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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.

This paper reports a study of foam characteristics: its consistency and stability in experiments conducted in a large scale flow loop, in order to simulate more realistic TLC conditions (including: flow, temperature, water condensation rate).The foam was generated pneumatically by sparging CO_2 through the mixture of a foaming agent and a corrosion inhibitor. The foam was then injected into the flow loop, forming a dense plug which is pushed forward by the gas. This provided uniform delivery of the inhibitor to the inner pipe wall. Hydrodynamic tests in 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. Corrosion rate was monitored under condensing conditions using electrical resistance (ER) measurements. The TLC rate of mild steel, as measured in the wet gas flow using the ER probe, was reduced by periodic treatment using the optimized foam composition.

Key words: corrosion inhibitor, foam matrix, flow loop, electrical resistance measurements

INTRODUCTION

Top-of-the-line corrosion (TLC) occurs in wet gas flow where significant temperature gradient between the outside environment and inner pipeline surface leads to higher condensation rates. The thin film of condensed water forms on the sides and at the top of the internal pipe walls and the presence of various corrosive species, such as carbon dioxide (CO_2) and acetic acid (CH_3COOH or shortly HAc) causes a severe corrosion problem.[1-7] The corrosive gases transported in the gas phase will condense together or dissolve in the water and increase solubility of iron as well as the TLC.[8-10]

Corrosion inhibition is one of the most commonly used methods for the corrosion control of carbon steel equipment in oil and gas production, but conventional mitigation methods can fall short in protecting the top of the line since the conditions do not allow the inhibitor to reach the top sections of the wall.[11,12] The most common method used in the case of TLC is batch treatment.

New inhibitor delivery methods are being investigated as an alternative to conventional batch treatment.[13,14] A novel idea consists of injecting the corrosion inhibitor within a foam matrix and delivering of corrosion inhibitor to locations where condensation occurs. A “proof of concept” validation of the novel TLC mitigation method was successfully conducted in a small scale laboratory setup.[15,16]

In order to raise confidence that the previously obtained results can be applied in the field, the novel TLC mitigation method needed to be first 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 (the gas temperature, the gas flow rate, CO_2 partial pressure, condensation rate) as well as flow conditions, encountered in the field.[17,13] The hydrodynamics of foam is especially challenging since the foam has a complex structure, with metastable characteristics, caused by the large interfacial area. For example, the foam stability and strength are affected by many parameters (liquid-phase properties, surfactant type, surfactant concentration, foam generator, pipe diameter, etc.).[18,19]

In this study, the foam was generated pneumatically by sparging CO_2 trough the mixture of foaming agent and corrosion inhibitor. The foam was then injected into the flow loop piping forming a dense plug which was pushed forward by the gas. This method was designed to try and uniformly delivery of the inhibitor to the inner pipe wall. It should have consequently lead to formation of strong chemical bonds that would allow the product to remain on the pipe wall for long periods of time between treatments.[11]

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 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. 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 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 the Figure 1.

