

Assessment of Precorrosion Methods for Inhibitor Testing Under Sour Conditions

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ABSTRACT

Qualification of corrosion inhibitors for field deployment involves performance testing in the laboratory. Especially for sour service, a common set of test methods and associated protocols or guidelines used across the oil and gas industry, chemical companies and laboratories does, however, not exist. Development and testing of robust methodology were at the core of a Joint Industry Project (JIP) carried out at the Institute for Energy Technology (IFE). This contribution presents a selection of findings related to precorrosion, one of the aspects addressed in the JIP.

A series of benchmark experiments assessing the performance characteristics of various inhibitor chemistries mitigating corrosion of carbon steel under sweet (CO_2) and sour ($\text{CO}_2\text{:H}_2\text{S}$ 1:1) conditions at 25 °C and 60 °C without any precorrosion raised concerns related to uneven attack and risk for developing undesirable experimental artifacts, e.g. localized corrosion. Subsequent study of several precorrosion methods, including natural and electrochemically accelerated (anodic polarization) corrosion either in the absence or presence of H_2S provided valuable insight into advantages and shortcomings of each approach.

From a methodology viewpoint the precorrosion approach and the selected conditions make it possible to generate corroding carbon steel surface either free of protective corrosion products, covered by non-protective FeS , pre-load the test solution with suspended FeS particles etc., which could be useful for tuning the inhibitor tests to various scenarios relevant to sour corrosion.

Key words: sour corrosion, sour inhibition, precorrosion

INTRODUCTION

Development of new oil and gas fields is likely to involve sour reserves to an increasing degree. Sour production often brings about difficulties in terms of asset integrity, related particularly to corrosion mitigation. Employing corrosion resistant alloys implies a considerable escalation in investment costs. On this basis the use of carbon steel and CO₂/H₂S corrosion inhibition remains a highly desirable option¹.

The use of carbon steel and corrosion inhibitors is, on the other hand, not without its challenges in the presence of H₂S. Inhibitor dose rates required to avoid localized corrosion may get very high, yet even so effectiveness may prove to be insufficient under certain conditions². Several aspects known to create difficulties in sweet service, such as under-deposit corrosion (UDC) or top of line corrosion (TLC), become even more complex in sour service³⁻⁶. Particularly the presence of iron sulfide either suspended or within deposits is known to worsen the corrosion generally and make inhibition particularly challenging^{5, 6}.

Corrosion inhibitors for sour service are commonly being tested and qualified for field application according to companies' internally available protocols and judgement. A set of test methods and associated protocols or guidelines used across the oil and gas industry, chemical companies and laboratories does not exist, albeit, to the authors' knowledge, efforts are being made within both commercial companies¹ and AMPP. More detail is needed for judicious choice of tests, methodology and procedures in order for the results to be both straightforward to interpret and give a realistic picture of the expected outcome in the field.

The presence of H₂S adds several layers of complexity to inhibition and inhibitor testing. Whereas under sweet conditions the specific or selective affinity to the bare steel is a key characteristic determining the performance, with H₂S present experience from this project shows that a FeS layer will form rather quickly regardless of the presence or absence of an inhibitor (that is, whether or not an inhibitor test is for example performed with or without precorrosion while H₂S is present). In addition, under certain circumstances FeS particles may also form and may either remain suspended or will settle to the bottom. These aspects translate very well to field conditions in the sense that in sour service pipelines inhibitors should provide protection on steel surfaces covered with pre-existing FeS scale, be available even when suspended fine FeS is present, and, ideally, protect also under deposits containing FeS (and other solids). In other words, the inhibitor should ideally have good affinity for the bare steel as well as steel covered with a FeS scale (film).

A Joint Industry Project concerned with various aspects of inhibitor testing under sour conditions was conducted. A series of benchmark experiments carried out assessing the performance characteristics of various inhibitor chemistries mitigating corrosion of carbon steel under sweet (CO₂) and sour (CO₂:H₂S 1:1) conditions at 25 °C and 60 °C without any precorrosion raised concerns related to uneven attack and risk for developing undesirable experimental artifacts, e.g. localized corrosion. Subsequent study of several precorrosion methods provided valuable insight into advantages and shortcomings of each approach. This paper discusses these findings, exemplified by a selection of results, restricted to only the sour tests at 60 °C due to space constraints.

