

Corrosion Inhibitor Screening and the Impact of Additives

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ABSTRACT

In order to successfully select an effective corrosion inhibitor, it is important to make a thorough assessment during a chemical qualification process. To efficiently make a selection, screening tests are generally performed prior to more complex field representative tests.

These screening tests can however misrepresent the performance of an inhibitor which would otherwise be deselected. One potential cause of this is the presence of minor, low concentration components in corrosion inhibitor formulations, commonly referred to as “additives”.

To illustrate this effect, a series of case scenarios and generic corrosion inhibitor tests will be presented, including standard low shear ambient tests, and also higher shear tests. These tests will demonstrate the impact additives can have on screening test results.

The examples show that relatively minor changes in formulated inhibitor chemistry can have a significant impact on the chemical performance and alter product rankings, and therefore affect the selection process.

The work will provide conclusions and recommendations on the best design of a screening program that reduces such test artefacts, and allows for easier interpretation of data. Along with comments that will be provided on the potential impacts this would have in the field.

Key Words: Corrosion Inhibitor, Screening, Additives, Laboratory, Testing

INTRODUCTION

Maintaining the integrity of oilfield equipment is essential to its safe operation and to maximize the efficiency of production. The integrity of oilfield equipment can rely on material selection and control of conditions, however, it is commonly maintained by the applications of chemical corrosion inhibitors (CI). Prior to use, these chemicals must be shown to perform as desired under the field conditions in question. To achieve this, chemicals are often evaluated using robust laboratory-based screening studies to identify potential candidates.

In order to be effective, an inhibitor must adsorb onto the metal surface and form a protective layer. Corrosion Inhibitors are typically amphiphilic with a charged hydrophilic head and long hydrophobic hydrocarbon chain tail. To form a film these hydrophilic heads need to adsorb to the metal surface. However, metal surfaces typically have a net positive charge in acidic environments which can disturb the formation of such layers. It is common for inhibitor formulations to contain species capable of forming a “bridge” between metal surface and inhibitor.¹ These “additives” in the formulation are typically sulfur containing molecules such as 2-mercaptoethanol, thioglycolic acid (TGA), and sodium thiosulfate.

The use of these sulfur containing additives in commercial corrosion inhibitor formulations has been the subject of numerous patent applications since the early 1990's. Naraghi and Prince² described the reaction products of mercaptocarboxylic acids and tertiary amines as economical corrosion inhibitors for a variety of environments in 1997. Following on from their claimed synergistic effect of thiosulfate on corrosion inhibitors¹, Phillips and Renwick patented thiosulfate ions as a corrosion inhibitor³. Subsequently 2-mercaptoethanol was claimed as an inhibitor of corrosion of metals by Ahn and Jovancicevic⁴. More recently thioglycolic acid salts of volatile amines have been proposed as condensing phase inhibitors for mitigation of top of line corrosion⁵.

Whereas the inherent toxicity of the mercapto derivatives requires the declaration of their addition on product safety data sheets even at low levels, the inorganic thiosulfate derivatives are essentially non-hazardous⁶. They were increasingly employed as synergist to enhance product performance in laboratory tests with no public record of their addition, often compensating for the relatively poor performance or low concentration of the underlying surfactant chemistry. Alongside this, operators began to suspect that thiosulfate was involved in the microbially induced corrosion of steel. The presence of thiosulfate and its utilization by the bacterial metabolism was considered a major risk factor⁷. Many operators precluded thiosulfate addition for oil system applications, instigating specific analyses of products tested to identify its presence⁸. The efficacy of the mercapto additives has also come under scrutiny claiming that thioglycolic acid based products exhibited poor localized corrosion performance under high shear conditions⁹.