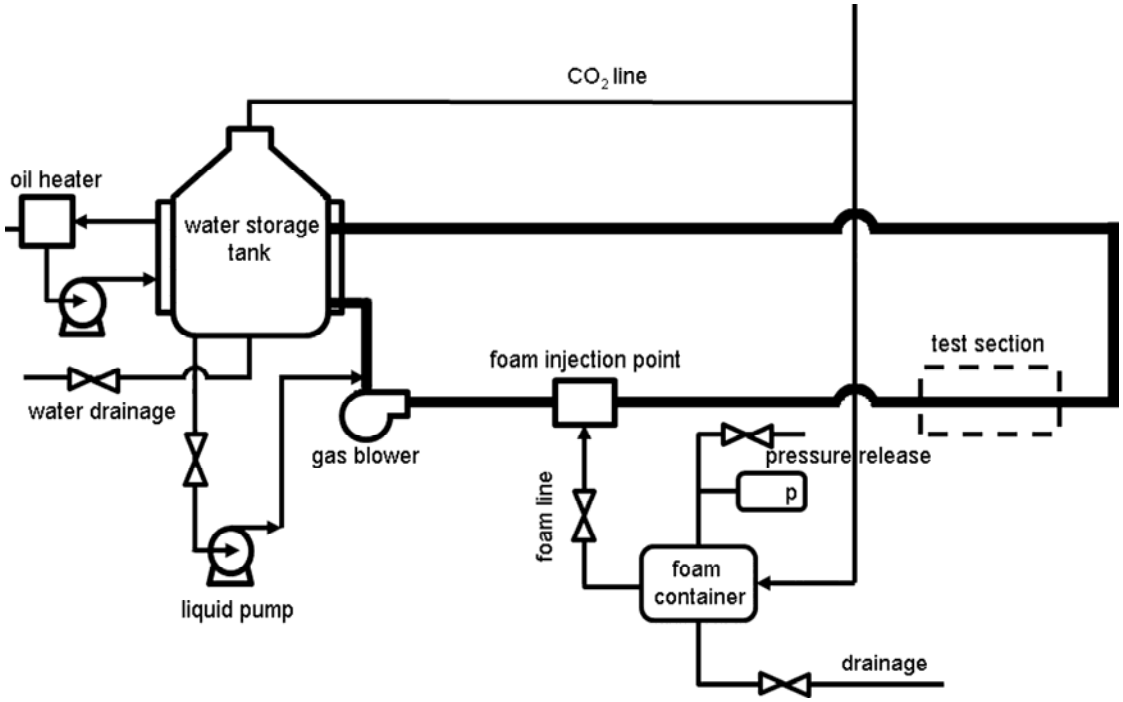

Figure 1: Schematic of the TLC flow loop.

The mixture of CO_2 and water vapor was circulated through the loop. The tank was filled with 150 gal (570 dm^3) of DI water with 1000 ppm_v of HAc injected. The loop was thermally insulated from the ambient. 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 started by injecting carbon dioxide (CO_2) into the loop at a specific pressure. The liquid phase was then heated in the tank to approximately 70ºC. The temperature of the circulating wet gas phase measured at the test section was approximately 60ºC. The liquid pump was then started. 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 pH3.5 and pH4 at pressure. Testing was conducted using a superficial liquid velocity below 0.01 m/s and superficial gas velocity of 1.4 m/s. The electrical resistance (ER) corrosion probes were introduced under pressure into the test section. A borescope was installed, in order to perform continuous visualization of the flow inside the pipe and for recording of the videos. The picture of the test section is presented in Figure 2, while the experimental conditions are summarized in Table 1.

Figure 2: Test section of the flow loop.

Table 1
Experimental conditions in the flow loop.

Parameters	Conditions
Test solution	DI water + 1000 ppm_v of HAc
Test gas	CO_2
Temperature in the liquid phase	70ºC
Temperature in the wet gas flow	60ºC
pH	3.5 to 4
Pressure in the system	1.1 bar
Superficial gas velocity	1.4 m/s
Superficial liquid velocity	< 0.01 m/s

Foam matrix formation

The foam was created pneumatically by sparging CO_2 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_2 bubbling was

performed for 2.5 min creating a plug of foam inside the pipe. The foam injection was performed under static conditions (the gas phase was not circulated at that time). After the CO_2 injection was stopped the gas blower and the liquid pump were restarted and the plug was pushed down the pipe. The foam stability and consistency were estimated by recording videos of the foam flow through the pipe using a borescope connected to a digital camera. 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. Different concentrations of the foaming agent were tested in the range of 5 vol % to 40 vol %. The effect of the superficial gas velocity on the foam plug consistency was also tested. Videos of the foam flow through the pipe were recorded at different superficial gas velocities in the range of 0.5 to 4 m/s while the superficial liquid velocity was held constant.

