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Corrosion Inhibition of Carbon Steel Pipeline Transporting Natural Gas at High Temperature

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ABSTRACT

Corrosion inhibition of carbon steel pipelines transporting natural gas containing CO₂ at high temperatures is very challenging to the oil and gas industry. The technical challenges to develop an effective corrosion inhibition program become even higher when the operating temperature reaches 145 degree Celsius or more. Other challenges include the changing of CO₂ corrosion mechanisms at high temperatures, the high technology demand of effective corrosion inhibition, thermal stabilities of chemical products, and the compatibility of corrosion inhibitors to scale control chemicals, and microbiologically influenced corrosion (MIC) concerns when the system temperature is reduced.

In this paper, the authors present the lab data of newly developed, robust chemical formulations with multiple functions. The chemical package demonstrated not only excellent corrosion inhibition performance in lab, but also enhanced reduction in microorganism concentrations after the formulation was aged held at high temperatures. Finally, the thermal stability of the product was evaluated.

Key words: HT CO₂ Corrosion, Corrosion inhibitor, CO₂-Corrosion, surfactant, corrosion inhibition, Partition

INTRODUCTION

CO₂-Corrosion mechanisms depend on many factors. One of the most important is the temperature. Many corrosion engineers and scientists have concluded in numerous publications that the CO₂-corrosion rate increases as the system temperature increases.¹⁻⁵ The corrosion rate reaches the maximum in the range 70 – 80°C and then begins to decline as the system temperature continues to increase. This is thought to be due to the formation of a protective carbonate scale that is produced more efficiently at higher temperatures.¹⁻⁵ These corrosion rates are referred to as general corrosion rates. There are many publications regarding CO₂ localized corrosion at high temperatures, e.g. temperature greater than 100 °C, but much fewer than those at low temperatures. It is obviously challenging to determine the precise corrosion mechanisms at high temperatures. It is also very challenging to characterize corrosion byproduct structures and properties formed *in situ* at high temperatures. Many novel corrosion inhibitors have been developed by the industry to help mitigate these challenges.⁶⁻⁸ In addition to the challenges, the high temperatures of tight natural gas reservoirs and deep water reservoirs set the bar even higher. This raises new opportunities for the chemical industry, which must design effective mitigation programs with corrosion inhibitors for high temperatures.⁹⁻¹¹ Additional chemical requirements, such as high thermal stability, low 'gunking', and injectability also need to be designed into these novel formulations. The natural question that follows would be, "Which type of corrosion inhibitor, oil soluble or water soluble, would have better chance to successfully treat a system at high temperatures?"

In this paper, the authors have made efforts to design oil soluble and water soluble corrosion inhibitors and new experimental approaches. These corrosion inhibitors were evaluated under high temperatures and standard test conditions. The results illustrated that these novel inhibitors were able to provide sufficient corrosion inhibition under the tested conditions. In addition, the chemicals maintained their ability to reduce bacterial counts after they have gone through high temperature aging.

EXPERIMENTAL PROCEDURE

Autoclave Corrosion Test

In this study, the performance of several corrosion inhibitors was evaluated with a set of electrochemical autoclaves. The setup of the autoclaves is shown in Figure 1. These 4 autoclaves are equipped with electrochemical techniques, such as linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), etc., allow the authors to evaluate the corrosion inhibition efficacy of the corrosion inhibitors with respect to four different variables in 4 different autoclaves at same time. These variables can be different temperatures, different chemicals, different treating rates, different water chemistries, etc. The net volume of these autoclaves is 382 ml. In this study, 250 ml testing fluid was used for all tests. Corrosion rates were measured and determined with the LPR technique. A constant B value 0.026 V/decade, which is calculated by anodic and cathodic Tafel slopes, was used in this study to compare the inhibitor performance. It was confirmed that B value was slightly lower with low dosage corrosion inhibitor. The scanning rate of LPR was 0.25 mV/s and the scanning range was 15 mV vs open circuit potential in cathodic and anodic directions. The reference and counter electrodes are made of corrosion resistant alloy UNS N10276, while the working electrode is made of the investigating material, UNS G10180. A thermocouple was used to control the testing temperature.