More recently operators have reported significant safety concerns over the generation of H₂S from aqueous, mercapto containing corrosion inhibitors. Particularly in locations where summer ambient temperatures can exceed 50°C. This had led to greater scrutiny of formulation stability and the possible generation of toxic degradation products¹⁰, and the prohibition of TGA containing products. This has led to a renewed interest in alternatives with comparable efficacy and improved stability. Organic disulfides were proposed by Harrington et al¹¹, whereas an alternative synergistic chemistry was suggested by Liu et al¹²

It remains unclear whether these additives are only effective within the idealized laboratory environment or also assist the active inhibitor component in the field. Conversely some inhibitors without these additives, which have given reliable performance in the field, have been found to be ineffective when tested under laboratory conditions. Additionally, there is evidence to suggest that sulfur based compounds can have detrimental effects on stainless steels, which can cause complications in certain cases.¹ To further complicate matters there is data that these sulfur based additives commonly display an inhibition effect in the laboratory.

To investigate this further a range of corrosion inhibitor analogues were assessed with many of the common additives used in the industry; along with an assessment of a formulation with additive removed. One possible hypothesis for the discrepancy between field and laboratory tests of inhibitor formulations lacking these bridging species is that sulfides are likely to be present, even in nominally “sweet” fields. There for we also examine this by testing our additive free analogue with a range of concentrations of sulfide in solution.

⁽¹⁾ Metals & Alloys in the Unified Numbering System, 13th ed.(Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2017)

EXPERIMENTAL METHODS

The results reported here were mostly obtained by low-shear bubble cell tests (kettle tests) with corrosion rate (CR) analysis by linear polarization resistance (LPR), see Figure 1¹³⁻¹⁶. Tests were conducted at ambient pressure with 100% CO₂ sparging using UNS⁽¹⁾ G10180 carbon steel electrodes with a synthetic formation water (Table 1) and condensed water (3% NaCl). This provides markedly different solution pH's; the formation water is predicted to be pH 5.5 whereas the unbuffered condensed water is pH 4 when saturated with CO₂. Additional conditions are specified below.

The typical industry requirement for effective mitigation of corrosion is to achieve a corrosion rate in the field of ≤ 0.1 mm/y (e.g., 3 mm corrosion allowance for 30 year lifetime)¹⁷, and although these low-shear LPR bubble tests tend to be less severe than more field-representative ones, this value provides a useful benchmark.

Additionally moderate shear stress rotating cylinder electrode (RCE) (see Figure 1) tests were conducted to evaluate the effect that shear stress would have on CI performance when additives were introduced.

Table 1
Synthetic Brine Composition Used

Ion	Formation Water (mg/l)	3% NaCl Condensed Water (mg/l)
Na ⁺	29358	12179
Ca ²⁺	3145	0
Mg ²⁺	503	0
K ⁺	372	0
[SO ₄] ²⁻	11	0
[HCO ₃] ⁻	494	0

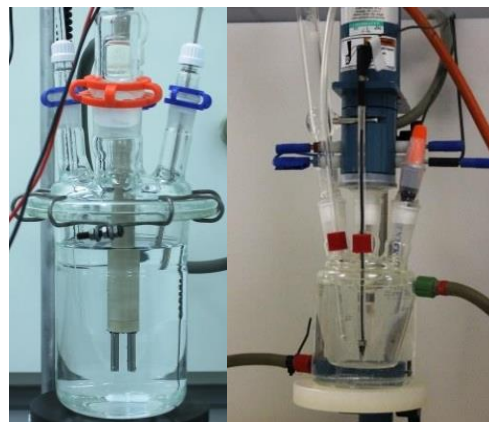


Figure 1: Images of LPR bubble cell and RCE equipment used

Generic Inhibitor Formulation

For this body of work a common quaternary ammonium salt was selected as the main active component, as shown in Figure 2.