Corrosion inhibitor and foam solution composition

The container used for foam formation was filled with 4 dm^3 of water containing 10 vol % foaming agent (sodium C14-16 olefin sulfonate) with different concentrations of corrosion inhibitors added. Two different generic formulations of corrosion inhibitors were tested in the present study:

- A commercial inhibitor with a known formulation based on talloil diethylenetriamine imidazoline (TOFA/DETA imidazoline)
- A mixture of dicyclohexylamine and oleylamine (1:1 vol %)

Both inhibitor molecule structures are comprised of nitrogenous surfactants (alkyl imidazolines and amine compounds). The full composition of foam matrix is shown in Table 2.

Table 2
Foam matrix composition.

Parameters	Conditions
Corrosion inhibitors	TOFA/DETA imidazoline dicyclohexylamine and oleylamine (1:1 vol %)
Inhibitor concentration, ppm_v	1000, 5000, 10,000, 20,000
Foaming agent	sodium C14-16 olefin sulfonate
Foaming agent concentration	10 vol %

Corrosion measurements in the flow loop

The corrosion rate data was acquired using electrical resistance (ER) measurements. ER probes were not introduced into the flow loop until the system had reached stable state (temperature, pressure, and flow velocities). The sensing elements of ER probes were pretreated with 78 wt % H_2SO_4 for 30 s, rinsed with distilled water for 10 s and then polished with emery paper grit 600 and rinsed with distilled water again. The ER probe sensing element after this preparation is shown in Figure 3. 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. The exposure time was between 30 h and 60 h.

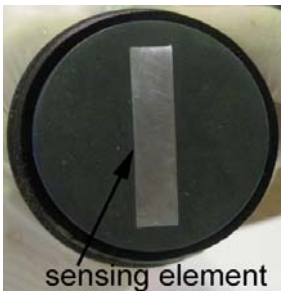

Figure 3: Electrical resistance probe head with the sensing element.

RESULTS AND DISSCUSSION

Foam matrix optimization

The objective of this part of the work was to optimize the conditions for foam formation. The advantages of the identified method for foam formation was its simplicity and the establishment of a relatively stable and dense 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, what would not be practical in the field. The application of other more efficient methods for foam formation and injection are currently being considered.

It was found that the most significant parameters that affect consistency and strength of the foam are the pressure of CO_2 used for foam formation and the foaming agent concentration. The most satisfying results were acquired when the pressure of 3 psi (20 kPa) and 10 vol % of sodium C14-16 olefin sulfonate foaming agent solution were applied. At these conditions the internal pipe wall surface was fully coated with foam. At lower pressure of CO_2, injection the foam wasn't stable enough and it easily decomposed when pushed towards the pipe section where the ER probes were mounted.

The effect of the superficial gas velocity on the foam plug consistency was also tested. At low superficial gas velocity (< 3 m/s) the foam was observed to be compact and stable, while with further increase in the gas velocity (> 3 m/s) the foam decomposed easily and failed to fully coat the internal pipe wall surface. The way the foam was generated carried considerable importance for the foam stability.

In order to attain necessary contact time between the foam and the ER probe, the superficial gas velocity chosen was 1.4 m/s. The contact time between the ER probe and the foam matrix was in this case around 15 s and shortly after that the foam film completely disappeared (Figure 4). This was a sufficiently long retention time for the foam matrix coating the metal surface which enabled the establishment of a viable corrosion inhibitor film.