Figure 1: Electrochemical Autoclave Setup

After the long duration experiments (96 hours), the used electrodes were evaluated for pitting corrosion with a surface profilometer, as shown in Figure 2.

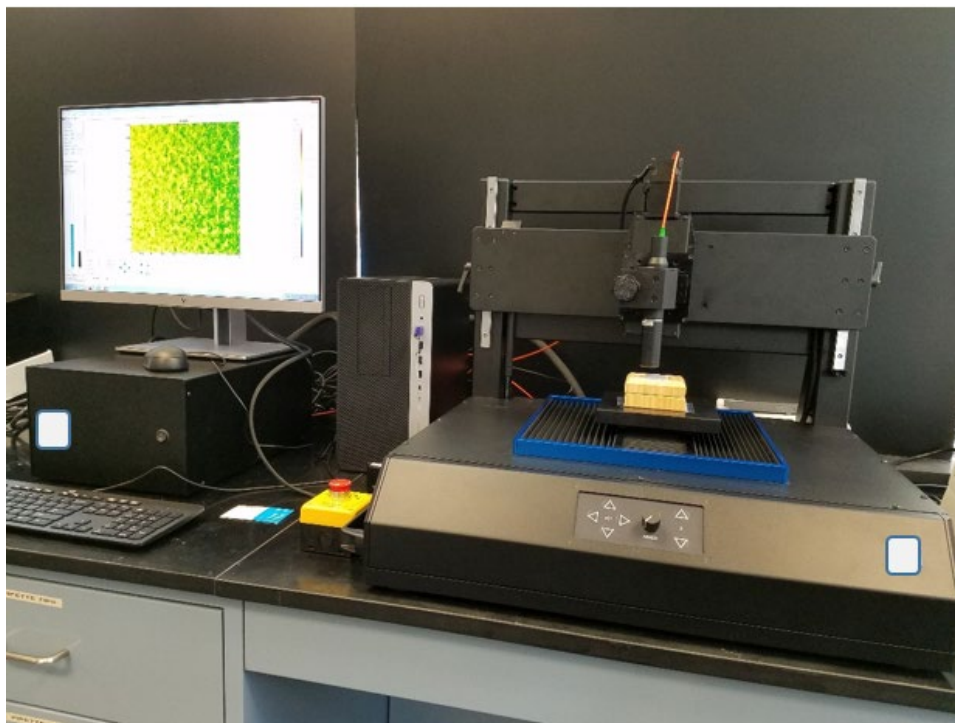


Figure 2: Surface Profilometer and Data Analysis Software

The corrosion testing electrodes were made of standard UNS G10180 steel. The electrodes were degreased in solvent while in an ultrasonic bath, and polished with 600 grit sandpaper directly

before each experiment started. The working electrodes were descaled in inhibited 10% HCl after each experiment. The working electrodes were analyzed for pitting corrosion with the surface profilometer, directly after the descaling of the electrodes. Otherwise, the cleaned electrodes were kept in a desiccator before they were scanned with the surface profilometer.

In a system producing natural gas at elevated temperatures (135°C), the free water is typically generated from condensation. Its brine chemistry is similar to that of a condensation water. The testing data presented in this paper used a brine with very low total dissolved solid (TDS), formula shown in Table 1. The synthetic brine used in this study was made with analytical grade salts based on the composition in Table 1. All testing fluids in this study were deoxygenated with CO₂ for more than one hour prior to the experiment.

Table 1
Brine Compositions in PPM

Chemical	Cl	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺
Concentration	200	5	10	100	30	10

For the partition tests, commercial chemical-free kerosene was used as the oil phase, and the synthetic brine was made from the above recipe. The water cut was determined for each specific experiment described later. A designated concentration of corrosion inhibitor was added to the mixture of the synthetic brine and kerosene. The mixture of the brine and kerosene either with or without corrosion inhibitor was vigorously shaken a total of 50 times, before it was deoxygenated with CO₂ for more than one hour. The system then allowed to rest at room temperature until the brine and kerosene phases had separated. To prevent oxygen ingress from happening, a low rate of CO₂ gas was continuously purged through the solution. After clear oil and water separation was observed, a known amount of brine and oil was transferred into the testing electrochemical autoclave without oxygen ingress. A pressure difference between the brine container and vacuumed autoclaves was maintained in order to help eliminate oxygen ingress during the transfer step.