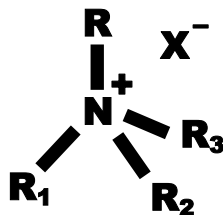


Figure 2: Quaternary ammonium salt structure

A range of formulations were prepared to investigate a variety of potential additive species. For these tests the same weight percentage of the active component was used, along with the same weight percentage of each of the solvents used. The sulfur additives were added at the same molar equivalent. A summary of the different corrosion inhibitor formulation is shown below:

⁽¹⁾ Metals & Alloys in the Unified Numbering System, 13th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2017)

- **Qu1:** The standard formulated quaternary ammonium salt, with 2-mercaptoethanol as the additive species.
- **Qu2:** Quaternary ammonium salt in the absence of any additive.
(These tests were also conducted in the presence of 0.1, 0.5, 1, or 5 mg/l sulfide, using Na₂S.9H₂O)
- **Qu3:** Quaternary ammonium salt with TGA as an additive
- **Qu4:** Quaternary ammonium salt formulated with sodium thiosulfate as an additive
- **Mer:** A formulation where quaternary ammonium salt replaced with 2-mercaptoethanol
- **“Additive Only”:** The additives were also assessed independently at a concentration equivalent to that present in 50 ppmv of the formulated corrosion inhibitor.

LPR Bubble Tests

In the low shear 100% brine LPR bubble tests, corrosion inhibitor is added to the brine phase and LPR corrosion rate measurements are made to determine the relative rate of corrosion rate reduction and the final corrosion rate achieved after 16 hours (h) in the presence of the inhibitor. Final corrosion rates are compared to a blank test with no corrosion inhibitor present. The method used is as follows:

Brine is sparged with carbon dioxide at test temperature in the cell until the measured oxygen level is less than 5 ppb, the pH of the brine is then measured. The UNS G10180 steel electrodes are then placed in the cell and connected to the potentiostat. LPR corrosion rate measurements are taken every 30 minutes. Corrosion inhibitor and/or other chemicals are added into the cell after the pre-corrosion stage. The results are a plot of the measured corrosion rate over time.

The test conditions are summarized as follows:

Brine:	Synthetic Formation Water (FW) or Condensed Water (CW) (see Table 1)
Temperature:	50°C
Pressure:	Ambient
pH:	FW: 5.5 CW: 4.0
Metallurgy:	UNS G10180
Gas:	100% CO ₂
Test Time:	18 h (2 h pre-corrosion, 16 h inhibitor dose)
Analysis:	LPR
Chemical:	Qu1, Qu2, Qu3, Qu4, Mer, additive only
Chemical Dose Rate:	10, 50 ppmv
Sulfide Concentration:	0, 0.1, 0.5, 1, 5 mg/l (added after pre-corrosion)

RCE LPR Tests

RCE testing is conducted under moderate to higher shear conditions to assess corrosion inhibitor performance under conditions more closely replicating pipe flow by rotating the electrode within the test fluid at a specified rotation speed to achieve the desired wall shear stress at the metal surface. Corrosion inhibitor is added to the brine phase and LPR corrosion rate measurements are made to determine the relative rate of corrosion rate reduction and the final corrosion rate achieved after 16 h in the presence of the inhibitor. Final corrosion rates are compared to a blank test with no corrosion inhibitor present. The method used is as follows:

Brine is sparged with carbon dioxide at test temperature in the cell until the measured oxygen level is less than 5 ppb, and the pH of the brine is then measured. The UNS G10180 steel working electrode, saturated calomel reference electrode and platinum auxiliary electrode are then placed in the test fluid and connected to the potentiostat. The working electrode is rotated at the desired rate, and LPR corrosion rate measurements are taken every 30 minutes. Corrosion inhibitor and/or other chemicals are added into the cell after the pre-corrosion stage. The results are a plot of the measured corrosion rate over time.

Test conditions were as the LPR bubble tests with a shear stress of 12 Pa applied using a rotating cylinder electrode to generate shear stress on the surface of the electrode.

RESULTS

Initial Quaternary Ammonium Salt Results

A range of 4 formulations were first examined at 10 ppmv in 100% brine bubble tests following 2 hours pre-corrosion as shown below:

We examined 4 formulations of our generic inhibitor:

1. Qu1 - Quaternary ammonium salt + 2-mercaptoethanol additive
2. Qu2 - Quaternary ammonium salt, no sulfur additive included
3. Qu3 - Quaternary ammonium salt + TGA additive
4. Qu4 - Quaternary ammonium salt + sodium thiosulfate additive

The results of these tests are displayed graphically in Figure 3, below.

