Formation Mechanisms of Iron Oxide and Iron Sulfide at High Temperature in H₂S Corrosion Environment

Shujun Gao, Bruce Brown, David Young, Srdjan Nesic, Marc Singer
Institute for Corrosion and Multiphase Technology
Department of Chemical & Biomolecular Engineering, Ohio University
342 West State Street
Athens, OH, 45701
USA

ABSTRACT

The mechanisms of corrosion of mild steel, and associated corrosion product formation, in high temperature sour environments are still largely unknown although they directly relate to pressing operating issues in the oil and gas industry. Previous studies have shown that, from 80°C to 200°C in an H₂S only environment, magnetite forms as an inner layer while iron sulfides are found in the outer layer. Although magnetite is thermodynamically less stable than iron sulfide, it was always observed as a defined inner layer. In this work, experiments were conducted to investigate the formation mechanisms of magnetite and iron sulfide in a H₂S environment at high temperature. The corrosion behavior of mild steel was first investigated in environments with and without H₂S at 120°C, showing that magnetite is the dominant corrosion product layer in the initial stages of corrosion, due to a much faster kinetics of formation than iron sulfide (mackinawite). Magnetite is assumed to be responsible for the initial rapid decrease of the corrosion rate in this environment. In another experiment, the conversion of magnetite into mackinawite was investigated by exposing a preformed magnetite layer on an inert steel substrate (nickel) to an H₂S environment. Consequently, it is postulated that Fe₃O₄ experiences a simultaneous and continuous process of formation at the steel/magnetite interface and conversion to mackinawite at the magnetite/mackinawite interface. A descriptive model for the formation mechanisms of magnetite and iron sulfide at high temperature is presented.

Key words: hydrogen sulfide, high temperature corrosion, iron sulfide, magnetite

INTRODUCTION

Persistent energy demand moves the exploration and production of hydrocarbons towards ever deeper and harsher reservoirs, both onshore and offshore. These wells are frequently operated under high temperature and high pressure conditions in the presence of H₂S.¹-⁴ As a result, these operating environments present a constant challenge for new developments in materials selection, design technology, corrosion management, and corrosion modeling in the oil and gas industry.⁵-⁸

H₂S corrosion at low temperature (< 80°C) has been extensively investigated in the past decades; some of the key issues have been well understood.⁹-¹³ However, at elevated temperatures (> 80°C), the

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mechanisms of H₂S corrosion have not been sufficiently studied and many aspects of corrosion kinetics and layer formation processes remain unclear.

The author’s previous research conducted at four elevated temperatures levels, 80°C, 120°C, 160°C, and 200°C, has shown that the initial corrosion rate increases with increasing temperature while the final stable corrosion rate decreased with temperature. Mackinawite, troilite, pyrrhotite, and pyrite were identified as the main iron sulfide phases in the outer layer at 80°C, 120°C, 160°C and 200°C, respectively. Iron oxide was detected as an inner layer at every studied temperature and was later identified as magnetite (Fe₃O₄) by electron diffraction performed in a transmission electron microscope (TEM). Thermodynamically, Fe₃O₄ is less stable than any iron sulfide and should not be present in an H₂S dominated environment. Indeed, it was never reported in similar environments at low temperature. However, further experiments with different test durations, ranging from 1 to 21 days, showed that Fe₃O₄ does not disappear as expected based on thermodynamic arguments, and was persistently found as an inner layer with a relatively constant thickness of 25 µm, as shown in Figure 1.

![Figure 1. Corrosion rate and layer thickness of Fe₃O₄ and iron sulfide change with time, T=120°C, pH₂S=0.1 bar, pH=4.0 (initial) ~ 5.5 (final), M: mackinawite, T: troilite, Py: pyrrhotite, P: pyrite.](image)

Reviewing these results, two interesting gaps in understanding can be identified:

1. The corrosion rate quickly decreased in the first day from 5.5 to 2 mm/yr (see dark blue data points in Figure 1). Yet, it is not entirely clear which layer, Fe₃O₄ or mackinawite, was responsible for the decrease of the corrosion rate. Was there a sequence in the layer formation? How fast are these layers forming?

