of this part was to compare the results obtained by electrochemical measurements in an aqueous phase with those measured by using an electrical resistance (ER) probe, in order to see its response and to prove its validity. The experiments were carried out in a 2 L glass cell equipped with cooling / condensing capabilities on the lid. Test solution was a 3 % wt. aqueous solution. It was deoxygenated by bubbling CO₂ for 1 hour prior to the experiment. CO₂ purging was maintained during the entire test. The temperature was increased and maintained at 70 °C using a hot plate. Finally, 1000 ppm of acetic acid was added. When the experimental conditions have been reached, an ER probe was immersed in the liquid phase. After a stable “baseline” uninhibited corrosion rate was obtained, 1000 ppm of inhibitor was injected into the solution. The temperatures of liquid and gas phases were continuously monitored during the test. The experimental conditions are summarized in Table 2.

Table 2
Experimental conditions for investigating inhibition efficiency of TOFA/DETA imidazoline in the aqueous phase using the ER probe.

| Parameters | Conditions |
|--|-----------------------|
| Total pressure (bar) | 1 |
| CO ₂ partial pressure (bar) | 0.69 |
| Liquid temperature (water) | 70 °C |
| Corrosion inhibitor | TOFA/DETA imidazoline |
| Inhibitor concentration (ppm) | 0 and 1000 |
| Acetic acid concentration (ppm) | 1000 |
| pH | 5 |
| Measurements | ER |

Corrosion inhibitor performance in the gas phase investigated using the ER probe

The objective here was to prove if the corrosion inhibitor can be carried by the foam matrix and provide sufficient corrosion inhibition on the top of the line. In order to achieve this goal, two glass cells were used as shown in Figure 2. The glass cell on the right, labeled the “corrosion cell”, contained 3 % wt. NaCl solution with 1000 ppm of acetic acid injected. The glass cell on the left, labeled the “foaming cell”, contained 400 mL of 20 % vol. foaming agent (sodium C14-16 olefin sulfonate) with 1000 ppm of corrosion inhibitor added. The experimental procedure was performed in the following order: CO₂ gas was bubbled in corrosion cell for 1 hour in order to deoxygenate the solution in the corrosion cell. The solution temperature was increased to 70°C and the pH was adjusted to pH 4. When the desired conditions were achieved ER probe was installed flush mounted at the bottom of a stainless steel lid of the corrosion cell. Cooling of the probe was maintained by using a heat exchanger, so the ER probe was exposed to water condensation. In order to limit water vapor loss during the test a reflux condenser was used in the exhaust line.

Once the uninhibited baseline corrosion rate was detected in the corrosion cell, the foam matrix was created by immersing the CO₂ gas bubbler into the solution of the foaming cell. When a plug of foam of good consistency was formed there, the ER probe was taken out from the corrosion cell and flush mounted onto the lid of the foaming cell where it was contacted by the foam for a set amount of time. It was then returned back to the corrosion cell. In this way, intermittent foam contact with the top of the line was simulated. Experimental conditions in the corrosion cell are summarized in Table 3, and those in the foaming cell are shown in Table 4.

Table 3
Experimental conditions in corrosion cell.

| Parameters | Conditions |
|--|------------|
| Total pressure (bar) | 1 |
| CO ₂ partial pressure (bar) | 0.69 |
| Liquid temperature (DI water) | 70 °C |
| pH | 4 |
| Measurements | ER |

Table 4
Experimental conditions in foaming cell.

| Parameters | Conditions |
|---|-----------------------|
| Corrosion inhibitor | TOFA/DETA Imidazoline |
| Inhibitor concentration (ppm) | 0, 1000 |
| Foaming agent (sodium C14-16 olefin sulfonate) concentration (% vol.) | 20 |
| Contact time with the foam matrix (second) | 5, 15, 30, 60 |

