Paper No.
C2025-00335

AMPP ANNUAL CONFERENCE + EXPO
APRIL 6-10, 2025 | NASHVILLE, TENNESSEE

Effects of Temperature and Presence of Hydrocarbon on Commercial Batch Inhibitor Persistency using a Developed Methodology

Kasra Shayar Bahadori, Bruce Brown, Marc Singer
Institute for Corrosion and Multiphase Technology
Department of Chemical and Biomolecular Engineering
Ohio University
334 W State St
Athens, OH, 45701
USA

ABSTRACT

Organic corrosion inhibitors (CIs) are widely used in the oil and gas industry to control pipeline corrosion. Batch treatment is a method commonly used to apply CIs for top-of-the-line corrosion mitigation in gas lines and in downhole tubulars. In this approach, the CI forms a thick protective film on the pipe surface, but this film gradually degrades due to various factors, leading to loss of inhibition. Therefore, understanding CI persistency and the parameters affecting its degradation is critical for improving the efficacy of batch treatments. A novel methodology and experimental setup were developed to address previous limitations and investigate CI persistency under batch treatment conditions. This setup effectively removed all CI residuals after application and prevented oxygen contamination during the film formation step. A commercial inhibitor was used to study the effects of temperature, presence of hydrocarbon, and contact time on CI persistency, by application in situ on API 5L X65 steel inside a deoxygenated glass cell. In addition, different model compound CIs with different solvents/carriers were tested for investigating their persistency. Electrochemical measurements were taken at intervals to track inhibitor performance over time.

Key words: corrosion inhibitor, persistency, batch inhibition, CO_2 corrosion

INTRODUCTION

Loss of metal due to CO_2 corrosion of the internal walls of mild steel pipelines has always been a significant problem in oil and gas industries. Different methods have been implemented to mitigate internal pipeline corrosion. Among these methods, the use of corrosion inhibitors provides advantages for minimizing pipeline wall loss as inhibitor treatment costs are lower than other mitigation techniques, such as corrosion resistant alloys (CRAs) and coated pipelines, and can be adjusted over time. Thus, chemical inhibitors are widely used as a conventional method to mitigate internal pipeline corrosion using two main methodologies: continuous inhibitor injection and batch inhibition treatment.[1–7] Continuous injection involves the constant application of an inhibitor at a low concentration, while batch inhibition uses periodic treatments at much higher concentrations. When continuous inhibitor injection fails to

provide adequate protection, batch inhibition can be implemented as an alternative approach. Different methods exist for administering inhibitors within a batch inhibition regime. In transportation pipelines, an inhibitor slug is introduced between two moving displacement devices (pigs or scrapers). The subsequent movement of these pigs results in the formation of a thick inhibitor film on the pipe internal surface. Alternatively, in downhole tubular systems, a highly concentrated inhibitor slug is injected from the wellhead, where it is allowed sufficient residence time to establish a uniform protective coverage on the pipe walls. Over time the inhibitor is gradually removed from the metal surface, resulting in loss of protection. The duration over which the inhibitor remains effective is referred to CI persistency.[7–11] Thus, understanding inhibitor persistency behavior is crucial for determining the time window of safe operation.

One of the most challenging steps in batch inhibition studies is the methodology that is employed in the laboratory to simulate the field application. The literature mentions two main methods to assess the persistency of batch inhibitors. In the first methodology, the specimen is first dipped into the neat or diluted inhibitor solution for a pre-defined time that represents the contact time. Then, the specimen is dripped dry and transferred to the uninhibited brine and electrochemical measurements are conducted on the specimen, with often only limited brine renewal.[8,9,11–14] This method is called “ex-situ dip and drip” method. The issues with this type of procedure are thought to be oxygen intrusion, since inhibitor is applied ex situ, and no control of inhibitor concentration if the solution in the glass cell is not continuously renewed. In the second methodology, inhibitor is applied to the specimen in a deoxygenated glass cell to avoid oxygen contamination. Then, the uninhibited brine is introduced to the glass cell without transferring the specimen.[15,16] This method is called “in-situ modified dip and drip” method. A modification of this method was proposed by Achour, et al.[15] and involved filling the entire cell with concentrated CI to avoid complications associated with the specimen transfer (O_2 contamination). However, this change was not without bringing its own sets of issues, leaving excessive residual inhibitor in the cell which must have been difficult to remove. Both methods exhibited limitations in brine renewal and CI concentration control during inhibitor application step and corrosion monitoring. Accordingly, an improved methodology is needed to simulate field applications without oxygen contamination, with a more controlled CI film formation and with the ability to remove all inhibitor residuals from the glass cell.

In addition to the inhibitor film formation procedure, the methodology that is used for batch inhibition study must consider other controlling parameters that play an important role in field application. Table 1 summarizes how the effects of these important parameters are treated in field applications and laboratory studies:

Table 1
Parameters from field application *vs.* laboratory studies [11,13,14]

Parameter	Field application	Laboratory studies
Presence of hydrocarbon	Flow in oil and gas pipelines consists of both oil and water phase	Presence of oil is often ignored
Contact time	Calculated based on the CI slug volume and velocity (at most 10-15 seconds)	Set based on the time that specimen is in contact with inhibitor
Film thickness	Estimated at 25 μm to 76 μm (1 to 3 mils) using “rule of thumb”	Not consistently measured or reported
Diluent to CI ratio	1:1 to 5:1	Neat CI
Solvent type	Field condensate, crude, diesel or aromatic solvents	“As received” in commercial inhibitor package (which contains solvents)

A number of literature studies investigated the effects of different operational parameters on CI persistency in batch treatment. De Marco, et al.[14], studied the effect of the presence of hydrocarbon on batch inhibition persistency. They used the dip and drip method using different model compound inhibitors and claimed that some inhibitors chemisorbed on the specimen while the other physiosorbed

on the metal surface based on assessment of their respective adsorption enthalpy and free adsorption energy (ΔH°_{ad} and ΔG°_{ad}). They also concluded that, in the presence of hydrocarbons, chemisorbed inhibitors experience higher persistency while physiosorbed inhibitors persistency decreases. Menendez, et al.[11], used an optical profilometer to measure the inhibitor film thickness of the specimens that were dipped into the inhibitor solution (dip and drip method), but did not conduct corrosion studies for confirmation of the results. Generally, the thickness of the inhibitor film on the specimens right after dipping step was in the range of 25 to 76 μm (similar to the reported value in the field). In addition, the authors investigated the effects of four different contact times on inhibitor film thickness, but differences observed were considered negligible. Moreover, inhibitor film thickness of two diluted commercial inhibitor packages were measured and compared to the neat measurements. Results showed that a decrease in the inhibitor package viscosity due to the dilution led to a lower inhibitor film thickness, which was thought to diminish the corrosion mitigation and persistency of the inhibitor. In prior research at the author's laboratory [10,17], the effect of temperature was examined using the Langmuir isotherm model, and the adsorption/desorption kinetics were calculated. The results indicated that higher temperatures lead to an increased desorption rate of the inhibitor, which also places it as another important operational parameter to examine.