2. The thickness of inner Fe₃O₄ layer did not change significantly with time (20 to 30 µm from day 1 to day 21), while the outer iron sulfide layer kept growing with time from 5 µm to reach 90 µm after 21 days (see light blue and red data points in Figure 1). So what was the layer growth mechanism of iron sulfide in the presence of a Fe₃O₄ layer?

**HYPOTHESES**

The following hypotheses were proposed to address the above two questions:

1st Hypothesis: At high temperature, Fe₃O₄ forms very quickly during the initial stages of corrosion. It is a protective layer that slows down the corrosion rate. Therefore, the growth of the Fe₃O₄ layer gradually slows down as the lower corrosion rates slow down the formation rate Fe₃O₄. At the same time the
conversion of Fe$_3$O$_4$ to FeS proceeds at a steady state until a balance is established and the thickness of the Fe$_3$O$_4$ becomes constant.

2$^{nd}$ Hypothesis: Iron sulfide growth mechanism is mainly through a conversion from Fe$_3$O$_4$. The Fe$_3$O$_4$ simultaneously forms at the steel/Fe$_3$O$_4$ interface and converts to FeS at the Fe$_3$O$_4$/FeS interface.

**METHODOLOGY**

To test the 1$^{st}$ hypothesis, Experimental Set #1 was conducted, as shown in Figure 2:

- **Step 1:** A X65 carbon steel specimen was immersed into 1 wt.% NaCl solution (purged by N$_2$) without H$_2$S. The experimental condition was 120$^\circ$C at an initial pH 4.0. After 1 day, the specimen with preformed Fe$_3$O$_4$ layer were retrieved, dried and stored in a nitrogen atmosphere.

- **Step 2:** The preformed Fe$_3$O$_4$ carbon steel specimen were exposed under the same condition (1 wt.% NaCl solution, 120$^\circ$C, initial pH 4.0) containing 0.1 bar H$_2$S, for 1 day.

According to the 1$^{st}$ hypothesis, the iron sulfide layer growth should be dominant in Step 2, since the initial Fe$_3$O$_4$ layer formation step would have already been completed. Therefore, a much thicker iron sulfide (mackinawite) layer would form compared with the same experiment conducted with no preformed Fe$_3$O$_4$ layer (see Figure 2 and the first point in Figure 1).

![Figure 2](image)

**Figure 2.** Experiment design to test hypothesis #1.

To verify the 2$^{nd}$ hypothesis, the Experimental Set #2 was performed, as shown in Figure 3:

- **Step 1:** Nickel (Ni) specimens, which should not corrode in the current experimental conditions with or without H$_2$S, were immersed into a 1 wt.% NaCl solution (purged by N$_2$) without H$_2$S. Some X65 steel specimens were also immersed in the cell at the same time solely to act as a source of Fe$^{2+}$. The test condition was still 120$^\circ$C at an initial pH 4.0. This was done in order to precipitate Fe$_3$O$_4$ on the Ni surface via Reaction (1):

\[
3\text{Fe}^{2+} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2e^- \tag{1}
\]

The cathodic reaction(s) associated with Reaction (1) is not identified with certainty as of yet but it is postulated that H$^+$ reduction and H$_2$S reduction could be involved.
• Step 2: The Ni specimens with preformed Fe$_3$O$_4$ were exposed to a 0.1 bar H$_2$S environment under the same conditions (120°C, initial pH 4.0) for 1 day.