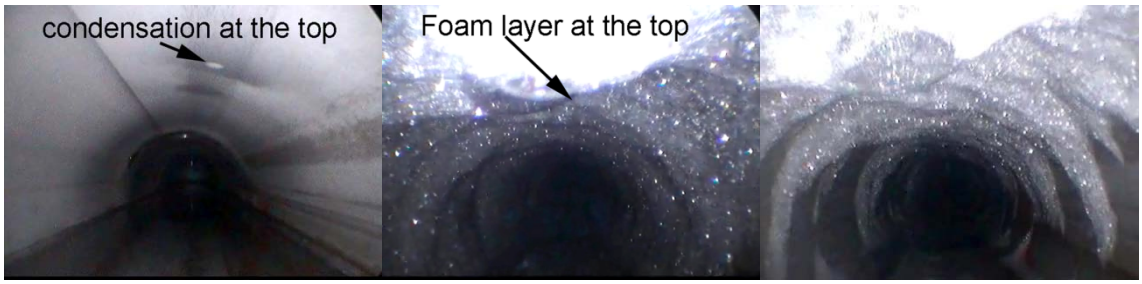

Figure 4: Inner pipe surface before and after the plug of foam was pushed through the pipe, recorded using a borescope.

Corrosion measurements

Inhibitive properties of the foam matrix without a corrosion inhibitor added

The time dependence of metal thickness loss (ER) for mild steel exposed at the top of the line to a wet CO_2 gas, before and after it was contacted by the foam plug (without any corrosion inhibitor) is shown in Figure 5.

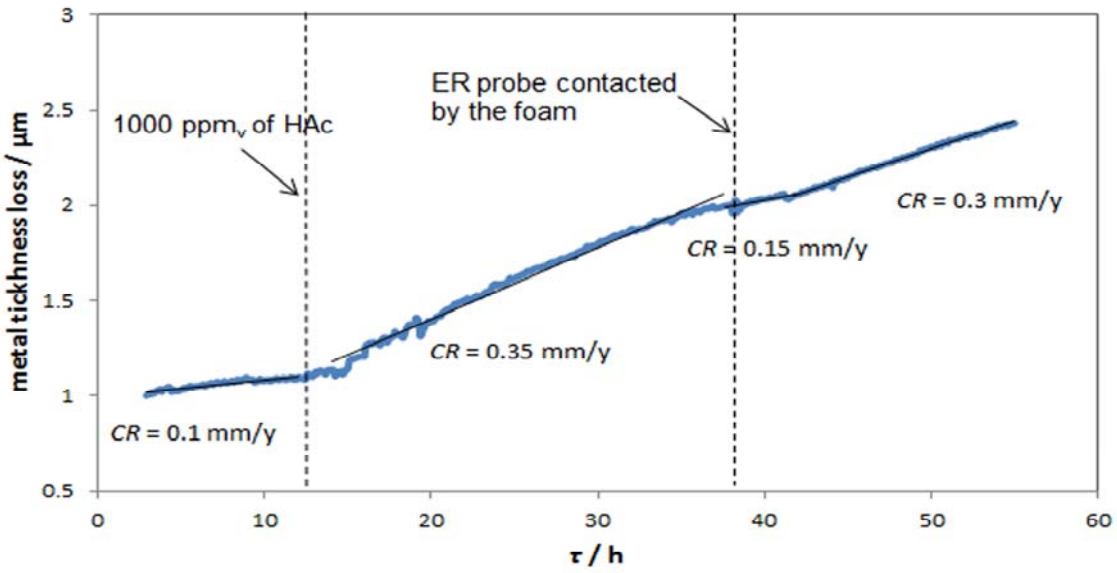

Figure 5: The time dependence of metal thickness loss, measured by ER, for mild steel exposed at the top of the line in wet CO_2 gas flow before and after being contacted by a foam plug without any corrosion inhibitor (test solution: DI water with 1000 ppm$_v$ of HAc, liquid temperature: 70ºC, gas temperature: 60ºC, pressure in the system: 1.1 bar, superficial gas velocity: 1.4 m/s)

The TLC rate (CR) was around 0.1 mm/y at the beginning of the experiment. As it can be seen in the Figure 5 an increase in corrosion rate occurred when 1000 ppm$_v$ of HAc was injected into the system and the corrosion rate increased to 0.35 mm/y. This type of influence of HAc on the corrosion rate in TLC has been previously reported in the literature.[3,10] The corrosion rate was steady for another 25 h when the ER probe was contacted by the plug of foam. The corrosion rate decreased approximately by a factor of two (0.15 mm/y), showing that the foaming agent alone has some retarding effect on the TLC rate, most likely by interfering with

condensation. With further exposure of ER probe to the corrosive wet gas environment, a gradual increase in the corrosion rate was detected and after 4 h the baseline corrosion rate of 0.3 mm/y was again established in the system, presumably due to the foam breaking up.