Accordingly, for laboratory batch inhibition studies, an appropriate methodology is needed to simulate the field application with no oxygen contamination and the ability to continuously remove inhibitor residuals from the glass cell. In addition, important parameters that are considered in field application of batch inhibition need to be studied to fill the knowledge gap on this topic. These parameters are inhibitor type, flow conditions (shear stress, temperature, etc.), film thickness, contact time, type of solvent, initial CI concentration, and presence of hydrocarbons or corrosion products. Among these parameters, temperature, presence of hydrocarbon, contact time, inhibitor type, and type of solvent were studied in this research.

EXPERIMENTAL PROCEDURE

All experiments were done in a 3-electrode glass cell apparatus connected to a 350 gallon (1325 liter) tank and the effluent container (Figure 1a). In this study, two different sets of experiments were conducted: batch inhibition experiments with commercial inhibitor (reaction products of fatty acid and amines with long hydrocarbon tail), and batch inhibition experiments with model compound inhibitors (quaternary ammonium and phosphate ester type CI).

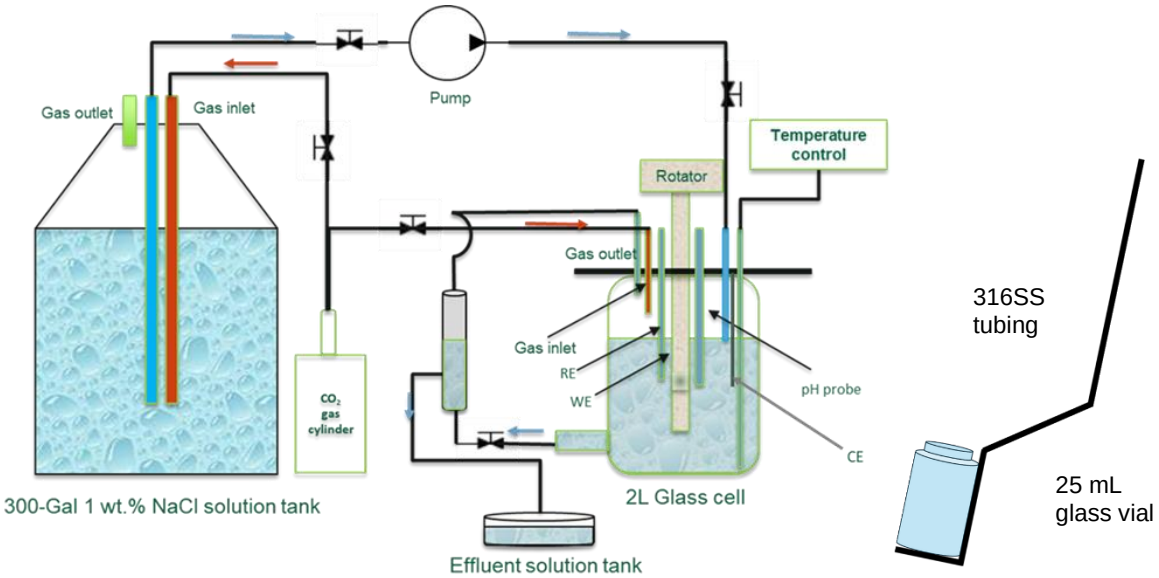

Figure 1: a) 3-Electrode glass cell setup schematic (left) b) and the inhibitor vial holder used for inhibitor film formation (right).

For each experiment the detailed steps were as follows:

1. Uninhibited brine was prepared and sparged overnight with CO_2.
2. The glass cell was emptied, dried and sparged for 30 min with CO_2 to deoxygenate the system before use.
3. Rotating Cylinder Electrode (RCE) was installed in the glass cell and the glass cell was sparged for another 10 min with CO_2.
4. Inhibitor solution was put in a separate vial attached to the holder (Figure 1b)
5. Stopper was removed and the vial was lowered into the glass cell and positioned around the RCE, avoiding direct contact between the vial and the RCE.
6. RCE rotation was set at (300 rpm) for a specific contact time (flow with inhibitor contact).
7. RCE rotation was stopped, and the inhibitor vial was removed, avoiding direct contact between the vial and the RCE.
8. The vial was taken out of the glass cell, the stopper was put back, and the glass cell was sparged with CO_2 for another 5 min.
9. Pre-sparged uninhibited brine was introduced to the glass cell continuously at a constant flow rate (40 mL/minute). Once the RCE was fully immersed in the brine, the outlet valve was open in order to maintain, at steady state, a constant aqueous phase volume in the cell. Excess inhibitor from dip and drip was flushed out of the bottom of the glass cell with the initial flow of brine.
10. After full contact between the RCE and the brine, RCE rotation was set at 1000 rpm and electrochemical measurements were taken at constant intervals until the end of the experiment.

Table 2 shows the experimental matrix for experiments with commercial inhibitor and model compound CIs.

Table 2
Experimental test matrix for the batch treatment persistency experiments

Parameters	**Description**
Working electrode	API 5L X65 (0.05 wt.% C)
Reference electrode	Saturated KCl Ag/AgCl
Counter electrode	Platinum coated titanium mesh
Electrolyte	1 wt.% NaCl
Sparge gas	CO_2
Total pressure	1 bar (10^5 Pa)
RCE rotational speed	1000 rpm
Temperature	30°C, 60°C, and 80°C
pH	4.0, 4.45, and 4.65 ± 0.1
Measurement methods	OCP, LPR, EIS
Inhibitor type	Commercial CI, Benzyldimethylammonium (BDA-C16), Phosphate ester (PE-C14)
Inhibitor initial concentration	1.5, 7.5 and 15 wt.% - neat
Residual inhibitor concentration measurement method	UV-vis spectroscopy (BDA-C16 only)
Inhibitor solvent (model compound inhibitor only)	Isopropanol, Butoxyethanol, Alkylphenolethoxylate, and LVT-200 model oil (light petroleum distillate)
Pre-corrosion	No pre-corrosion
Contact time	5 minutes or 10 seconds
Presence of hydrocarbon	0 or 1% (v/v) model oil

The electrochemical measurements that were taken during the experiments were open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and linear polarization resistance (LPR). OCP was monitored before other measurements to check if the system was stable (ΔOCP < 5 mV/minute). EIS was used to measure the solution resistance (R_s), which was used to correct LPR results in all corrosion rate measurements shown in this study. Measurements in the sequence of OCP-EIS-OCP-LPR were repeated approximately every 30 minutes throughout each experiment. Data collected for R_S and OCP associated with these tests is under review, so these details are not provided in this paper.

In a previous study[10], benzyldimethylhexadecylammonium (BDA-C16) was used as a model CI to investigate batch corrosion inhibition. It was used again in this study because it is a chemical which is synthesized in-house, has been used in several studies, and has been shown to have repeatable CI residual measurements obtained using UV-vis spectroscopy. The UV-vis method was not able to be used for commercial inhibitors or phosphate ester CIs, so it was only reported for use with BDA-C16.

After each experiment, the RCE were visually inspected for general or localized corrosion. If localized corrosion was observed, the RCE was analyzed using the Alicona Infinite Focus Microscope (IFM) for the profilometry measurement.

