Localized Corrosion of Mild Steel in Marginally Sour Environments

Saba Navabzadeh Esmaeely,‡ Wei Zhang,* Bruce Brown,* Marc Singer,* and Srdjan Nešić*

ABSTRACT

Localized corrosion has been a challenge for the integrity of mild steel pipelines, specifically at operating conditions where a trace amount of H$_2$S is present alongside CO$_2$ at lower temperatures. The presence of H$_2$S will lead to the formation of a protective iron sulfide layer that will decrease the general corrosion rate; however, a trace amount of H$_2$S may only form a partially protective mackinawite layer that could result in localized corrosion. In the current study, mild steel specimens (API 5L X65) were exposed to a 1 wt% NaCl solution sparged at 0.096 MPa pCO$_2$ and 15×10$^{-6}$ MPa or less pH$_2$S (≤150 ppm H$_2$S/CO$_2$). At pH 5.0 and 30°C the bulk solution was undersaturated with respect to iron sulfide—mackinawite and iron carbonate. At these marginally sour conditions, a H$_2$S/CO$_2$ threshold of approximately 100 ppm was deduced, below which localized corrosion happened. No localized corrosion occurred for the same environmental conditions when H$_2$S/CO$_2$ ratio was above 100 ppm or when there was no H$_2$S present.

KEY WORDS: carbides, carbon dioxide, hydrogen sulfide, localized corrosion, marginally sour

INTRODUCTION

Localized corrosion presents a threat to the integrity of mild steel pipelines and equipment in the oil and gas industry, given that it often proceeds at a much faster rate than uniform corrosion at the same conditions. It frequently results in failure, when the penetration depth exceeds far beyond the built-in corrosion allowance, which is based on the predicted uniform corrosion rates. The lack of ability to predict localized corrosion and to detect it by using conventional corrosion monitoring methods makes a difficult situation even worse.

Because the presence of H$_2$S in upstream oil and gas pipelines has been associated with an increased risk of localized corrosion,$^1$ a significant research effort has been focused on understanding H$_2$S corrosion mechanisms. Mild steel corrosion in such environments has been investigated since the 1940s, and was mostly concentrated on uniform corrosion.$^2$–$^{19}$ Rather few studies available in the open literature have addressed localized corrosion in H$_2$S-containing environments. There, most of the effort was on aqueous solutions that contain moderate to high amounts of H$_2$S (pH$_2$S = 0.01 MPa to 0.5 MPa) with temperatures ranging from 50°C to 150°C.$^{20}$–$^{24}$

There are two postulated mechanisms of localized corrosion in H$_2$S environments: the first one associated with the presence of elemental sulfur$^{25}$–$^{28}$ and the second one related to formation of conductive iron sulfides, such as pyrite and pyrrhotite, in the corrosion product layer.$^{29}$–$^{34}$ Both of these mechanisms result in galvanic corrosion and are typical for conditions with higher H$_2$S partial pressures and higher temperatures, such as those listed above. The presence of chloride was also listed as a risk factor for localized corrosion in H$_2$S-containing environments.$^{35}$ One explanation is that chloride impact is via changing the electrolyte conductivity and iron sulfide solubility, which are directly linked to the two abovementioned mechanisms.$^{36}$


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In the oil and gas industry, one frequently encounters conditions with lower temperatures and only trace amounts of H₂S (in the ppm range), which are also referred to as “marginally sour” conditions. One example is sweet wells which become marginally sour over the lifetime of production, resulting from microbiological (sulfate-reducing bacteria) activity in the reservoir. Under these marginally sour conditions, CO₂ is the main cause of corrosion and it has been suggested that trace amounts of H₂S lead to formation of a thin iron sulfide corrosion product layer, which has protective properties. Therefore, uniform corrosion rates of mild steel in marginally sour conditions were found to be lower than those seen under the same conditions without H₂S. An early example was given by Lee, where with only 3 ppm H₂S/CO₂ (at atmospheric pressure) the sweet corrosion rate was halved, while at 15 ppm and higher the corrosion rate was almost an order of magnitude lower compared to conditions where there was no H₂S.

