

Localized Corrosion Studied via Interferometry using Modified Surfaces

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ABSTRACT

Localized corrosion in the oil industry is a dominant area of study that still remains elusive to researchers. Most infrastructure failures in the oil industry result from localized corrosion defects not general corrosion. Most corrosion testing relies on polished surfaces and relatively short tests resulting in detection of small features that may not be representative of field conditions. This paper looks at media blasted surfaces that are imaged at high resolution before and after corrosion testing. This method of corrosion testing shows that the modified surfaces contain populations of features that can be studied in aggregate to evaluate the effectiveness of corrosion inhibitors. This technique maximizes the utility of interferometry as a microscopy technique while also providing a surface that may be more representative of field conditions than a 600 grit polished surface.

Key words: localized corrosion, pitting, interferometry, media blasted surfaces, multi-region analysis

INTRODUCTION

Corrosion failures in the oil and gas industry are dominated by localized failures in carbon steel; however, the industry has yet to develop standards for localized corrosion specifically for low alloy carbon steels (CS) such as UNS⁽¹⁾ K03014 (API⁽²⁾ 5LX65 [X65]) or UNS G10180 (C1018).¹ The reasons for the lack of standardization are understandable as they are not trivial. The challenges are as follows: 1) CS pitting is more complex than pitting on stainless steels (SS) and can be impacted by corrosion byproducts and other forms of scales, and 2) surface finish of a test coupon or electrode has a significant impact on the three phases of pitting: initiation, propagation, and termination.

The first challenge of localized corrosion on CS is that the protective films are not as predictable as for the SS metallurgies. The predictability of passive films on SS is illustrated in the ASTM G46 standard.² The new lessons learned section in the 2021 version of G46 compares the complexities of passive film formation on SS and CS in more detail and cautions against using G46 in CS applications. The scales formed on CS are dependent on the concentration of iron(II) in solution and the speciation of iron(II) involves a complex set of parameters including temperature, acid gases, acid gas concentration, system pressure, brine composition, and many others. System temperature may be the most significant parameter, owing to the fact that iron(II) solubility in brine is highly temperature dependent. Corrosion tests conducted at or below 50°C may not show protective scales on CS while tests run at 90°C may have scales that are as protective as some forms of chemical inhibition.^{3,4}

The second challenge which compounds the complexity of localized corrosion on CS in a lab setting is the surface finish of the metal. Surface finish has a significant impact on the scales that are formed and the initiation and growth of localized features. Choosing a surface finish for a laboratory test that will demonstrate the same representative localized corrosion as the field can be difficult. Some standards suggest a 120 grit finish.⁵ It should be no surprise that different surface finishes have been shown to have different corrosion rates, but for CS it is not always so straightforward.⁶ Some researchers report that corrosion rate decreases with decreasing surface roughness.^{7,8} Yet others show that it depends on the environmental conditions because in some cases corrosion rate increases with decreasing surface roughness.⁹ These conflicting studies are a result of the change in protectiveness of iron scales on CS. Liu et. al. showed that calcium scales can also play an important role. They show that scaling brines and non-scaling brines respond differently to polished or media blasted surfaces.¹⁰ Uninhibited corrosion tests of media blasted surfaces in a scaling brine will show a steadily decreasing baseline due to the ease of protective scale formation on roughened surfaces. However, in a non-scaling, uninhibited brine the baseline corrosion rates for polished surfaces tend to increase steadily until they reach a steady state corrosion rate. Use of scale inhibitors in lab tests further add to this complexity.

A high grit polish (>600 grit) is commonly used because it provides the fewest pitfalls for testing various brines and it makes finding small features much easier especially without the use of expensive imaging equipment like an interferometer. In addition, some inhibitors will show better performance at lower minimum effective dosages so screening unknowns or new molecules is typically performed with polished electrodes. Polishing also seems to favor shorter tests. Most corrosion testing labs do not have the resources to run numerous long term (4 to 6 week) tests. To maximize throughput, tests are typically run for seven days. However, when the tests are short and the pitting criteria are low, this poses a challenge. Since the time is short the polished surface makes identification of small features more practical.