RESULTS

Prior to corrosion inhibitor experiments, baseline corrosion rates were established through numerous glass cell experiments conducted under identical conditions without the presence of hydrocarbon at 30°C, 60°C, and 80°C. These experiments yielded a corrosion rate of 3.95 ± 0.25, 8.2 ± 1.8, 11.7 ± 1.9 mm/year at 30°C, 60°C, and 80°C respectively in the absence of any inhibitor. To isolate the effects of model oil on RCE corrosion rates, experiments were conducted using the same methodology as the CI experiments, but with the vial filled solely with model oil. No significant effects on corrosion rates were observed.

Batch Inhibition experiments using a commercial corrosion inhibitor

The first series of experiments were performed with a commercial batch inhibitor, known for its persistency. The aim of these experiments was to validate the methodology and to identify the main parameters that could have an influence on the CI persistency.

Effects of temperature and contact time

A commercial inhibitor that had shown excellent performance from a previous set of proprietary testing was used in these experiments. In addition, the influence of two parameters speculated to affect CI persistency was investigated: contact time and temperature. Figure *2* shows the corrosion rate versus time for two repeats of the experiment in which a neat (as received) inhibitor was applied to the RCE for 5 minutes of contact time and exposed to flowing conditions at 30°C. The commercial inhibitor was used ‘as received’ and the exact composition was proprietary. The excessive contact time was chosen for proof of concept (this was adjusted in subsequent experimentation). The commercial CI showed high persistency in the testing conditions: excellent inhibitor efficiency (close to 100%) and persistency for over 18 days.

Since such low LPR corrosion rates were observed for these experiments, further tests were conducted for confirmation. Cathodic potentiodynamic sweeps (from E_{OC} to E_{OC}-700mV) and one short anodic sweep (from E_{OC} to E_{OC}+20mV) were conducted at the end of these two experiments to observe the change in corrosion mechanisms. Figure 3 shows that, compared to the uninhibited conditions, charge transfer rates and limiting currents of all reactions decreased by multiple orders of magnitude in experiments with this commercial inhibitor, confirming its mitigating effect on all corrosion mechanisms. Mass loss measurements of the RCE from these tests also showed no measurable change, confirming

the electrochemical measurements. With confirmation of the results, inhibition efficiency was calculated at 99.997% based on solely the LPR measurements from the inhibited and uninhibited experiments (Equation (1)):

$$\varepsilon = \frac{CR_{uninhibited} - CR_{inhibited}}{CR_{uninhibited}} \quad (1)$$

where ε is the corrosion efficiency, $CR_{uninhibited}$ is the steady state corrosion rate (3.95 ± 0.25 mm/year baseline corrosion rate at 30°C) without inhibitor and $CR_{inhibited}$ is the steady-state corrosion rate (mm/year) in the presence of inhibitor.

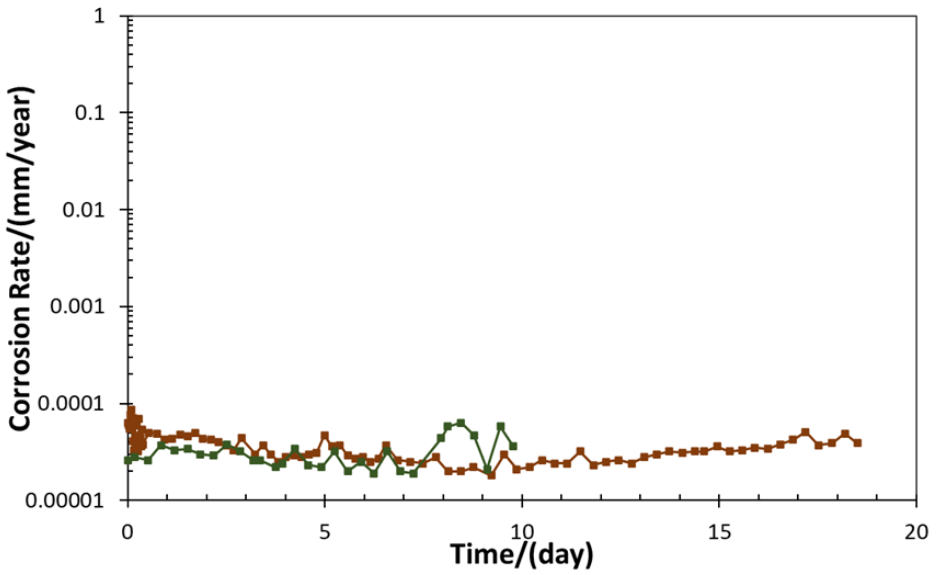

Figure 2: Batch inhibition persistency experiments (2 repeats) with commercial inhibitor (30°C, 5 min contact time, 1000 rpm, pH 4.0, 1 wt.% NaCl). Corrosion rates are measured with LPR.

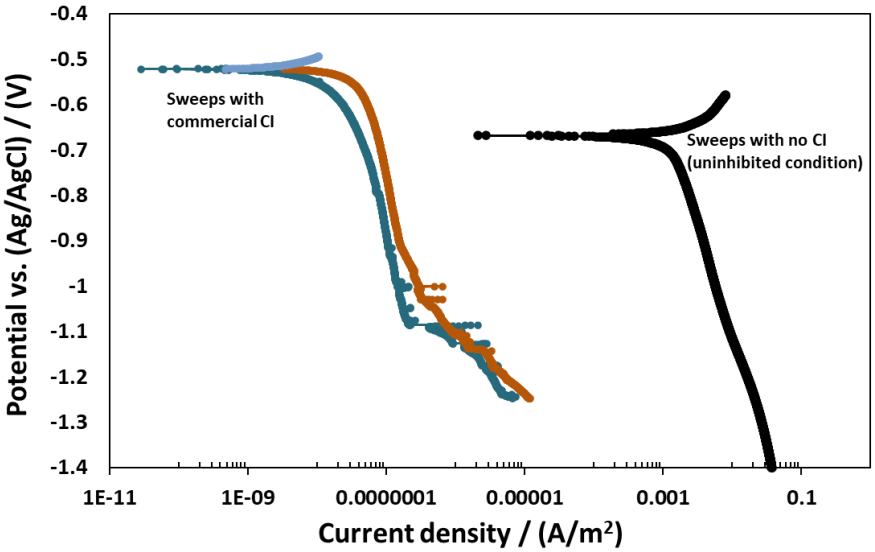

Figure 3: Potentiodynamic sweeps of the specimen with commercial Cl (2 repeats) vs. uninhibited conditions (30°C, 5 min contact time, 1000 rpm, pH 4.0, 1 wt.% NaCl).

Given the excellent persistency demonstrated by this commercial batch CI in these experiments, further investigation was undertaken to determine which changes in experimental conditions would have a detrimental effect on its performance. Thus, for the next step, the effects of shorter contact time and higher temperature were studied. Figure 4 shows three different repeats of an experiment in which the contact time was 10 seconds, and the temperature was initially 30°C for 1.5 days. Then, the temperature was increased to 45°C to investigate the effects of an increase in temperature. Results showed that, with the shorter contact time, the same inhibitor efficiency for 30°C was observed. The increase in temperature caused an increase in the corrosion rate, however, the inhibitor remained persistent and was assumed to have a similar inhibitor efficiency based on an expected higher baseline corrosion rate at the higher temperature. Baseline conditions were not tested at 45°C due to this assumption.