Despite this apparently beneficial effect of a trace amount of H₂S on uniform corrosion of mild steel, there are some indications that such conditions might lead to a serious risk of localized attack. In a recent study, focused on top-of-the-line corrosion in sour environments, Yaakob, et al., reported localized corrosion at 15 ppm and 30 ppm H₂S, at room temperature and 1 MPa CO₂ partial pressure. In the same study localized corrosion was not observed at 80 ppm and 150 ppm H₂S. This seems to suggest that there may be a threshold concentration of H₂S below which localized corrosion occurs in marginally sour environments.

It is therefore of importance to investigate whether such a threshold exists. In an effort to prove this, the experiments described below were conducted with trace amounts of H₂S at low temperature (30°C). The experiments were conducted in a small scale glass cell at atmospheric pressure.

**EXPERIMENTAL METHOD**

Experiments were conducted in a conventional three-electrode glass cell with the experimental conditions summarized in Table 1. In this setup, the cylindrical cell was filled with 2 L of deionized (DI) water and 20.2 g of sodium chloride (NaCl) to obtain a 1.0 wt% NaCl electrolyte. The temperature was set to room temperature (30°C). Electrochemical measurements were conducted using a three-electrode setup with a platinum mesh plate serving as the working electrode (WE), a saturated silver/silver chloride (Ag/AgCl) reference electrode (RE) connected via a Luggin capillary, and a platinum counter electrode (CE). The H₂S gas concentration at the inlet was adjusted using gas rotameters and the accuracy was confirmed by taking a gas sample using a pump with colorimetric H₂S detector tubes. The gas outlet was scrubbed through a 1 M sodium hydroxide solution (NaOH) and a dry carbon scrubber to capture H₂S.

In order to ensure that the solution was deoxygenated, it was purged with CO₂ gas for at least 2 h prior to adding H₂S gas at the desired concentration. The solution pH was set to pH 5.0 by adding a deoxygenated 1 M sodium hydroxide (NaOH) solution. The electrolyte was stirred at 300 rpm with a 0.5 in (1.27 cm) stir bar to ensure mixing.

In addition to the cylindrical WE, flat square specimens, with a surface area of 3.4 cm² and made from the same material, were suspended in the solution for the purpose of measuring weight loss and performing surface analysis. Prior to immersion all specimens were sequentially polished with silicon carbide sandpaper from 150 grit to 600 grit, rinsed with DI water, cleaned with isopropanol in an ultrasonic bath, and air dried and weighed.

The corrosion process was monitored by recording the open-circuit potential (OCP), and by performing linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) measurements using a Gamry Reference 600 potentiostat. The polarization resistance (Rp) was obtained by polarizing the WE, sweeping the potential from 5 mV to 150 mV at a scan rate of 0.125 mV/s. The B value of 23 mV was used in all cases to calculate the LPR corrosion rate. The Rp was corrected for ohmic drop using the solution resistance (Rs) measured by EIS at high frequencies (ca. 5 kHz).

Surface and compositional analyses were performed using scanning electron microscopy (SEM) and x-ray diffraction (XRD), respectively. XRD analyses were executed through a CuKα source (λ = 1.5405 Å = 0.154 nm, 40 kV and 44 mA), scanning from 10 to 80° 2θ.

### Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
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<td>Total pressure</td>
<td>0.1 MPa</td>
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<tr>
<td>Temperature</td>
<td>30°C</td>
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<tr>
<td>Solution</td>
<td>1 wt% NaCl</td>
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<tr>
<td>Flow condition</td>
<td>Agitated, 300 rpm 0.5 in (1.27 cm) stir bar</td>
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<tr>
<td>Material</td>
<td>API 5L X65 steel</td>
</tr>
<tr>
<td>Corrosion measurement methods</td>
<td>LPR, EIS, and weight loss</td>
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<td>pCO₂</td>
<td>0.096 MPa</td>
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<tr>
<td>pH₂S in the gas phase</td>
<td>0 4 × 10⁻⁶ MPa (40 ppm) 9 × 10⁻⁶ MPa (90 ppm) 15 × 10⁻⁶ MPa (150 ppm)</td>
</tr>
<tr>
<td>pH</td>
<td>5.0±0.1</td>
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</table>

### Table 2

<table>
<thead>
<tr>
<th>API 5L X65 Elemental Analysis (wt%)</th>
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<td>C</td>
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<tr>
<td>-----</td>
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<tr>
<td>0.13</td>
</tr>
</tbody>
</table>

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1. Trade name.
to 70 20 at a scan rate of 1° per min. An Alicona Infi-
teFocus’ profilometer microscope was utilized to
measure the pit depth after the corrosion product layer
was chemically removed. The Fe²⁺ concentrations were
measured by ultraviolet-visible (UV-vis)
spectrophotometry.

RESULTS

For each of the H₂S concentrations, the experi-
ments were repeated at least three times except for the
experiment with 150 ppm H₂S that was conducted
twice. The uniform corrosion rates and the measured
OCP are shown in Figure 1 as a function of time. The
points are averages across the different repeats. The
error bars denote the maximum and the minimum
deviation from the average value.

The measured OCP (Figure 1[a]) of each specimen
shows a potential increase between 30 mV and 50 mV.
This could be as a result of two possible mechanisms,
an increase in the cathodic reaction rate or a decrease in
the anodic reaction rate.

In the absence of H₂S, the CO₂ LPR corrosion rate
increased over time (Figure 1[b]). This was a result of the
iron carbide, the part of the steel structure that is left
on the steel surface as it does not corrode. It is well
known that iron carbide is conductive and therefore
this porous layer increases the cathodic surface area,
and as a result of a galvanic effect it leads to an
increase in the corrosion current/rate.⁴²⁻⁴⁵ This was
reflected in the measured Rp, however, the magni-
tude of the corrosion rate increase is overestimated
there, as the LPR method cannot properly account for
different cathodic and anodic surface areas. The in-
crease in the cathodic reaction rate also explains the
positive shift in the specimen OCP shown in Figure 1(a).

For the two conditions at 40 ppm and 90 ppm H₂S,
the LPR corrosion rate (Figure 1[b]) started out lower than
in the absence of H₂S, resulting from formation of a
protective iron sulfide—mackinawite layer. The corrosion
rate decreased further during the first day of exposure
and then increased until the end of the experiment. One
would be tempted to ascribe this increase to iron car-
bide layer formation, however, most of the surface was
covered by a significantly thin layer, possibly made of a
mixture of mackinawite and iron carbide, which could not
produce any significant galvanic current. Another
possibility is non-uniform attack that initiated and de-
veloped over time. As LPR records the total current that
is averaged across the surface area of the specimen, any
failure of the protective mackinawite layer and localized
attack would present itself as an apparent increase in the
LPR corrosion rate. Without proper surface analysis
this assumption cannot be confirmed.

For the experiment conducted with 150 ppm
H₂S, the LPR corrosion rate decreased upon exposure
and stayed low over the course of the experiment. This
could be an indication of a more protective mackinawite
layer which formed at this higher H₂S concentration.
The lower LPR corrosion rates seen in the presence
of H₂S are the result of a retardation of the anodic
reaction that resulted in a positive shift on the OCP
seen in Figure 1(a).

Figure 2 shows the changes in bulk solution
properties over the course of the experiments. Figure 2(a)
shows the pH variation; in order to keep the
bulk pH value relatively stable, diluted deoxygenated HCl
was occasionally injected into the experimental cell.