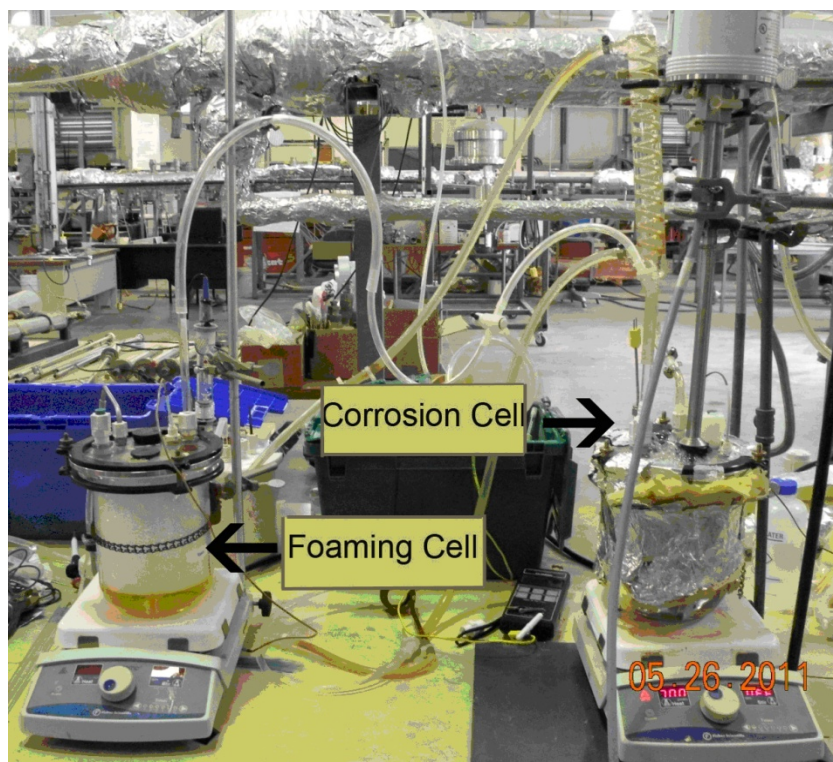


Figure 2: The glass cell setup which consists of a foaming cell and a corrosion cell.

RESULTS AND DISCUSSION

Electrochemical study of corrosion inhibitor efficiency in the aqueous phase

The EIS data were analyzed using the electrical equivalent circuit represented in Figure 3, where R_{Ω} is the solution resistance, C_{dl} is the double layer capacitance and R_{ct} is the charge-transfer resistance.

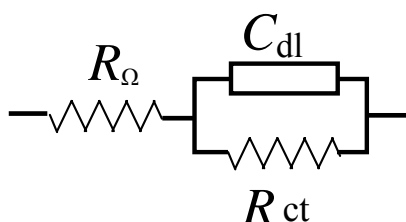


Figure 3: Electrical equivalent circuit.

The Nyquist plots of the mild steel in 3 % wt. NaCl saturated with CO_2 at room temperature and 70°C , pH 5, without and with 70 ppm TOFA/DETA imidazoline added are shown in Figure 4. From the Nyquist plots, it could be seen that the EIS response changes with the addition of inhibitor molecules. All experimental plots have a depressed semicircular shape in the complex plane, with the center under the real axis, which is a typical behavior for solid metal electrodes that show frequency dispersion of the impedance data.¹¹ The existence of a single semicircle indicates the presence of simple-charge transfer process during dissolution. The values of charge-transfer increase with added inhibitor and decrease at higher temperature.

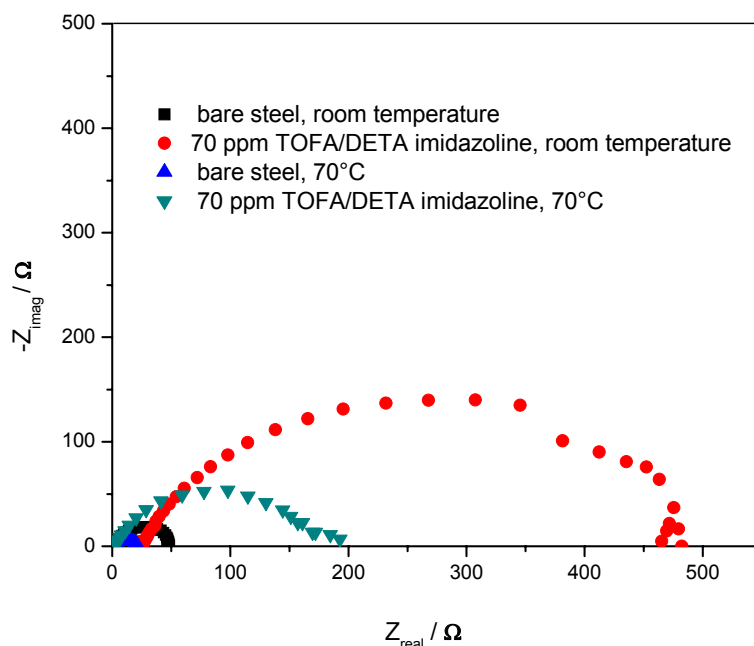


Figure 4: Nyquist plots for mild steel in 3 % wt. NaCl at room temperature and at 70°C, pH 5, without and with 70 ppm TOFA/DETA imidazoline