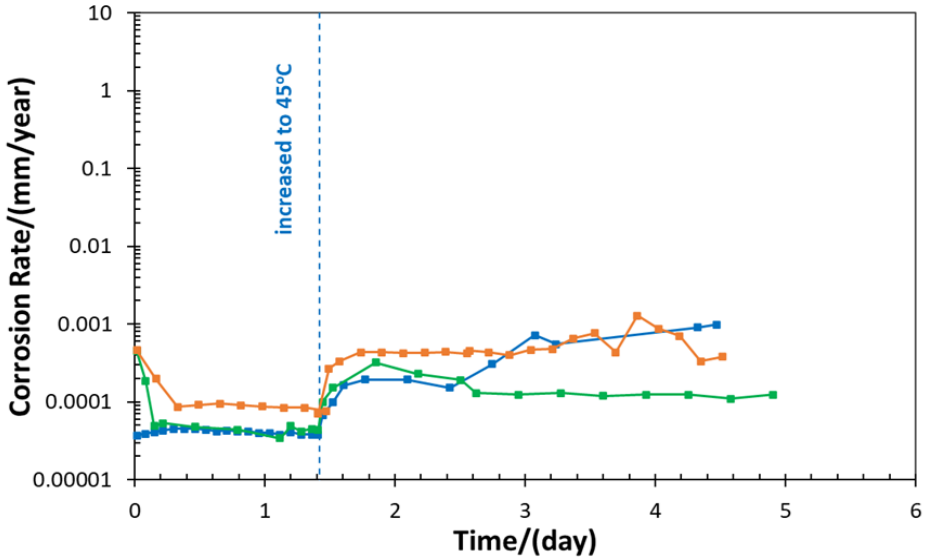

Figure 4. Batch inhibition persistency experiments (3 repeats) with commercial inhibitor with shorter contact time and increase in temperature (30°C to 45°C, 1000 rpm, pH 4.0, 1 wt.% NaCl).

Since this commercial batch CI showed excellent persistency throughout the laboratory testing period further investigations were warranted, particularly at elevated temperatures (60°C and 80°C). In all experiments at 60°C, an increase in the corrosion rate occurred after 3.5 days, which indicates a partial loss of inhibition. These experiments represent an interesting case study since it showed a measurable persistency period (followed by a relatively rapid loss of persistency) and is the focus of deeper analysis. Figure 5 shows five repeats for experiments at 60°C. In addition, in all experiments localized corrosion was observed after loss of CI persistency. This implies that this commercial batch CI, when employed for protection at 60°C with a 10 second contact time, exhibits a persistency window of approximately 3 days before partial failure that results in local area corrosion.

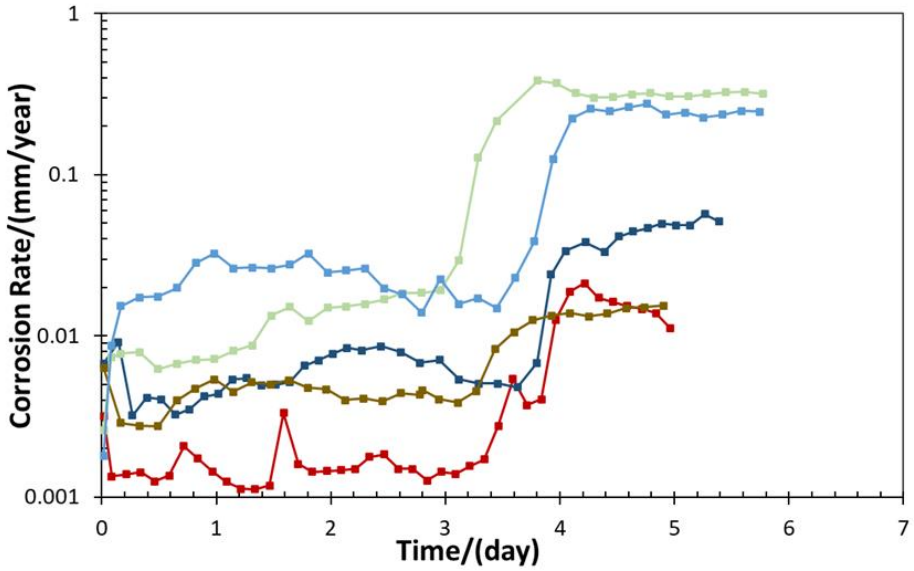

Figure 5: Different repeats for batch inhibition persistency experiments (5 repeats) with commercial inhibitor at 60°C (10s contact time, 1000 rpm, pH 4.45, 1 wt.% NaCl.)

Figure 6 shows the image of the RCE as retrieved and the profilometer surface analysis. The deepest depth of the pitting corrosion measured was 273 µm (the experiment represented in green line in Figure 5 was run for 9 days and pitting corrosion calculation was done for 6 days after inhibition which equals to 16.6 mm/year (Equation (2)). This means that the ratio of the localized corrosion rate to measured corrosion rate after the loss of persistency in Equation (3) is 55.3 which is considered as very high localized corrosion.[18] Even when compared to the uninhibited general corrosion rate under the same environmental conditions, which was measured at 8.2 ± 1.8 mm/year for 60°C, it seems the RCE specimen has undergone a harsh localized corrosion after loss of persistency.

$$CR\left(\frac{mm}{year}\right) = \frac{273\ \mu m}{6\ days} \times \frac{365\ days}{1\ year} \times \frac{1\ mm}{1000\ \mu m} = 16.6\frac{mm}{year} \quad (2)$$

$$\frac{localized\ corrosion\ rate}{measured\ corrosion\ rate} = \frac{16.6}{0.3} = 55.3 \quad (3)$$

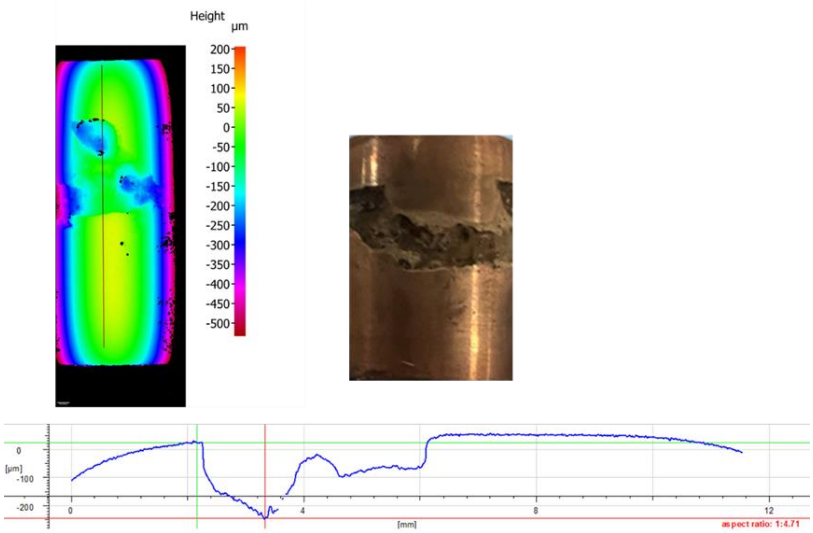

Figure 6: Profilometer analysis (left and bottom) with associated picture of the RCE with severe localized corrosion after loss of inhibition at 60°C.