(1) Unified Numbering System for Metals and Alloys (UNS). UNS numbers are listed in Metals & Alloys in the Unified Numbering System, 10th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2004)

(2) American Petroleum Institute, 1220 L Street, Washington, DC 20005

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Ironically this may be self-defeating because it is known that a high polish delays the onset of crack initiation and pitting.¹¹

This leaves the testing laboratories and perhaps the operators in a quandary on how to assess chemical inhibitors for protection against pitting. Polishing allows for detection of small features in short tests, but then longer tests are needed for the delay of pit initiation imparted by polishing. Media blasting hardens the surface which increases the corrosion activity, and it can embed particles that can act to increase pitting from crevice corrosion. However, media blasting has a quality over polishing that plays to the strength of the interferometer. With polished surfaces, pits can be found easily using a microscope of sufficient power. What is the advantage of scanning a polished coupon to find a handful of pits? How many pits does it take to declare a chemical inhibitor a “poor performer”? In practice throwing away a lower cost chemical product that has three pits may be overly conservative and not advantageous to the operator. This paper discusses how one can use the strengths of the interferometer coupled with roughened surfaces to better assess the performance of a chemical inhibitor for localized corrosion mitigation.

An interferometer is an incredibly sensitive and accurate instrument capable of nanometer resolution in the Z dimension under certain conditions. Implementation of an interferometer is time consuming, and for polished surfaces it offers little value when it reports back a handful features. There is no conclusive evidence, historical study, or standard indicating that a single pit means a product will or will not perform well in the field. Often this handful of features could be associated with voids or inclusions inherent to the coupon metallurgy. The advantage of an interferometer is its ability to scan a high resolution image and process that image for thousands of features. This is where a marriage of interferometry and media blasting could provide more insight into pitting of CS with and without corrosion inhibitor. The study that follows looks at media blasted surfaces before and after corrosion testing and compares the population changes of the hundreds of features found in the pre-scans to gauge the pitting performance of two corrosion inhibitors and two scale and corrosion inhibitor combination products after exposure to corrosive conditions. The authors realize that this new study does not amount to a perfect method for pit evaluation. The goal is to try new techniques and continually advance this area of localized corrosion which contains considerable gaps in knowledge, especially where chemical inhibition is concerned.

EXPERIMENTAL PROCEDURE

High Speed Autoclave Testing (HSAT)

HSAT testing was similar to that previously described.¹² For this project two duplicate UNS G10180 (C1018 carbon steel) coupons (45 mm × 12 mm or 1.75" × 0.5") were included in each coupon holder for each autoclave test. The coupons were media blasted on all sides to a consistent finish using an aluminum oxide particle. After surface preparation, the coupons were pre-scanned with an interferometer. After scanning, the coupons were assembled on a rotating cage holder, and mounted on the center shaft of the autoclave. The coupons were installed with the numbers facing inward and upward. Since the rotation of the motor is counter clockwise this means that the right side of the coupon was the leading edge when the numbers are shown facing the viewer and at the top. For photos and profiling purposes the numbers were always on the left even when showing the back of the coupon. When the numbers are facing the reader the top is the leading edge. When showing the back of the coupon the bottom is the leading edge. After holder installation the autoclave was then sealed and pressure pumped from vacuum to 50 psi N₂ a total of three times to remove all oxygen from the test vessel. After oxygen removal, the test vessel was pressurized with N₂ to 345 kPa (50 psi) for half an hour to perform a leak test.

The test brine was purged with CO₂ for ~1 hour before it was anaerobically transferred to the autoclave vessel by putting the vessel under vacuum and loading the liquids from specially designed loading

vessels. The desired concentration of chemical was injected into the fluid stream during the fluid transfer process using a chemical injection port attached to the liquid transfer line. Upon completion of the fluid transfer process, the autoclaves were sealed and heating and rotation were started.

The test vessel was charged with 276 kPa (40 psi) CO₂ at room temperature and temperature was allowed to increase to 124°C (200°F), CO₂ was topped to 552 kPa (80 psi) when at 124°C (200°F), if it was required. This pressure was held for ~1 hour to allow the test fluids to become saturated with CO₂.