Similar behavior was observed from potentiodynamic sweep curves shown in Figure 5. Addition of TOFA/DETA imidazoline shifts the corrosion potential slightly in the positive direction and decreases the corrosion rate. Reduction of corrosion rate and increase in corrosion potential confirm the inhibitive properties of TOFA/DETA imidazoline.

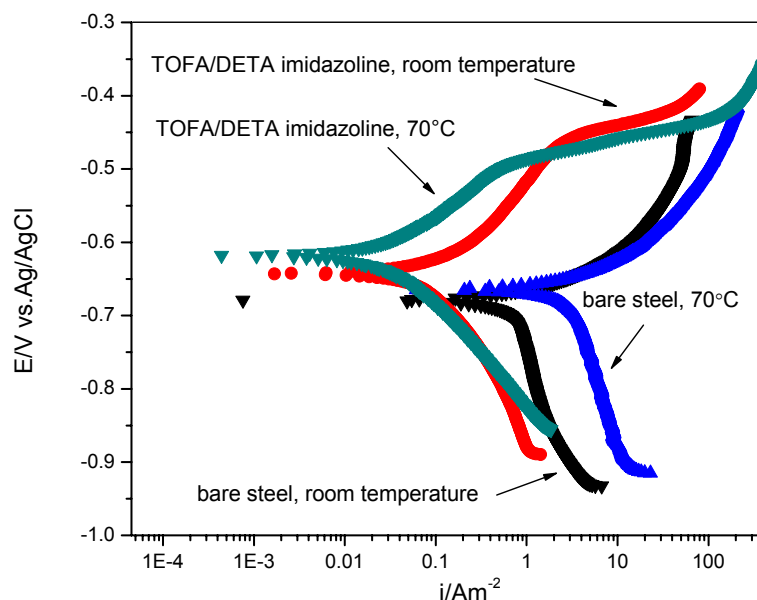


Figure 5: Polarization curves of mild steel in 3 % wt. NaCl at room temperature and at 70°C, pH 5, without and with 70 ppm TOFA/DETA imidazoline.

Corrosion rate was measured using linear polarization resistance (Figure 6) for 24 hours. It was found that corrosion rate of mild steel in 3 % wt. NaCl, pH 5, at room temperature decreased from 1 mm·yr⁻¹ for bare steel to 0.1 mm·yr⁻¹ when 70 ppm of TOFA/DETA imidazoline was added. The corrosion rate also decreased from 4 mm·yr⁻¹ for bare steel to 0.2 mm·yr⁻¹ by adding 70 ppm of TOFA/DETA imidazoline at 70°C.

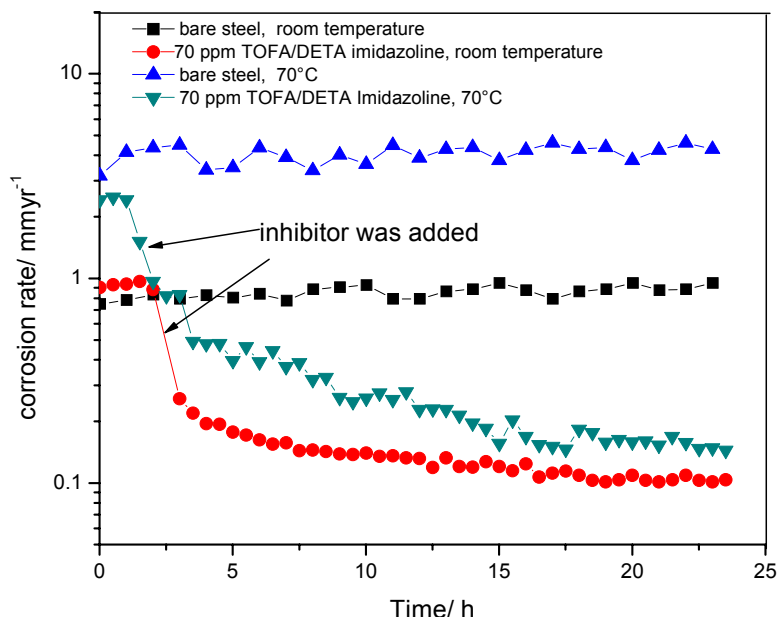


Figure 6: Corrosion rate of mild steel in 3 % wt. NaCl at room temperature and at 70°C, pH 5, without and with 70 ppm TOFA/DETA Imidazoline, measured with LPR.