Evaluating the effects of certain types of precorrosion (or the lack thereof) on the outcome of inhibitor tests was one of the main aspects within the framework of this project. There are several reasons why precorrosion is both a necessity and at the same time a challenge when it comes to inhibitor testing under sour conditions.

It is well established and accepted in inhibitor testing under sweet conditions (i.e. without H₂S present) that allowing the exposed specimens to corrode naturally for some time before the inhibitor is injected is beneficial:

- the corrosion process initiates and encompasses the entire specimen surface rather uniformly; in this fashion the starting point for testing inhibitor performance is a uniformly “activated” surface
- sometimes surface oxides protect areas of a specimen, but spontaneous pre-corrosion is usually effective in reactivating; occasionally short anodic or cathodic polarization may be used to achieve the same without significant impact on the specimen, yet rendering the outcome of the test more reliable
- obtaining a uniformly corroding surface at the start of inhibitor tests is assumed to eliminate (or minimize) local attacks developing as experimental artifacts; this lends more confidence to using the results for assessment of the risk of localized corrosion.

It is very desirable to take advantage of these benefits also when testing under sour conditions. The presence of H₂S, however adds complexity and uncertainty to procedures that are otherwise robust under sweet conditions. Some of the particularities that pose challenges:

Rapid formation of FeS film/scale

The solubility of FeS is extremely low and precipitation occurs almost instantly even at lower temperatures. This is in stark contrast to e.g. FeCO₃ that can form in CO₂ corrosion, which allows sufficient time for pre-corrosion while maintaining bare steel under most conditions except very high temperatures. This implies that if pre-corrosion is carried out in the presence of H₂S, the steel surface will be covered by FeS and the inhibitor must also be efficient on a scale-covered surface. The affinity towards bare steel is, however, not less important, as the inhibitor should be able to protect at sites of damaged or missing FeS layer.

Rapidly forming FeS layers have repercussions also on the methodology: FeS films can be very protective even while they are still very thin. The corrosion rate will then be reduced over time, possibly obscuring the effect of the inhibitor. It is therefore often necessary to have baselines to compare the performance against on one hand, and to aid timing the inhibitor addition, on the other hand.

Formation of FeS particles by precipitation in the bulk solution

Especially with pre-corrosion in the absence of H₂S (but to some degree in any sour corrosion/inhibition experiment) FeS particles may precipitate in the bulk and produce a certain “loading” of fine solids. This can lead to “parasitic” consumption by adsorption of the inhibitor that will consequently reduce its availability to protect the steel, and, if settling on corroding steel surfaces, to under deposit corrosion that may cause severe localized attacks.

EXPERIMENTAL PROCEDURE

The experiments were performed at ambient pressure in jacketed glass cells equipped with airtight lids with a number of feedthroughs allowing purging with the desired gas (mixture) and mounting of specimens and accessories (see schematic illustration in Figure 1). All experiments were started with deaerated solutions, purged for at least two hours at the target temperature of 60 °C, maintained by an external bath. Gentle mixing was applied throughout the experiments by means of magnetic stirring. The solutions were continuously purged with a 1:1 volumetric mixture of CO₂ and H₂S. Test duration was typically ca. 1 week.

Three liters of a low-salinity brine, i.e. 1 g/L NaCl, 1 mM NaHCO₃ (both technical grade) was used in all experiments. The pH under the test conditions was typically between 5.0-5.4, in good agreement with the calculated value of 5.0.



Figure 1. Schematic illustration of the test cell used in the experiments

The specimens were machined from carbon steel (UNS K03014) and were either cylindrical (1 cm high, 1 cm diameter) or flat (1 cm wide, 2.5 cm long). All specimens were abraded using SiC paper (P400 and P1000), degreased with acetone, and rinsed with isopropanol before exposure. One cylindrical specimen for electrochemical measurements was present in each test. Two flat specimens (for mass loss and surface assessment) were also suspended in the cells in some of the experiments (omitted in tests with electrochemical preconditioning).