Inhibitive properties of the foam matrix with the TOFA/DETA imidazoline 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_2 gas flow before and after it was contacted by a foam plug containing 1000 ppm_v and then 10,000 ppm_v of TOFA/DETA imidazoline, is shown in the Figure 6.

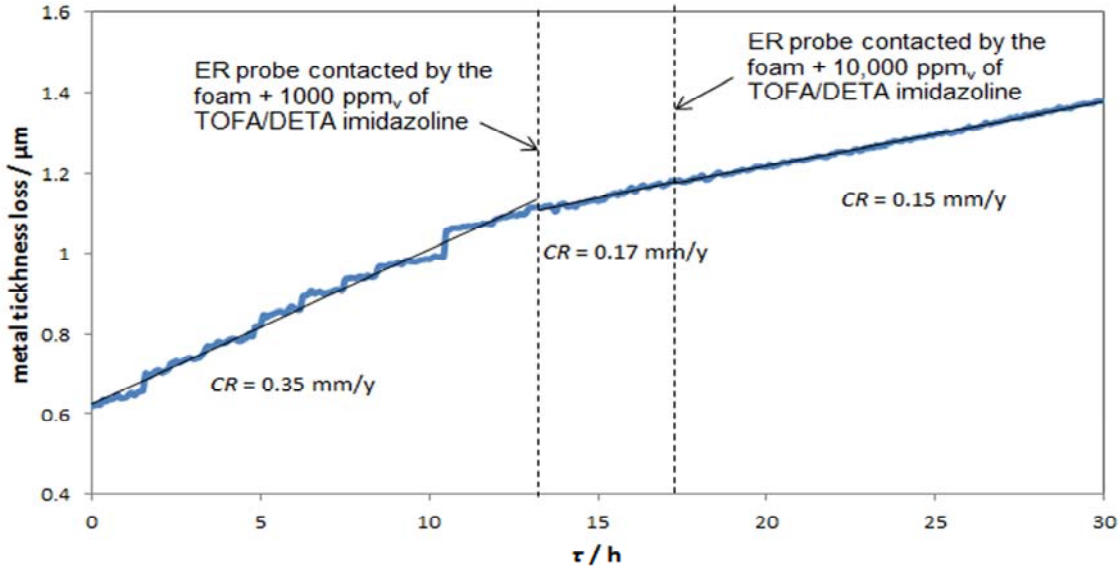

Figure 6: The time dependence of metal thickness loss for mild steel, measured by ER, exposed at the top of the line in wet CO_2 gas flow before and after being contacted by a foam plug containing 1000 ppm_v and then 10,000 ppm_v of TOFA/DETA imidazoline corrosion inhibitor (test solution: DI water with 1000 ppm_v of HAc, liquid temperature: 70ºC, gas temperature: 60ºC, pressure in the system: 1.1 bar, superficial gas velocity: 1.4 m/s).

As it can be seen in Figure 6 the baseline corrosion rate was 0.35 mm/y. A plug of foam containing 1000 ppm_v of TOFA/DETA imidazoline was pushed through the flow loop and the resulting corrosion rate decreased by a factor of two. The procedure was then repeated with 10,000 ppm_v of TOFA/DETA imidazoline and the corrosion rate was approximately the same. While the effect of inhibitor was seen with 1000 ppm_v, further increase of TOFA/DETA imidazoline concentration to 10,000 ppm_v did not seem to have any significant effect on the TLC rate. The corrosion rate remained the same during the following 15 h. Compared to the results obtained with the pure foam matrix, without the corrosion inhibitor, the corrosion rate in did not decrease to very low values. These corrosion rates were not as favorable as those measured with the same inhibitor at the same concentrations in a glass cell setup.[15] This seems to indicate that the inhibitor performance was somehow affected by the flow conditions.