The protective action of the TOFA/ DETA imidazoline can be explained taking into account the interaction that takes place between the inhibitor molecules and the metal substrate. The pyridine-like (sp^2) nitrogen atom in the imidazoline would act as a Lewis base, while Fe^{3+} , Fe^{2+} and metallic Fe would behave like acids, acting as electron acceptors, with higher acidity corresponding to higher oxidation state.¹² Consequently, the inhibitor can act by blocking the active sites or generating a sort of physical barrier to reduce the transport of corrosive species to the metal surface. The presence of TOFA long hydrocarbon chains in the structure of the corrosion inhibitor is responsible for their capacity of forming protective barriers against aggressive ions from the bulk solution.¹³

Corrosion inhibitor properties in the aqueous phase investigated using the ER probe

The time dependence of metal thickness loss (Figure 7) was obtained using ER probe in liquid phase, 3 % wt. NaCl solution, pH 5, where the temperature of solution was held constant at 70°C. As it can be seen in Figure 7, the metal thickness loss was steady for bare steel and it practically stopped when 1000 ppm of TOFA/DETA imidazoline was injected.

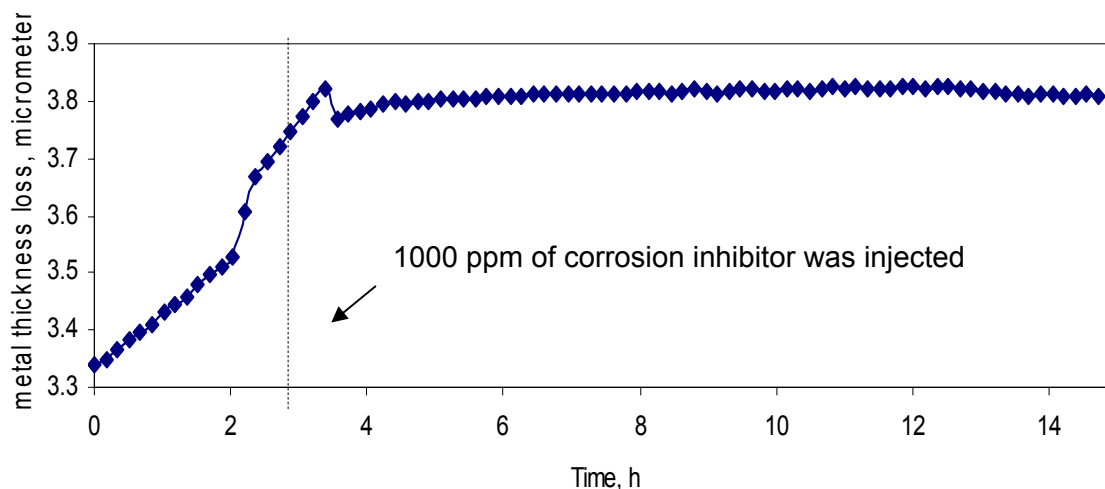


Figure 7: The time dependence of metal thickness loss for mild steel in 3 % wt. NaCl at 70°C, pH 5 with 1000 ppm of acetic acid and 1000 ppm of TOFA/DETA imidazoline.

The corrosion rate was calculated from metal thickness loss measurements. The change of the corrosion rate with exposure time is shown in Figure 8. The corrosion rate increased during the first 3 hours and reached approximately 2.5 mm·yr⁻¹. After 3 hours, 1000 ppm of TOFA/DETA imidazoline was injected directly in the solution, and corrosion rate decreased to under 0.1 mm·yr⁻¹. These results show the efficiency of the TOFA/DETA imidazoline in the liquid phase and qualitatively agree with the electrochemical measurements shown above.