The commercial inhibitors to be used in the tests were selected to represent various typical inhibitor chemistries and they all had documented good inhibition effectiveness against CO₂ corrosion. For this paper results from only two classes are included for brevity:

- imidazoline (Inhibitor 1)
- polymeric ester amine (Inhibitor 2)

A fixed concentration of 200 ppm (formulated) inhibitor was used in all tests except the baseline experiments.

1 % (vol.) of hydrocarbon was added to each cell. A refined, low aromatic oil product (commercially available) with properties resembling a light hydrocarbon condensate was used in the tests.

Electrochemical measurements were performed using a potentiostat with a multiplexer in a three-electrode configuration. The cylindrical steel specimens served as working electrodes and the counter electrodes were made of titanium. The Ag/AgCl internal reference half-cells of long-shaft pH probes were used as reference electrodes. The corrosion rates were monitored electrochemically by linear polarization resistance (LPR) polarizing the specimen from -5 mV to $+5$ mV vs. the open circuit potential (E_{corr}), with a scan rate of 0.1 mV/s. The LPR data were adjusted subsequently to match the average mass loss corrosion rates. Potentiodynamic polarization sweeps (cathodic first, from the OCP to -300 mV vs. E_{corr} then anodic, from the OCP to $+150$ mV vs. E_{corr} , both with 0.1 mV/s scan rate) were also performed, usually towards the end of the exposure period. There were no LPR measurements performed during the time period for recording the polarization curves, which consequently appears as a gap in the LPR plots. The solution resistance for IR compensation was determined by means of electrochemical impedance spectroscopy (EIS).

After exposure the specimens were rinsed with isopropanol, dried, and weighed. The corrosion products were chemically removed from the cylinder specimen and selected flat specimens to determine the mass loss and assess the surface morphology.

Specimens were weighed on an analytical balance with a precision of 0.1 mg. This corresponds to a lower limit of measurable corrosion rate averaged over seven days of exposure of 0.0021 mm/y for the cylinder specimens and 0.0007 mm/y for the flat specimens.

Preconditioning of the specimens was performed in several ways:

- Natural precorrosion in the presence of H_2S and CO_2 at 60 °C
- Natural precorrosion in the presence of CO_2 only at 60 °C for 2 hours
- Natural precorrosion in the presence of only CO_2 at 60 °C for 24 hours
- Precorrosion by anodic polarization in the presence of CO_2 only
- Precorrosion by anodic polarization in the presence of H_2S

RESULTS AND DISCUSSION

No precorrosion

Several experiments, both in the presence and in the absence of H_2S have been performed in the initial phase of the project without precorroding the exposed steel specimens, i.e. the inhibitor was dosed before inserting the specimens, whereas the hydrocarbon was dosed right after. While the necessity of precorrosion has been generally accepted, these initial tests were used to assess whether negative implications (or any effect for that matter) of such an approach can be documented. The expectation was that results would reveal tendencies for developing experimental artifacts, particularly localized corrosion.

The full effect of corrosion inhibitors is often established in stages with duration from a few hours to even days. Without precorrosion, in most tests without H_2S (not presented in detail here) there was a visible initiation of corrosion attack (darkening of small areas) before the inhibitor's effect was established, especially at the higher temperature where the corrosion process is comparably faster. This suggest at least the possibility of introducing initiation of local attacks that otherwise would not have occurred, even though the overall corrosion inhibitor performance would be quite good based on the electrochemical and mass loss measurements. In the presence of H_2S , however, the steel coupons were darkened in most cases almost instantly, because the formation of a (dark) FeS layer is very fast. The FeS layer may obscure incipient local differences in the establishment of corrosion attack vs. establishment of inhibition; on the other hand the rapid establishment of FeS layers may in principle also contribute to a more even corrosion in the starting phase. Still, signs of uneven corrosion were observable even in sour tests without precorrosion (see examples in Figure 2).



Figure 2. Examples of visibly uneven corrosion in tests with no precorrosion. Inhibitor 1 (left) and Inhibitor 2 (right)