To investigate the effects of temperature on this commercial batch CI, another set of experiments were conducted at 80°C. Figure 7 shows the results of two different repeats at this temperature. Results showed that although the inhibition efficiency is high (~99%), the inhibited corrosion rate was close to the acceptable corrosion rate (assumed to be 4 mil/year or 0.1 mm/year [19]).

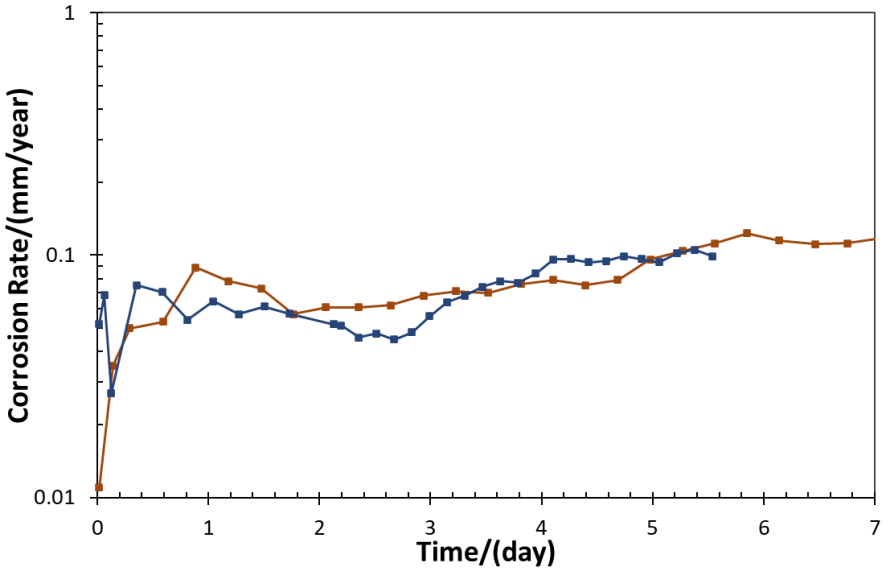

Figure 7. Batch inhibition persistency experiments (2 repeats) with commercial inhibitor at 80°C (10s contact time, 1000 rpm, pH 4.65, 1 wt.% NaCl).

Effect of presence of hydrocarbon

Previous studies have shown that both partitioning and oil wetting of the corrosion test specimen can affect the corrosion rate and the inhibitor behavior (efficiency & persistency).[20,21] As shown in Figure 8, the hypothesis is that aliphatic hydrocarbon molecules dispersed in the water phase can interact with inhibitor hydrocarbon tails to enhance the inhibitor performance and persistency time.

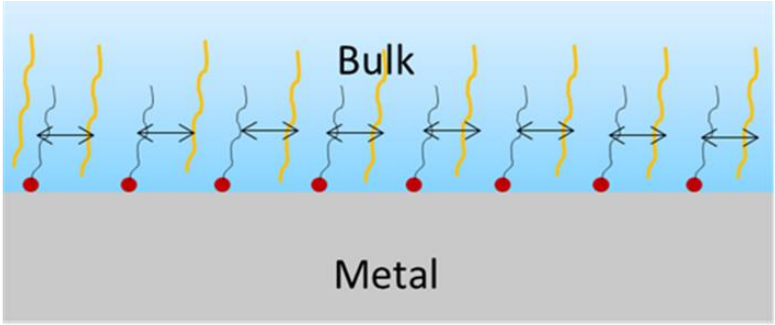

Figure 8: Interaction between inhibitor and oil molecules near the metal surface.

To investigate the impact of a hydrocarbon presence on the commercial batch corrosion inhibitor (CI), experiments were conducted involving the introduction of 20 mL of model oil on top of 1780 mL of brine (1wt.% NaCl). The experimental procedure entailed the initial addition of 1780 mL of brine into the glass cell, followed by the subsequent introduction of 20 mL of pre-sparged model oil into the system. The entire solution was continuously flushed with pre-sparged uninhibited brine at 60°C at a rate of 40 ml per minute. The continuous addition of fresh solution through the oil layer into the glass cell was observed to entrain and disperse oil droplets into the bulk solution. To counteract the dispersion of hydrocarbon molecules and the gradual loss of oil due to continuous dilution, model oil was replenished every 24 hours, ensuring the sustained presence of the oil phase until the conclusion of the test. Figure 9 shows

different repeats of the batch inhibition experiments with the presence of hydrocarbon molecules. Results showed that the presence of hydrocarbon and its subsequent dispersion into the brine phase enhanced the commercial CI efficiency and persistency as hypothesized. The loss of persistency observed at 60°C for about 3 days without oil was not observed in this experiment. In addition, no visual indication of localized corrosion was observed.

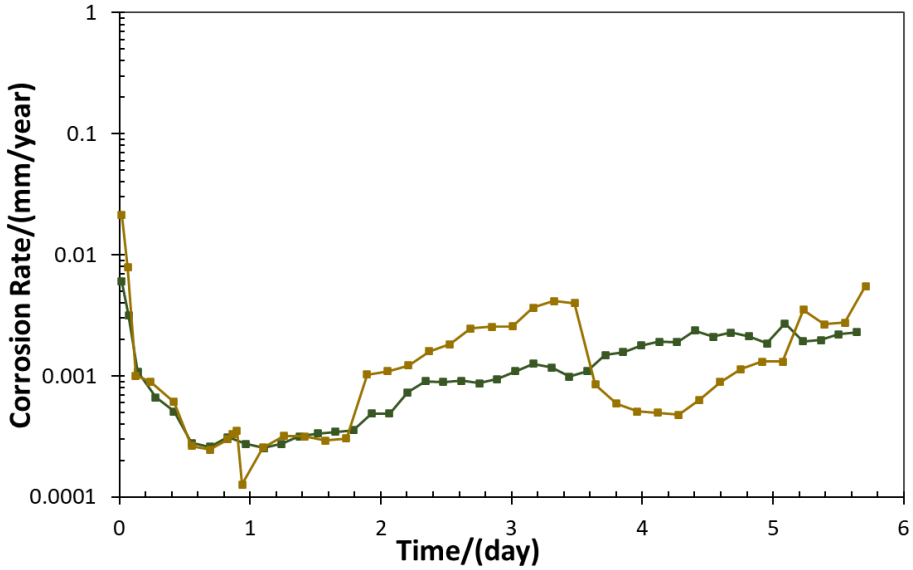

Figure 9: Two repeats of commercial batch CI experiments (2 repeats) with presence of model oil as the hydrocarbon phase (60°C, 10s contact time, 1000 rpm, pH 4.45, 1 wt.% NaCl)

Batch Inhibition experiments using model compound corrosion inhibitors

Experiments with a commercial CI limit the mechanistic understanding of the process involved in batch inhibition persistency since the CI composition is unknown. Therefore, the next step was to test single-molecule model compound corrosion inhibitors with known structure and composition in these tests as batch inhibitors, in similar experimental conditions as conducted with the commercial inhibitor. Since these are model compounds used as inhibitors, the focus of this part of the study was on the characteristics of the solvents or carriers used to deliver the inhibitor to the metal surface.