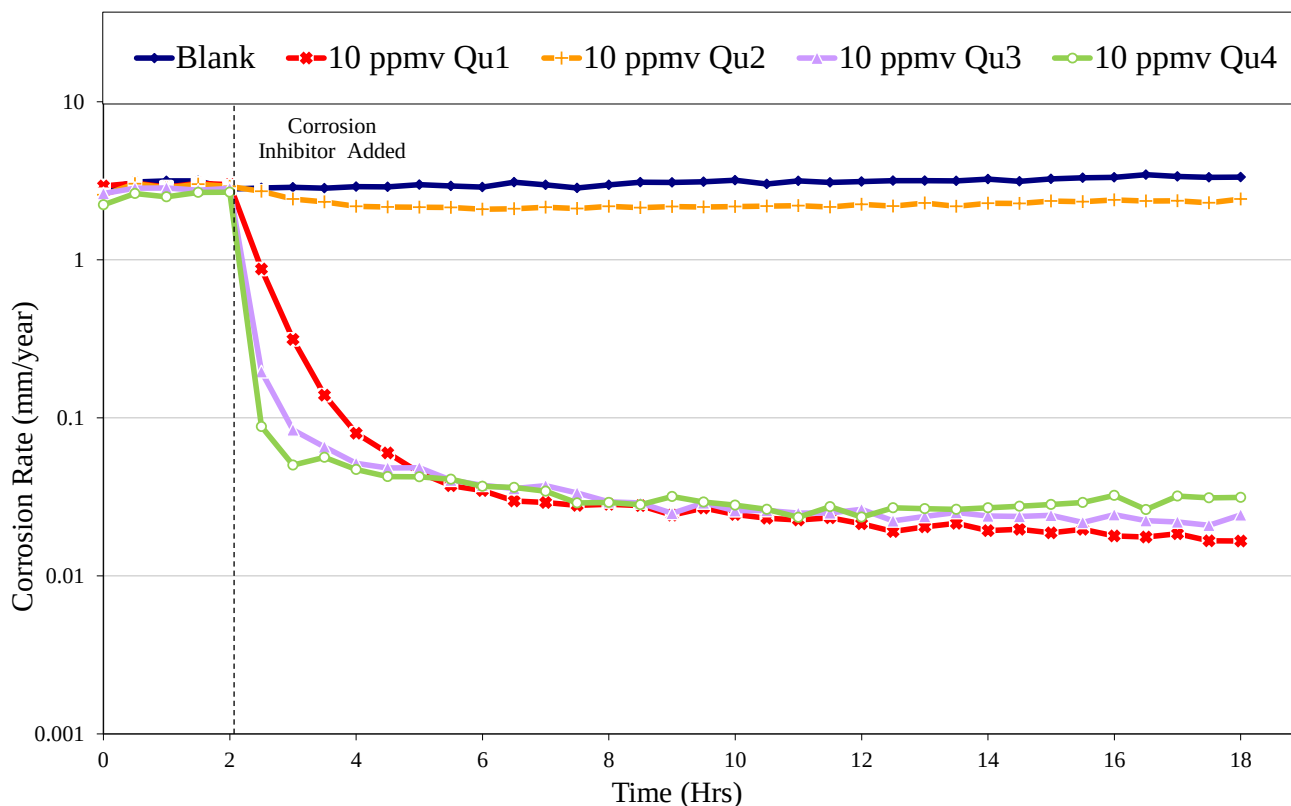


Figure 3: LPR Bubble Tests, 10 ppmv Generic Quaternary Ammonium Formulations, Synthetic Formation Water, 50°C, Ambient Pressure, 100% CO₂, 2 Electrode LPR (UNS G10180), Surface Area 2.375 cm², $\beta_a = \beta_c = 120$ mV/decade