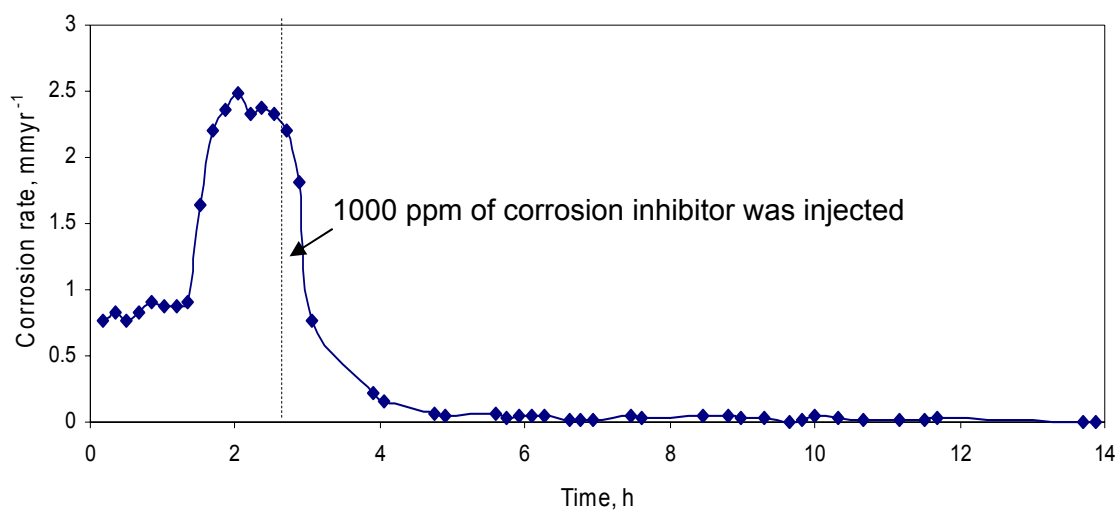


Figure 8: Corrosion rate of mild steel in 3 % wt. NaCl at 70°C, pH 5, with 1000 ppm of acetic acid and 1000 ppm of TOFA/DETA imidazoline

Corrosion inhibitor properties in gas phase investigated using ER probe

In order to investigate if the corrosion inhibitor carried by foam matrix can provide sufficient inhibition at the top of the line, sodium C14-16 olefin sulfonate was used as foaming agent in concentration 20 % vol. In order to simulate intermittent foam contact, ER probe was taken from corrosion cell and flush mounted on the lid of the foaming cell (shown in Figure 9) for several seconds and then returned back to the corrosion cell lid.



Figure 9: Foaming cell with developed foam.

Check of inhibitive property of the foam matrix without corrosion inhibitor added

The time dependence of metal thickness loss (Figure 10) was obtained by using ER probe in vapor phase saturated with CO₂ and H₂O at a total pressure of 1 bar. The temperature of the solution was held constantly at 70°C while the temperature of the vapor phase was around 60°C. As it can be seen in Figure 10, the metal thickness loss increased in the uninhibited system and kept on increasing with further exposure time even when the ER probe was taken from the corrosion cell and flush mounted on the lid of the foaming cell for 60 seconds at the time. So, it can be concluded that foaming agent sodium C14-16 olefin sulfonate alone has very poor inhibitive property (if any) and does not protect the mild steel at the top of the line.