Batch inhibition experiments with BDA-C16 using different solvents

The first experiment was conducted with BDA-C16 and isopropanol as solvent, because of the higher solubility of BDA-16 (15 wt%) in isopropanol. BDA-C16 had also been previously tested as a continuous type CI and was shown to mitigate corrosion to 0.1 mm/yr at a concentration as low as 50 ppm_w.[22] This inhibitor was, however, not expected to be very persistent as it is considered to be a continuous type CI. Using the same experimental procedure as the first commercial inhibitor experiment, the specimen was dipped into the 15 wt.% BDA-C16 in isopropanol for 5 minutes contact time to provide the “excessive amount of time” for the batch treatment methodology. After conducting the inhibitor film formation procedure, the uninhibited brine was introduced to the glass cell and electrochemical measurements were conducted.

Figure 10 shows two repeats of this experiment with 15 wt.% BDA-C16 dissolved in isopropanol and their associated change in corrosion rate/inhibitor concentration with time. The results show that after introducing the brine to the glass cell, the residual inhibitor concentration dropped significantly showing the ability of inhibitor removal in this methodology. It can be observed that the corrosion rate started at

higher value than the baseline inhibited corrosion rate (measured at 0.1 mm/y [22]) and increased to uninhibited value (~4 mm/year) after 50 hours, showing no persistency.

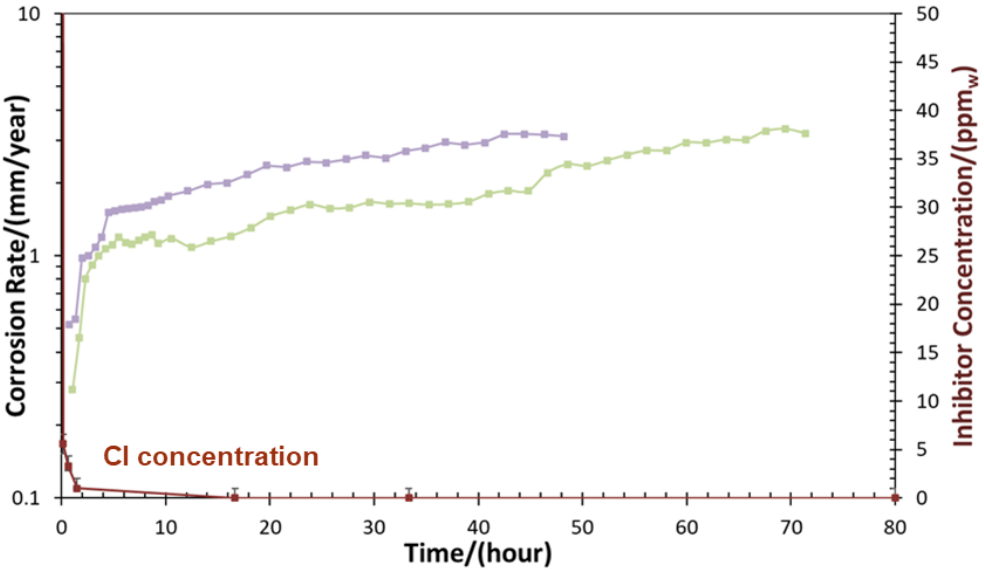

Figure 10: Batch inhibition persistency experiment with 15 wt.% BDA-C16 in isopropanol (30°C, 5 min contact time, 1000 rpm, pH 4.0, 1 wt.% NaCl).

Since the presence of a hydrocarbon (model oil) had a positive effect on the persistency of the commercial CI, the next step was to use it as the solvent or carrier for BDA-C16. The hypothesis behind these experiments, shown in Figure 8, was that the straight chain hydrocarbon molecules incorporate with the inhibitor adsorbed layer and enhance the persistency of the inhibitor. Thus, for the next step, the model oil was used as the solvent for BDA-C16. The specimen was dipped into an inhibitor solution with 7.5 wt.% BDA-C16 in model oil, which is the highest solubility of BDA-C16 in the model oil. Figure 11 shows the results for corrosion rate/inhibitor concentration versus time.

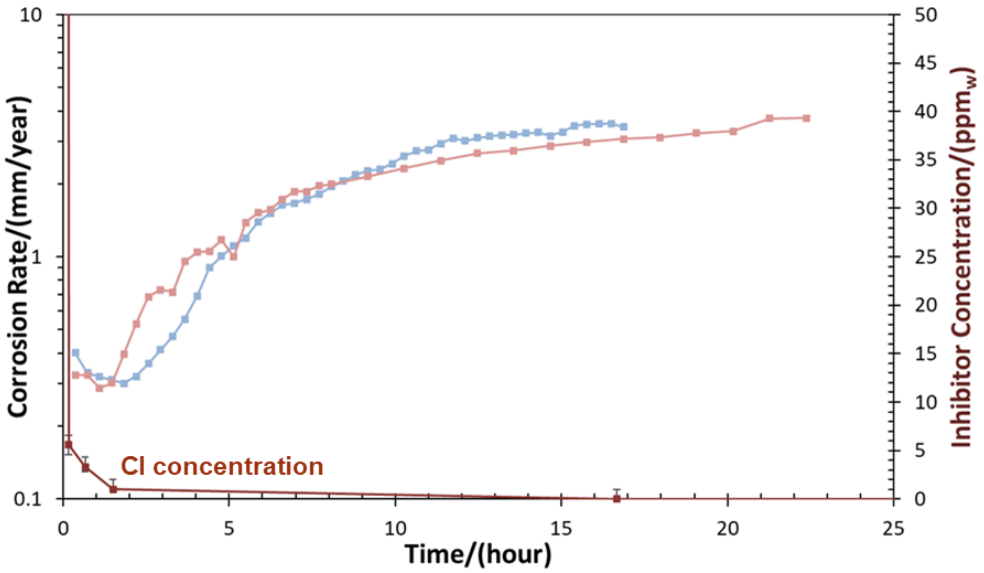

Figure 11: Batch inhibition persistency experiment with 7.5 wt.% BDA-C16 in model oil (30°C, 5 min contact time, 1000 rpm, pH 4.0, 1 wt.% NaCl).

Results show that, although the initial corrosion rate was again higher than the baseline inhibited corrosion rate for BDA-C16, the corrosion rate remained low for 2 hours and then gradually increased

over 15 hours to eventually reach the uninhibited value. This suggests that the presence of alkanes in the system seems to lead to an improved, yet short, persistency (which was not seen with using isopropanol). Therefore, incorporation of hydrocarbon into the CI adsorbed layer is hypothesized to cause a slight improvement in the persistency of this model inhibitor compound.