In the subsequent experiment, the concentration of the inhibitor 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_2 gas flow, before and after it was contacted by a foam plug containing

20,000 ppm_v of TOFA/DETA imidazoline, is shown in the Figure 7. The baseline corrosion rate was again around 0.3 mm/y. When the concentration of TOFA/DETA imidazoline in the foam matrix was increased to 20,000 ppm_v, the corrosion rate after the treatment approached very low values (0.01 mm/y).

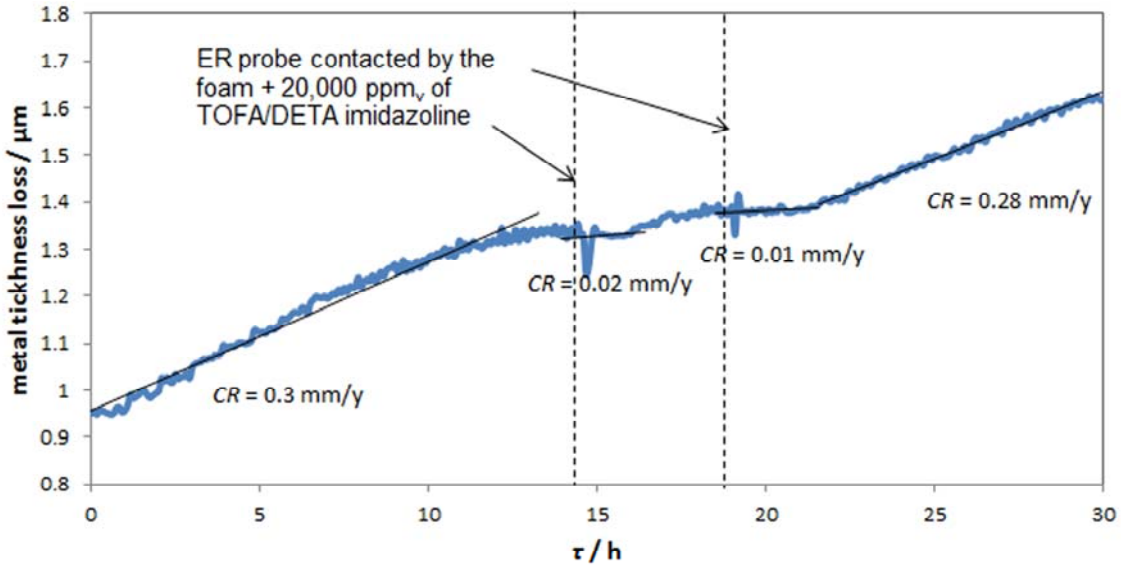

Figure 7: The time dependence of metal thickness loss for mild steel, measured by ER, exposed at the top of the line in wet CO_2 gas flow before and after being contacted by a foam plug containing 20,000 ppm_v of TOFA/DETA imidazoline (test solution: DI water with 1000 ppm_v of HAc, liquid temperature: 70ºC, gas temperature: 60ºC, pressure in the system: 1.1 bar, superficial gas velocity: 1.4 m/s).

The inhibition effect lasted for approximately 3 h. After 3 h the corrosion rate gradually increased to the baseline value of 0.3 mm/y suggesting that the applied inhibitor film was not persistent enough and was washed away by the condensation of water.

Inhibitive properties of the foam matrix with DCHA+OA 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_2 gas flow, before and after it was contacted by a foam plug containing 5000 ppm_v of DCHA+OA is shown in the Figure 8.