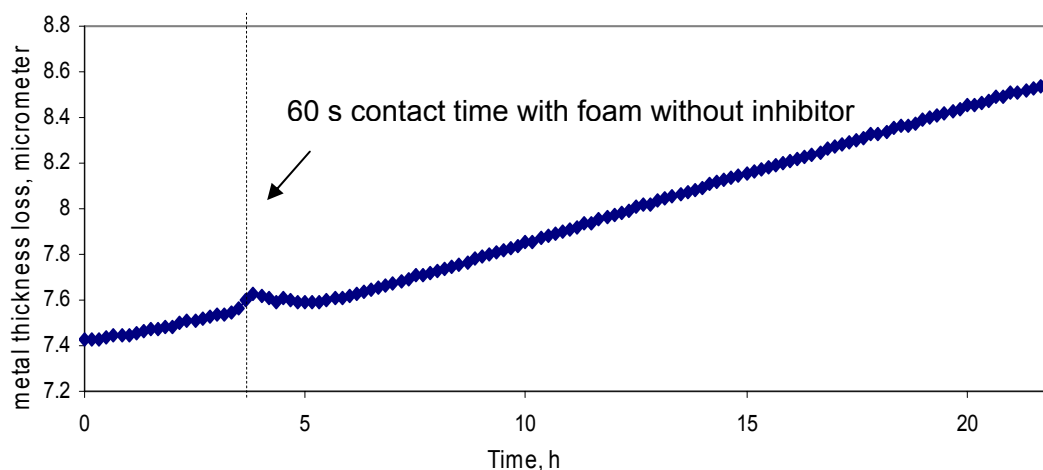


Figure 10: The time dependence of metal thickness loss for mild steel in vapor phase in presence of the foaming agent, contact time 60 seconds, 3 % wt. NaCl solution at 70°C, pH 4 with 1000 ppm of acetic acid.

The TLC rate of mild steel, measured in vapor phase with an ER probe, is shown in Figure 11. The corrosion rate in the vapor phase increased during the first 4 hours and reached approximately $0.5 \text{ mm}\cdot\text{yr}^{-1}$. After the ER probe was taken from corrosion cell and flush mounted on the lid of foaming cell for 60 seconds, the corrosion rate kept the same value, showing that the foaming agent alone has no effect on the TLC rate.

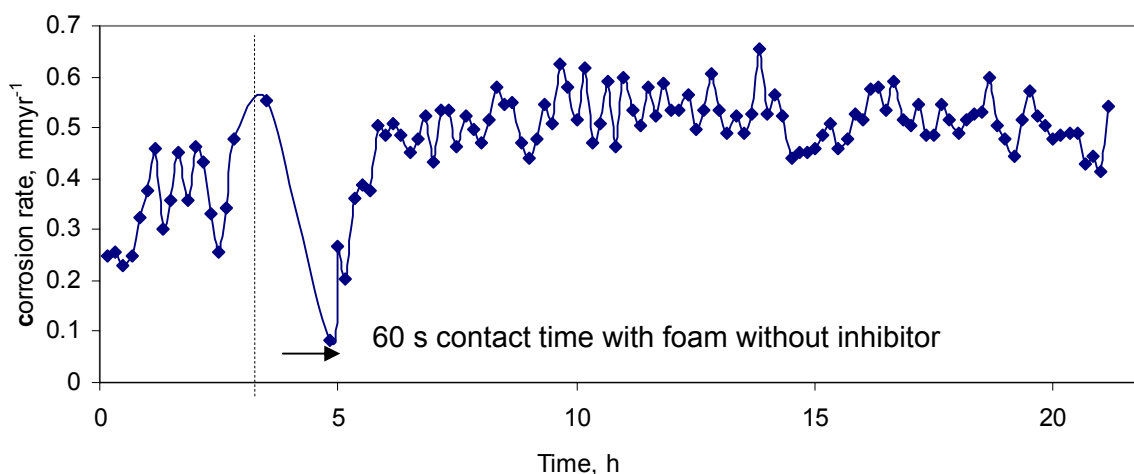
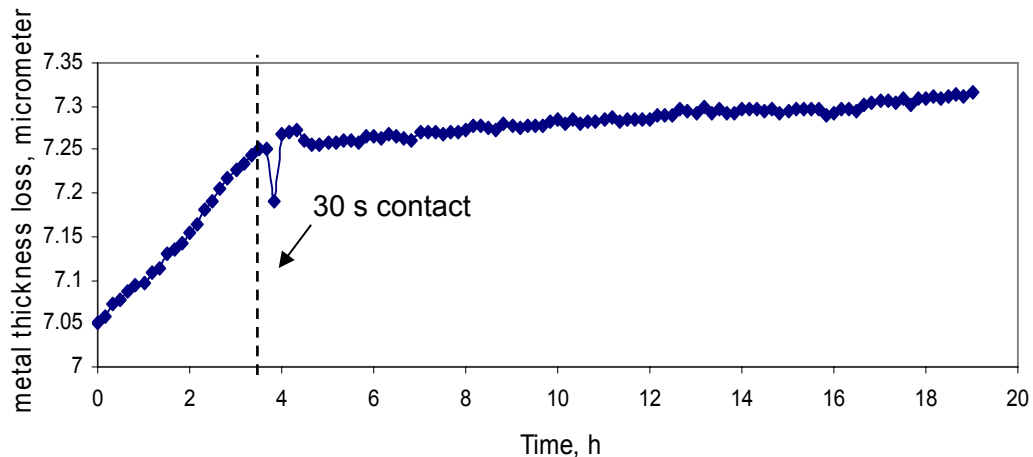