Batch inhibition experiments with PE-C14 using different solvents

Since the BDA-C16 did not show acceptable persistency in batch treatment, it was proposed that a phosphate ester model compound inhibitor (PE-C14) be used. PE-C14 previously showed high efficiency in continuous treatment and exhibited a lower water solubility as compared to BDA-C16.[22] The hypothesis was that PE-C14, if used with a viscous solvent such as alkylphenolethoxylate (AE), should provide both an excellent initial inhibition and delay the loss of persistency over time because of a combination of high efficiency and high solvent viscosity. However, PE-C14 has a very low solubility in AE. Therefore, another solvent that has high solubility for PE-C14 was needed in this "known" inhibitor package. Given the relatively high solubility of PE-C14 in 2-butoxyethanol (BE), it was postulated that an inhibitor package composed of PE-C14, AE, and BE would be more suitable for investigating the underlying mechanisms governing CI persistency during batch treatment. Figure 12 and Figure 13 show the molecular structures associated with this model compound inhibitor and the two solvents respectively.

Figure 12: Molecular structures of in-house synthesized tetradecyl phosphate ester (PE-C14) (73.5% monoester & 25.5% diester).

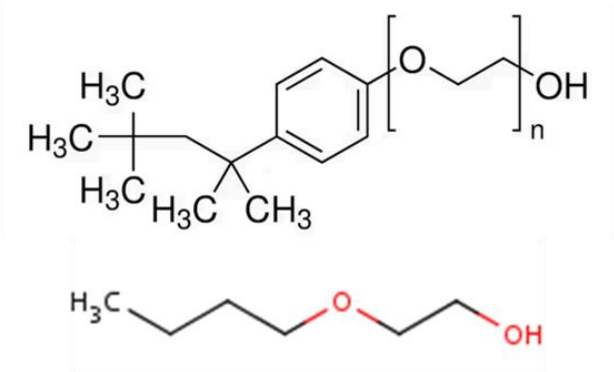

Figure 13: Molecular structure of the viscous alkylphenolethoxylate type solvent (top) and 2-butoxyethanol (bottom).

The influence of each component in the inhibitor package can be assessed, while using a 10 second contact time for each, by conducting batch inhibition persistency tests with different inhibitor packages (AE+BE+PE-C14, AE+BE, BE+PE-C14, AE only), as shown in (Figure 14). The short contact time of 10 seconds was used as PE-C14 was shown to have a high efficiency when tested previously as a continuous CI.[23] The concentration of 1.5 wt.% was selected because it represents the maximum solubility of PE-C14 in the solution containing AE and BE. Maintaining this concentration across all formulations allowed for a consistent basis of comparison when evaluating different solvents and carriers.

First, PE-C14 was dissolved in BE (1.5 wt.%) to investigate the persistency of PE-C14 in solvent with low viscosity but high solubility for PE-C14. These results (BE+PE-C14) show that although PE-C14 is highly soluble in BE, the inhibitor molecules desorbed from the surface as soon as the fresh uninhibited brine

was introduced into the glass cell. This was expected since BE is highly soluble in water and has a low viscosity.

Before using AE with PE-C14 and BE, experiments were necessary to examine the effects of AE only on CO_2 corrosion. These results show that AE has a slight inhibition effect on the corrosion rate, however the inhibition efficiency and persistency are negligible and can be ignored. For the next step, 1.5 wt.% PE-C14 was made with 18 mL AE and 3 mL BE. Results with this inhibitor package (AE+BE+PE-C14) suggest that PE-C14 can be used for further investigation in batch inhibition persistency study when it is dissolved in viscous solvent that increases the persistency.

To complete the study, the effect of both solvents together without inhibitor was tested (AE+BE). Although the mixture of viscous AE and BE without inhibitor showed some level of inhibition, inhibition efficiency and persistency were not as good as the full package.

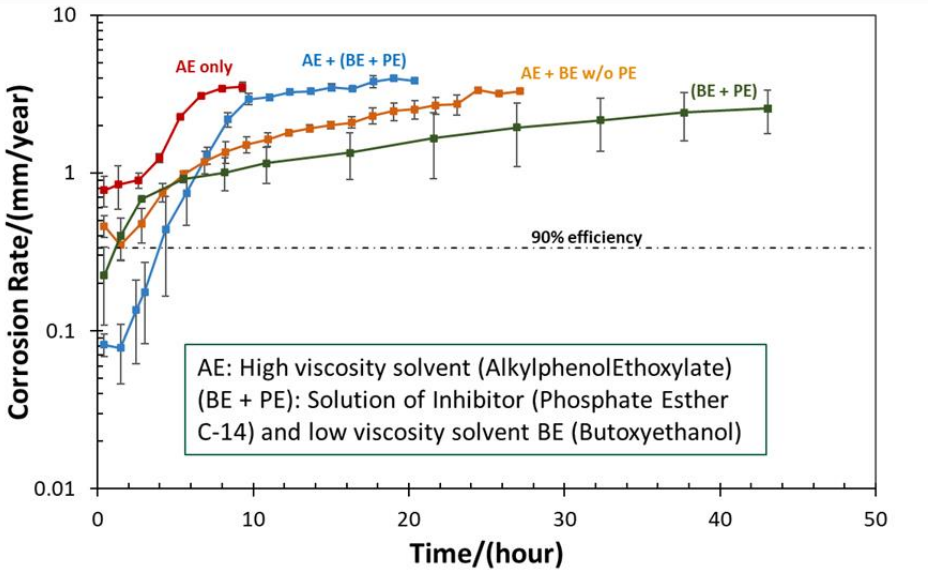

Figure 14: Batch inhibition with different CI packages and PE-C14 (30°C, 10s contact time, 1000 rpm, pH 4.00, 1 wt.% NaCl).

Table 3 shows a summary of these experimental results (CI efficiency and persistency) using the model compound inhibitor with two known solvents/carriers. Inhibitor efficiency was calculated using Equation (1).

Table 3
Summary of inhibition efficiency and persistency for 4 different packages.

Inhibitor package	Initial inhibition efficiency	Persistency
BE + PE	93.8 %	< 1 hour
AE (without PE)	87.5 %	N/A
AE + BE (without PE)	55.8 %	N/A
AE + PE + BE	97.6 %	4 hours

CONCLUSIONS

Commercial CI:

Although the commercial inhibitor had excellent efficiency and persistency at room temperature, it showed only 3 days persistency at 60°C. In addition, the following conclusions can be taken from these experiments:

- Continuous replenishment of the test fluids is one of the key parameters of the batch inhibition experiment in the laboratory as it ensures minimum residual of the inhibitor in the bulk similar to field conditions.
- All the observed failures of inhibition at 60°C and loss of persistency resulted in pitting corrosion of the metal surface.
- Presence of a model oil dispersed in the water phase enhanced the persistency of the inhibitor, which suggests that the incorporation of hydrocarbon molecules (either as the model oil or as a solvent in the CI package) with the CI film plays a key role in persistency.
- Without the presence of hydrocarbon, it can be speculated that the loss of persistency was associated with:
  - breakage of bonds between hydrocarbon (in inhibitor package) and CI molecules within the film,
  - desorption of CI molecules at the steel surface.