Two categories of corrosion inhibitors were formulated and blended in the authors' laboratory. The three water soluble corrosion inhibitors were named as WCI-1, WCI-2 and WCI-3. The two oil soluble corrosion inhibitors were named as OCI-1, OCI-2. OCI-1 and were also modified to become OCI-1a and OCI-1b to improve the water dispersibility of the inhibitor molecules.

To test corrosion inhibitor performance used for continuous injection application, 1000 ppm corrosion inhibitor was injected into the testing autoclaves via a plastic capillary at 75°C, to avoid the brine boiling risk at the experimental temperature. The autoclaves were pressurized and maintained at 84 psi with CO₂ at 138°C.

Biocidal Test

In general, there will be little to no threat of microbiologically influenced corrosion (MIC) in such system at so high temperature. However, at points of intervention at the pipeline, such as pigging activity, inline inspection or even cutout at lower temperature section of the pipeline, the temperature is typically lower, MIC becomes a true threat. Therefore, the authors have evaluated the biocidal efficacy of corrosion inhibitors to reduce the bacteria count, using the corrosion inhibitors before and after aging at high temperature. The objective of these tests was to examine if these corrosion inhibitors maintain the property of reducing the bacteria count at lower temperature section of a pipeline, even if they were injected at the section of pipeline at high temperatures. Corrosion inhibitors with biocidal property activity would be useful in nonregulated

markets. If a corrosion inhibitor was used as a joint corrosion inhibitor and biocidal package, the authors acknowledge that such a package would have to be properly registered with the proper government's environmental protection agency.

Bacteria Culturing

A general heterotrophic bacteria culture, *Pseudomonas aeruginosa* (ATCC 15442^{1†}), was used to test biocidal efficacy of corrosion inhibitor products WCI-1 and OCI-1. The bacterium was cultured overnight at 30°C in Tryptic Soy Broth (TSB) prior to performing the kill study. The overnight culture of *Pseudomonas aeruginosa* was then added into a synthetic brine at dilution rate of 0.001X to create the biological testing brine.

The biological testing brine was generated by using a partition test procedure. 30% synthetic brine and 70% kerosene were mixed at room temperature. WCI-1 and OCI-1 at two concentrations of 1,000 and 2,000 ppm were studied. The partitioned brines were separated from the partitioned kerosene with serological pipettes. One half of partitioned brine aliquot was used for biocide kill study. The other one half of partitioned brine aliquot was aged at 138°C for 1 hour before being used for biocide kill study.

Biocide Kill Study

The biocide kill study was performed at contact times of 2 hours, 1 day, 4 days, and 13 days and at 30°C. A newly developed generation of the Adenosine Triphosphate (ATP) test kit from a supplier was used to extract ATP from samples and determine the biocidal efficacy of both corrosion inhibitor products with respect to that of the control.

RESULTS AND DISCUSSION

An effective corrosion inhibition program will contain the Right Chemical (corrosion inhibitor), Right application, Right dosage, and be applied at the Right time. This concept was introduced by the authors as the Four "Rs" in a previous publication.⁶ Obviously, the correct selection of corrosion inhibitor is essential to the success of the project. In this paper, we attempted to expand on the use of the Four Rs in with respect to how the correct selection of corrosion inhibitor should be made in terms of chemistry, testing methods, and processes.

One of the most important factors in selecting the right corrosion inhibitor for the system is its ability to mitigate all the potential threats under the conditions of the application. The current system under investigation posed the technical challenges of high temperature CO₂ corrosion, inhibitor transportation in dry gas, pitting corrosion, and elevated harmful bacterial populations.

To overcome the above mentioned challenges, the successful corrosion inhibitor should meet the following technical requirements:

- (1) It is a water soluble corrosion inhibitor or oil soluble corrosion inhibitor with high partition tendency into low TDS brine
- (2) It requires a meaningful methodology to determine the oil and water partition properties of these corrosion inhibitors,
- (3) It will successfully inhibit pitting at the system temperature

^{1†} Trade name – American Type Culture Collection, organism number 15442