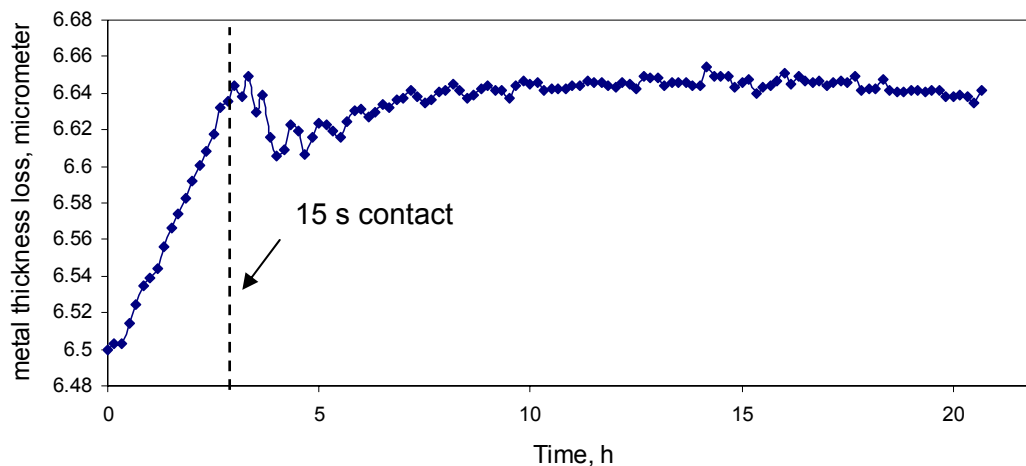
Figure 11: Corrosion rate of mild steel in vapor phase in presence of the foaming agent, contact time 60 seconds, 3 % wt. NaCl solution at 70°C, pH 4 with 1000 ppm of acetic acid.

Inhibitive property of the foam matrix with the corrosion inhibitor

Once the baseline corrosion conditions were established in the corrosion cell, the TLC rate of bare steel was around $0.5 \text{ mm}\cdot\text{yr}^{-1}$. The ER probe was then taken from corrosion cell and flush mounted on the lid of foaming cell, containing 1000 ppm of corrosion inhibitor, for 60, 30, 15 and 5 seconds at a time, and then returned back to the corrosion cell. Figures 12 and 13 show the time dependence of metal thickness loss and corrosion rates, respectively, for contact times of 30 seconds and 15 seconds, indicating that in both cases the corrosion rate was below $0.1 \text{ mm}\cdot\text{yr}^{-1}$ even after 15 hours of exposure. The same results were obtained for contact times of 60 seconds and 5 seconds (data are not shown here). Consequently, it can be considered that the TOFA/DETA imidazoline carried by the foam matrix significantly decreased the TLC rate.



a)



b)

Figure 12: The time dependence of metal thickness loss for mild steel in vapor phase when 1000 ppm TOFA/DETA imidazoline was added in the foam, 3 % wt. NaCl solution at 70°C, pH 4 with 1000 ppm of acetic acid, contact time: a) 30 seconds and b) 15 seconds.