Figures 2(b) and (c) show calculated saturation values
with respect to iron carbonate⁴⁶ (Equation [1]) and
mackinawite⁴⁷ (Equation [2]), respectively.

\[
S_{\text{FeCO}_3} = \frac{C_{\text{Fe}^{2+}} C_{\text{CO}_3^{2-}}}{C_{\text{H}^+} K_{\text{sp,FeCO}_3}} \quad (1)
\]

\[
K_{\text{sp,FeCO}_3} = -59.3498 - 0.041377 T - \frac{2.1963}{T} + 24.5724 \log(T) + 2.518 T^{0.5} - 0.6571 \quad (2)
\]

\[
S_{\text{FeS(Mackinawite)}} = \frac{C_{\text{Fe}^{2+}} C_{\text{HS}^{-}}}{C_{\text{H}^+} K_{\text{sp,FeS(Mackinawite)}}} \quad (3)
\]

\[
K_{\text{sp,FeS(mackinawite)}} = 10^{\frac{-2848.772 - 6.347 \log(K_{1})}{T}} \quad (4)
\]

\[
K_{(\text{H}_2\text{S})} = 10^{\frac{782.43945 + 0.361261 T \cdot 1.6722 - 10^{-4.6571 T^{0.5} - 7.1121 - 142.741722 \ln T_{2}}{T}} \quad (5)
\]
where $C_{\text{Fe}^{2+}}, C_{\text{CO}_2^{-}}, C_{\text{HS}^{-}},$ and $C_{\text{H}^+}$ are the ion concentrations for ferrous iron, carbonate, bisulfide, and hydrogen ions in mol/L, respectively. $K_{\text{sp}}$ stands for the solubility limit, $T$ is temperature (K), $I$ is the ionic strength, and $K_1^{48}$ is the first dissociation constant of $\text{H}_2\text{S}$ (mol/L). In all of the experiments, the bulk solution was undersaturated with respect to both iron carbonate and mackinawite. It should be emphasized that the surface pH is expected to be higher than the bulk pH which would result in higher saturation values in the vicinity of the corroding surface. It has been previously shown that the surface pH could vary from the bulk pH by 1 unit to 2 units depending on the level of mixing.49

This suggests that both iron carbonate and mackinawite were likely supersaturated at the steel surface, which is a necessary precondition for formation of solid corrosion product layers.

Figure 3 shows the SEM images of the surface of exposed specimens. In the absence of $\text{H}_2\text{S}$, a fractured layer on the surface is observed (Figure 3[a]). With $\text{H}_2\text{S}$ present, the specimen surface was covered with a thin compact layer that seems to be following the original shape of the steel surface including the polishing marks. For the case of 40 ppm and 90 ppm $\text{H}_2\text{S}$ there are some local failures of the layer, which can be seen in Figures 3(b) and (c). The surface of the specimen exposed to 150 ppm $\text{H}_2\text{S}$ does not show any such features (Figure 3[d]).

XRD was utilized in order to identify the makeup of the corrosion product layer. Iron carbide was identified on the specimen exposed to a solution without $\text{H}_2\text{S}$ (Figure 4[a]). However, the XRD patterns of the specimens exposed to 40 ppm and 90 ppm $\text{H}_2\text{S}$ do not show any peaks that could correspond to mackinawite, iron carbonate, nor iron carbide (Figures 4[b] and 4[c]). The peaks on these two patterns at 44.28° and 65.28° are the $\alpha$-Fe peaks.50 This shows that the layers formed on these surfaces were so thin (order of $\mu$m) that the conventional XRD was not able to detect the layer. XRD was not conducted on the specimen exposed to 150 ppm $\text{H}_2\text{S}$. The elemental analysis using EDS showed sulfur on the surface of the specimens exposed to 40 ppm, 90 ppm, and 150 ppm $\text{H}_2\text{S}$ after 6 d to 7 d of exposure.