Model compound CI:

- BDA-C16 showed no acceptable persistency in batch treatment. However, using a hydrocarbon solvent (model oil) slightly increased CI persistency suggesting incorporation of hydrocarbon molecules with CI molecules on the specimen.

PE-C14 tested for batch inhibition showed little to no persistency in combination with butoxyethanol for solubility.

- The use of a high viscosity solvent as a carrier for PE-C14 in combination with BE enhanced CI persistency by diminishing the inhibitor dissolution rate from the specimen surface.

ACKNOWLEDGEMENTS

The author would like to thank the following companies for their financial support: Ansys, Baker Hughes, ChampionX LLC, Chevron Energy Technology, Coastal Chemical Co., ConocoPhillips, ExxonMobil, SLB, Occidental Oil Company, Pertamina, Saudi Aramco, Shell Global Solutions and TotalEnergies. Dr. David Young is thanked for synthesizing the corrosion inhibitor model compounds used in this research with much appreciation given for the technical support from Mr. Alexis Barxias and Mr. Cody Shafer.

REFERENCES

1. A. Kahyarian, B. Brown, S. Nesic, “Electrochemistry of CO_2 Corrosion of Mild Steel: Effect of CO_2 on Iron Dissolution Reaction,” *Corrosion Science* 129, (2017): pp. 146-151.

2. H. A. Craddock, S. Caird, H. Wilkinson, M. Guzzman, “A New Class of “Green” Corrosion Inhibitors: Development and Application,” *SPE Projects Facilities & Construction* 2, 4 (2007): pp. 1-8.

3. M. Lopez, J. Porcayo-Calderon, M. Casales-Diaz, I. Carrillo, J. Canto, L. M. Martinez de la Escalera, C. Cuevas-Arteaga, I. Regla, R. M. Melgoza-Aleman, L. Martinez-Gomez, “Internal Corrosion Solution for Gathering Production Gas Pipelines Involving Palm Oil Amide Based Corrosion Inhibitors,” *Int J Electrochem Sci* 10, 9 (2015): pp. 7166-7179.

4. P. Roberge, Corrosion Inhibitors. In: *Handbook of Corrosion Engineering*, 1st ed. (New York, NY: Mc-Graw Hill Education, 2000), pp. 833-862.

5. S. Papavinasam, *Corrosion Control in the Oil and Gas Industry*,1st ed. (Gulf Professional Publishing, 2014), p. IV.

6. J. Sonke, W.D. Grimes, “Guidelines for Corrosion Inhibitor Selection for Oil and Gas Production,” CORROSION/2017, paper no. 8842 (New Orleans, LA: NACE, 2017).

7. J. Yang, V. Jovancicevic, S. Mancuso, J. Mitchell, “High Performance Batch Treating Corrosion Inhibitor,” NACE-International Corrosion Conference Series, paper no. 07693 (Nashville, TN: NACE, 2007).

8. Y. J. Tan, B. Kinsella, S. Bailey, “An investigation of the Formation and Destruction of Corrosion Inhibitor Films Using Electrochemical Impedance Spectroscopy (EIS),” *Corrosion Science* 38, 9 (1996): pp. 1545-1561.

9. W. Mosher, T. Crosby, T. Lam, “Methodology for the Evaluation of Batch Corrosion Inhibitor Films and their Integrity,” *CORROSION*/2021, paper no. 16632 (Virtual, AMPP, 2021).

10. M. Pan, K. Shayar Bahadori, M. Eslami, B. Brown, M. Singer, “Development of Methodologies for Continuous and Batch Inhibitor Film Persistency Investigation in the Laboratory,” CORROSION/2022, paper no. 18056 (San Antonio, TX, AMPP 2022).

11. C.M. Menendez, J.M. Bojes, J. Lerbscher, “Obtaining Batch Corrosion Inhibitor Film Thickness Measurements Using an Optical Profiler,” *Corrosion* 67,3 (2011): pp. 035003-1-035003-

12. J.M. Bojes, M. Maddison, M. Girgis, H. Fear, “Batch Inhibitor Film Distribution Studies: Correlation of Field Data with Laboratory Results,” *CORROSION*/*2001*, paper no. 01028 (Houston, TX: NACE, 2001).

13. J.J. Wylde, M. Reid, A. Kirkpatrick, N. Obeyesekere, D. Glasgow, “When to Batch and When Not to Batch: An Overview of Integrity Management and Batch Corrosion Inhibitor Testing Methods and Application Strategies,” *SPE International Symposium on Oilfield Chemistry*, (2013), p. SPE-164080-MS.

14. R. De Marco, W. Durnie, A. Jefferson, B. Kinsella, A. Crawford, "Persistence of Carbon Dioxide Corrosion Inhibitors," *Corrosion* 58, 4 (2002): pp. 354-363.

15. M. Achour, J. Pierce, D. Daniels, “A Novel Laboratory Test Method to Determine Film Persistency of Batch Inhibitors used to Mitigate Top of the Line Corrosion,” CORROSION/2010, paper no. 10101, (Dallas, TX: NACE 2010).

16. M. Pan, M. Eslami, Y. Ding, Z. Belarbi, D. Young, M. Singer, “Methodology of Batch Inhibition Applied for Top and Bottom of the Line Corrosion Mitigation,” *CORROSION*/2021, paper no. 16751 (Virtual, AMPP 2021).

17. K. Shayar Bahadori, M. Singer, B. Brown, D. Young, “Investigation of CO_2 Corrosion Inhibitor Adsorption and Desorption Behavior Using Langmuir Isotherm Model and Effects of Iron Carbide on CI Persistency,” *CORROSION*/2023, paper no. 19451, (Denver, CO: AMPP 2023).

18. B. Brown, S. Nesic, “Aspects of Localized Corrosion in an H_2S / CO_2 Environment,” *CORROSION*/2012, paper no. 1559, (Salt Lake City, UT, NACE 2012).

19. A. Crossland, R. Woollam, J. Vera, J. Palmer, G. John, S. Turgoose, “Corrosion Inhibitor Efficiency Limits and Key Factors,” *CORROSION/2011*, paper no. 11062, (Houston, TX, NACE 2011).

20. N. Norooziasl, D. Young, B. Brown, and M. Singer, “Effect of Oil/Water Intermittent Wetting on CO_2 Corrosion in the Presence of Acridine and Myristic Acid,” *Corrosion* 80, 1 (2023): pp. 102–112.

21. Z. M. Wang and J. Zhang, “Corrosion of Multiphase Flow Pipelines: The Impact of Crude Oil,” *Corrosion Reviews* 34, 1–2 (2016): pp. 17–40.

22. N. Moradighadi, S. Lewis, J. D. Olivo, D. Young, B. Brown, S. Nesic, “Determining Critical Micelle Concentration of Organic Corrosion Inhibitors and its Effectiveness in Corrosion Mitigation,” *Corrosion Science* 77, 3 (2020): pp. 266-275.

23. Sh. Ren, Y. He, X. Wang, D. Young, M. Singer, M. Mohamed-Said, S. Camperos, “The Change of Corrosion Inhibition Behavior of Tetradecyl Phosphate Ester at Elevated Temperatures,” *CORROSION/2022*, paper no. 18053, (Houston, CO: AMPP2022).