Once the baseline corrosion conditions were established in the flow loop, the TLC rate of bare steel was repeatable: approximately 0.3 mm/y. A foam slug with 5000 ppm_v of DCHA+OA was then pushed into the line. This was repeated twice. As it can be seen in the Figure 8 the time dependence of metal thickness loss indicates that in both cases, after the application of the inhibitor, the corrosion rate was below 0.1 mm/y for approximately 5 h of exposure. The corrosion rate then increased to 0.15 mm/y and was constant for over 20 h. Consequently, it can be considered that the inhibition using 5000 ppm_v of DCHA+OA was more persistent in reducing the TLC rate. More work is planned to test different chemical formulations and delivery methods in longer tests.

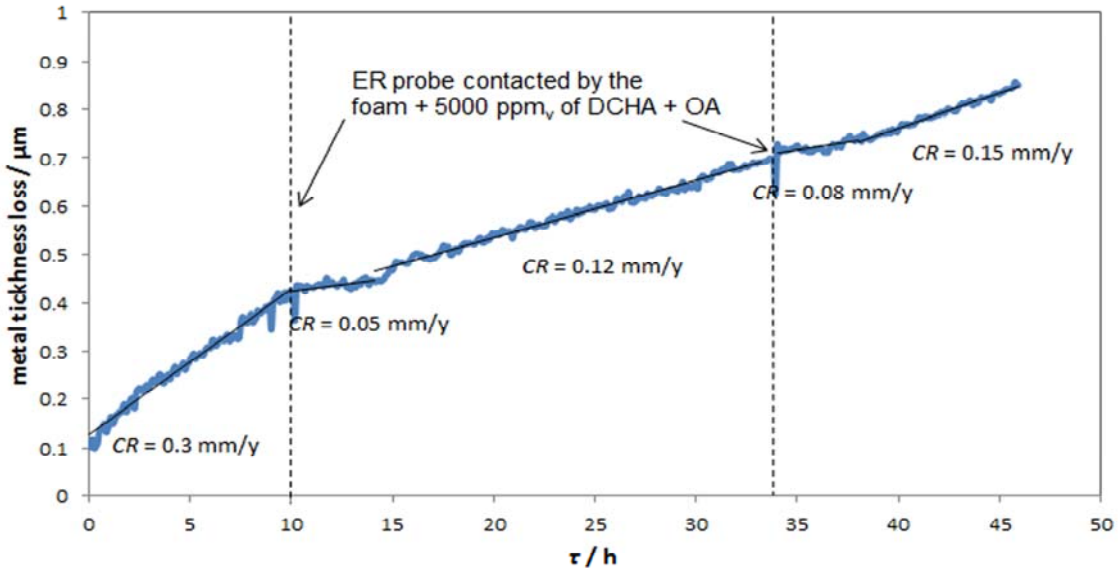

Figure 8: The time dependence of metal thickness loss for mild steel, measured by ER, exposed at the top of the line in wet CO_2 gas flow before and after being contacted by a foam plug containing 5000 ppm_v DCHA+OA (test solution: DI water with 1000 ppm_v of HAc, liquid temperature: 70ºC, gas temperature: 60ºC, pressure in the system: 1.1 bar, superficial gas velocity: 1.4 m/s).

CONCLUSIONS

- A novel TLC mitigation method was evaluated under simulated field conditions in large scale multiphase flow loop. The use of a flow loop enabled a more realistic simulation 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_2 through the foaming agent. It was observed that the foam characteristics were depended on the pressure of CO_2 used for foam formation, and the foaming agent concentration.

- 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, showing 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 by the foam containing a high concentration of a TOFA/DETA imidazoline corrosion inhibitor. However, the effect was not persistent, and the inhibition effect lasted between 3 h and 15 h.

- Using a DCHA+OA inhibitor led to more persistent inhibition and the effect lasted over 20 h.

- The foam matrix is an effective method to deliver a corrosion inhibitor which can control the TLC rate in wet CO_2 gas flow. Additional experimentation is needed to find more efficient chemical formulations and delivery methods in longer tests.

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