Cross-section images of the specimens were analyzed in order to investigate the corrosion product layer thickness and the appearance of the pits. The specimen exposed to the aqueous $\text{CO}_2$ solution (in the absence of $\text{H}_2\text{S}$) shown in Figure 5(a) has a very porous and detached fragmented layer on the surface, which is made of iron carbide and lacks any protective properties. The specimens exposed to 40 ppm and 90 ppm $\text{H}_2\text{S}$ are shown in Figures 5(b) and (c), respectively, showing pitting. These pits are partially filled with some corrosion product, which is not dense, nor is it well attached; therefore, it is likely that these pits had remained active throughout the experiment. A very thin layer is seen on the steel surface in the vicinity of the pits, which explains the inability of the XRD to detect this layer. The specimen exposed to 150 ppm $\text{H}_2\text{S}$ is shown in Figure 5(d), where a very thin layer is present. No pitting was found on this surface.

In order to investigate the morphology of the corrosion attack, the corrosion product layer was chemically removed following the procedure given in ASTM Standard G151 using Clarke’s solution. Figure 6 shows the SEM images of the specimen surface after the corrosion product layer was removed. Figure 6(a) shows the specimen exposed to aqueous $\text{CO}_2$ in the absence of $\text{H}_2\text{S}$ and exhibits a relatively rough surface, which shows that the specimen underwent severe uniform corrosion. The specimens exposed to 40 ppm
and 90 ppm H₂S still have the original polishing marks on the majority of the surface, along with locally corroded areas (Figures 6[b] and [c)]. There are much smaller and shallower pits on the specimen exposed to 150 ppm H₂S in Figure 6(c).

Profilometry was utilized to measure the depth of the pits on the surface and the deepest pit depth was used to calculate the maximum pit penetration rate (PPR) (Figure 7). The specimen exposed to aqueous CO₂ solution (in the absence of H₂S) does not show any features on the surface that could be considered as localized attack, just general roughening. The profilometry of the specimens exposed to 40 ppm and 90 ppm H₂S shows evidence of pitting, more widespread at 40 ppm. A pit depth of more than 200 μm can be seen on both specimens in Figures 7(b) and (c). The image of the specimen exposed to 150 ppm H₂S shows very small pits with the depth less than 10 μm, which cannot be considered as localized corrosion.

The specimens were weighed after the corrosion product layer was removed; the time averaged weight loss corrosion rate (Δm/t in mm/y) and the PPR of the specimens versus the H₂S concentration are compared in Figure 8. The data show that the overall mass loss decreased with an increase in H₂S concentrations; however, 40 ppm and 90 ppm H₂S triggered localized corrosion. For these two experiments, the PPR was at least five times higher than the uniform corrosion rate of the specimen exposed to similar aqueous environment without H₂S confirming localized corrosion. In the presence of 150 ppm H₂S, localized corrosion was not observed and the weight loss corrosion rate shows the lowest value as compared with other experiments.

**DISCUSSION**

It was shown above that localized corrosion occurred on mild steel specimens exposed to aqueous CO₂ solutions with trace amounts of H₂S. The bulk solution in all experiments was undersaturated with respect to corrosion products: iron carbonate and mackinawite. However, a corrosion product layer was observed on the corroded specimen SEM images. Based on XPS analysis reported by Lee and Nend and Choi, et al., it is likely that the layer was mackinawite. This was not unexpected, because a corrosion process results in different water chemistry at the surface as compared to the bulk, with both the pH and Fe²⁺ concentrations being higher at the corroding steel surface. This is particularly pronounced in
quiescent conditions, while the surface and the bulk water chemistry values converge in turbulent flow conditions.