After 168 hours, the autoclave was cooled and safely depressurized; the coupons were retrieved from the coupon holder and were cleaned using the cleaning procedure shown below

- Solvent wash (water, IPA, and acetone)
- Weight measurement
- Clark's solution wash (2 minutes)
- Weight measurement
- Solvent wash (Water, IPA, and acetone)
- Final weight measurement

Weight loss calculations (following the procedure listed in ASTM G1-90) were then performed to determine the corrosion rate.¹³

The HSAT test conditions and brine composition are shown in Table 1 and Table 2, respectively. The two corrosion inhibitors are identified as CI-A and CI-B and the two combination scale and corrosion inhibitors are identified as CMB-A and CMB-B.

Table 1: HSAT test conditions

Parameters	Condition
Temperature, °C (°F)	124 (200)
Coupon material	UNS G10180 (1018 carbon steel)
CO ₂ partial pressure, kPa (psi)	552 (80)
Rotational speed	100 rpm
Brine/Oil ratio	70:30
Test duration (hours)	168
Chemical tested	CI-A, CI-B, CMB-A, CMB-B
Inhibitor dosage (ppm)	200 (400 for CMB-B)

Table 2: Synthetic brine composition for this study

Component	Concentration (mg/L)
Chloride	140,000
Bicarbonate	548
Sodium	56,630
Calcium	4,533
Magnesium	601
Potassium	989
Strontium	389
Barium	27
Acetate	1,154
Sulfate	184
Bicarbonate	548

Interferometry

Interferometry was performed with a Bruker Contour GT⁽³⁾ optical profiler equipped with an adjustable objective and automated stage. An interferometer is an optical microscope equipped with a parallel mirror interferometer below the objective lens (see Figure 1). A monochromatic light beam is split at a beam splitter with half of the light reaching the sample while the other half reflects between the mirrors. The light will recombine and interfere on its way to the charge-coupled device (CCD) camera. The interference is used to determine when a point on the sample is in exact focus, since the instrument is adjusted to give maximum constructive interference at best focus. By scanning the objective lens towards the surface, the height of all pixels in the image can be determined with high precision, provided enough light is reflected from the sample back into the lens. This instrument has a depth resolution of 3 nm under the right conditions and a lateral resolution based on coupon size. The lateral resolution is generally limited by the size of the file that is collected. For 1" × 2" coupons the highest practical resolution is 3.7 μm in both the x and y dimensions. For this study a resolution of 2.0 μm × 2.0 μm was used.

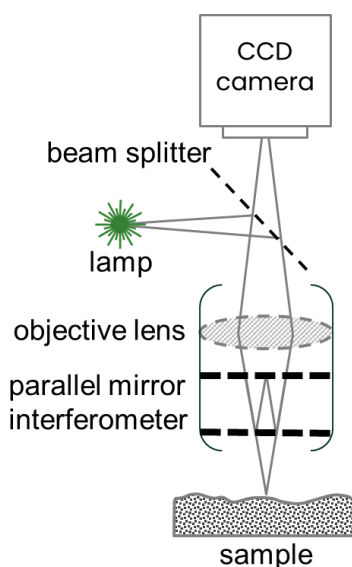


Figure 1: Schematic of an interferometer

After the interferometer scans were collected they were evaluated for missing data. If insufficient data were present in the images they were rescanned. If the data in the image were sufficient the images were then post-processed. Post-processing was performed with the Bruker Vision64⁽⁴⁾ software and involved the following:

1. Tilt and rotation correction to level the x, y, z plane and align the coupon edges for cropping
2. Median smoothing using a 3x3 median filter to remove shot noise common to CCD cameras
3. Data restoration using the standard method optimized for high quality
4. Cropping the image to remove exposed coupon edges to allow for Gaussian smoothing
5. Finally Gaussian smoothing using a short wavelength pass, robust, 2nd order Gaussian filter the following parameters: a) Long wavelength cutoff of 1.0 mm, b) CutoffX/CutoffY of 1, and c) Tolerance % of 0.001

⁽³⁾ Trade name

⁽⁴⁾ Trade name

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