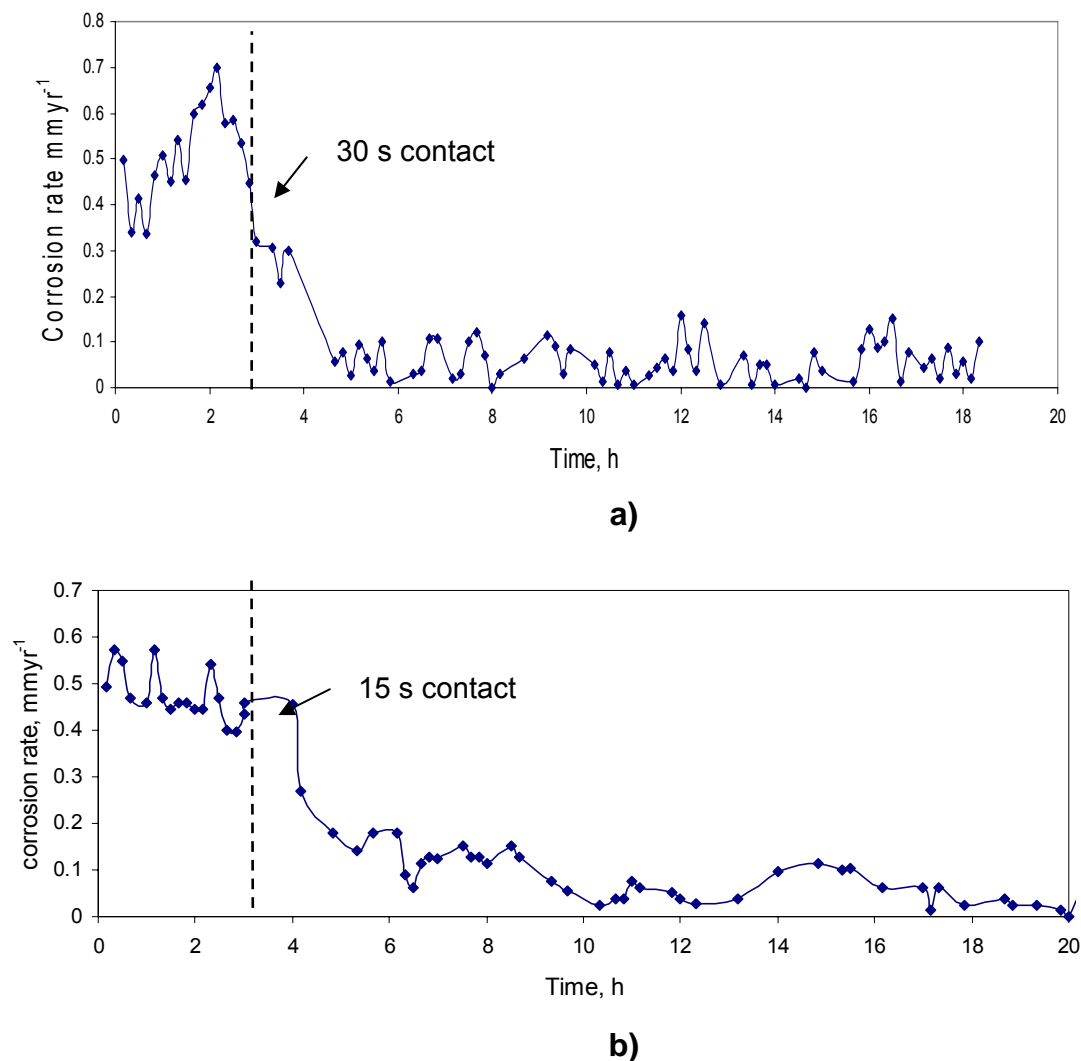


Figure 13: Corrosion rate of mild steel in vapor phase when 1000 ppm TOFA/DETA imidazoline was added in the foam, 3 % wt. NaCl solution at 70°C, pH 4 with 1000 ppm of acetic acid, contact time: a) 30 seconds and b) 15 seconds.

CONCLUSIONS

Based on the results presented in this work, the following conclusions can be made:

- The innovative experimental glass cell setup, which consisted of a foaming cell and a corrosion cell used to simulate intermittent contact between the foam and the steel surface, was successful in creating an environment representative of a field TLC situation, periodically inhibited by a foam plug containing a corrosion inhibitor.

- The electrochemical study of corrosion inhibitor efficiency in liquid phase showed that corrosion rate of mild steel decreased at least an order of magnitude when 70 ppm or more of TOFA/DETA imidazoline was added.
- The investigation showed that the ER probe could adequately measure the inhibitive effect of the chemical compound in the aqueous phase.
- The foam matrix had no corrosion inhibitive properties and does not affect on the TLC rate.
- The TLC rate of mild steel, as measured in the vapor phase using an ER probe, was reduced by periodic treatment by the foam containing a TOFA/DETA imidazoline corrosion inhibitor. Repeatable results were obtained for all contact times in the range of 5-60 seconds, and lasted for at least 15 hours.
- It appears that the foam matrix with TOFA/DETA imidazoline can be used to effectively apply batch inhibition of corrosion at to the top of the line.

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