In marginally sour environments, such as the one used in the current study, the higher pH and Fe$^{2+}$ concentration at the surface allowed mackinawite layer formation, even if the bulk solution was undersaturated. As the mackinawite layer formed and grew in thickness it presented a diffusion barrier, which led to a reduction in the corrosion rate. Because of ongoing corrosion that was undermining the layer, it did not form uniformly.55 It is well known that protectiveness of a corrosion product layer depends on the so-called scaling tendency, which is a ratio of the precipitation rate and the corrosion rate.56 When the scaling tendency is high, the precipitation overwhelms corrosion and protective layers form. Conversely, when rapid corrosion overpowers the precipitation and undermines the layer, nonprotective layers form. In the current study, when there was more H$_2$S, the precipitation proceeded at a faster rate, thus a more protective layer formed and vice versa. At lower H$_2$S concentrations, faults in the layer allowed the corrosive species to reach the steel surface. This resulted in localized corrosion at those locations. In addition, the outer surface of the growing mackinawite underwent dissolution. Therefore, the stability of this layer depended on the balance of: undermining by corrosion, precipitation at the steel/mackinawite interface, and dissolution at the mackinawite/solution interface.

The observed localized corrosion rates in the present study were higher than the bare steel corrosion rate exposed to similar conditions without the presence of H$_2$S. It should be noted that while H$_2$S provided partial protection in these marginally sour environments, it would not have significantly contributed to the uniform corrosion rate because of the very low concentrations. It was the much higher content of CO$_2$ that led to the high corrosion rate (the corrosiveness of carbonic acid has been well documented).57 However, iron carbonate, which is the product of CO$_2$ corrosion, was not found at the surface of the steel under these conditions because of a much slower kinetics of formation when compared to that of mackinawite.58 Therefore, it is believed that the observed localized corrosion was the result of a galvanic effect. The galvanic effect was driven by a positive shift in the surface potential59 at the mackinawite-covered steel surface (Figure 1[a]). It is not entirely clear at this time whether the increase in potential was the result of an increase of the cathodic surface area, or due to the retardation of the anodic reaction as a result of coverage by the mackinawite layer. Either way, the potential difference between the large surrounding steel surface covered by mackinawite (that was more positive) and the uncovered steel in the pits (that was more negative) was the driving force for a galvanic couple, which led to localized corrosion.

Based on the finding in the current study, there seems to be a threshold value of pH$_2$S which led to localized attack that was observed at concentrations up to 90 ppm H$_2$S in CO$_2$, but not at 150 ppm or more.24 For the sake of the present argument, one can assume that this threshold was of the order of 100 ppm H$_2$S in CO$_2$ in the present study. It is expected that the threshold will vary with temperature and water chemistry (mostly affected by pH). At significantly higher temperatures and higher pH a lower threshold value is expected. It is of key importance to emphasize that this threshold actually refers to the ratio of H$_2$S to CO$_2$ gas partial pressures (pH$_2$S/pCO$_2$ = 10$^{-4}$) and not the actual H$_2$S gas concentration as reported from the field, which is different because of the presence of hydrocarbon gases.
FIGURE 5. Cross-section image of X65 specimen after 6 d of exposure to an aqueous CO₂ solution at 30°C and pH 5.0: (a) no H₂S, (b) 40 ppm H₂S, (c) 90 ppm H₂S, and (d) 150 ppm H₂S, 1 wt% NaCl.

FIGURE 6. SEM image of X65 specimen after exposure to a saturated CO₂ solution at 30°C and pH 5.0 without corrosion product layer: (a) no H₂S, (b) 40 ppm H₂S, (c) 90 ppm H₂S, and (d) 150 ppm H₂S, 1 wt% NaCl, 6 d exposure.
CONCLUSIONS

In aqueous CO₂ environments with a trace amount of H₂S at low temperatures where the solution was undersaturated with respect to both iron carbonate and mackinawite:

- Mild steel underwent localized corrosion when there was not enough [H₂S]_aq to form a stable mackinawite layer.
- Below 100 ppm H₂S (when the ratio of H₂S to CO₂ gas partial pressures was below 10⁻⁴) localized attack was observed, while above this threshold the mackinawite layer provided a uniform protection to the steel surface.
- It is hypothesized that at lower H₂S concentrations, faults in the corrosion product layer allowed the corrosive species to reach the steel surface. This resulted in localized corrosion.

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