Based on the 2$^{nd}$ hypothesis, the preformed Fe$_3$O$_4$ layer should convert to iron sulfide in Step 2, via Reaction (2). Since there was no replenishment for Fe from the steel substrate to form new Fe$_3$O$_4$ (Reaction (1)), the Fe$_3$O$_4$ found at the end of Step 2 should be either very thin or even non-existent if it completely converted to iron sulfide.

\[
Fe_3O_4 + 3H_2S + 2H^+ + 2e^- \rightarrow 3FeS + 4H_2O
\]  

(2)

The anodic reaction(s) associated with Reaction (2) is also not clearly identified but Fe oxidation and/or reaction (1) are likely.

Figure 3. Experiment design to test hypothesis #2.

H$_2$S corrosion experiments were conducted in a 7 L Hastelloy autoclave, shown in Figure 4. Linear polarization resistance (LPR) measurements were carried out in a conventional three-electrode electrochemical setup using a potentiostat. The working electrode was a cylindrical UNS K03014 (API 5L X65) carbon steel, its chemical composition is shown in Table 1. A Pt-coated Nb cylinder served as the counter electrode. Due to the lack of a reliable reference electrode in the high temperature H$_2$S environment, a commercial Zr/ZrO$_2$ high-temperature, high-pressure electrode within the pH probe was used as a pseudo-reference electrode. This is doable as long as its potential is stable under the experimental conditions, while the exact potential with respect to a SHE is unknown. Some flat specimens were fastened to a fixed shaft using a PTFE-coated 304SS wire. A centrally positioned impeller with 1000 rpm rotation speed was used to keep the solution well mixed during each experiment.
The experimental conditions such as pH and pH$_2$S, summarized in Table 2, were calculated based on an in-house water chemistry model (reviewed in previous publications$^{14}$). Before each experiment, the carbon steel specimens were polished with 400# and 600# grit abrasive paper, then thoroughly rinsed with deionized water and isopropanol. The 1 wt.% NaCl solution was purged with N$_2$ overnight at room temperature. Then the pH was adjusted according to the water chemistry calculation and H$_2$S added to the autoclave at room temperature to achieve a solution pH of 4.0 and desired 0.1 bar pH$_2$S when the temperature reached 120$^\circ$C. After each experiment, the corroded specimens were retrieved and examined by X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS). Other experimental details can be found elsewhere.$^{14}$ For the tests without H$_2$S, the same procedure was followed except that no H$_2$S was involved.

Table 2. Test matrix for the effect of temperature

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>120$^\circ$C</td>
</tr>
<tr>
<td>pH$_2$S</td>
<td>0.1 bar</td>
</tr>
<tr>
<td>Initial pH</td>
<td>4.0</td>
</tr>
<tr>
<td>Rotation speed</td>
<td>1000 rpm</td>
</tr>
</tbody>
</table>

RESULTS

Sequence of Fe$_3$O$_4$/FeS Formation

The corrosion rates obtained in Experimental Set #1 with H$_2$S (0.1 bar), and without H$_2$S, are shown in Figure 5. For clarity, these two are respectively labeled as experiment “with H$_2$S”, “without H$_2$S” and “with preformed Fe$_3$O$_4$”.

Looking first at the results from experiment “with H$_2$S” and experiment “without H$_2$S”, the LPR corrosion rates are both shown to decrease relatively quickly at high temperature. The LPR corrosion rate from experiment “without H$_2$S” gradually decreased during the first 50 hours of exposure and reached a stable corrosion rate of 0.5 mm/yr. The LPR corrosion rate from experiment “with H$_2$S” reduced dramatically in the first 2 hours from over 5 mm/yr to about 2.8 mm/yr. Then it kept decreasing in a slower manner and eventually stabilized around 1 mm/yr.

The results from experiment “with preformed Fe$_3$O$_4$” are plotted in red in Figure 5, including the 1 day, representing the time needed to preform the Fe$_3$O$_4$ layer. The corrosion rates experienced by the specimen during the Fe$_3$O$_4$ layer formation (red dots in Figure 5) are the same to the corrosion rates during the first day of the experiment “without H$_2$S” (green dots in Figure 5) as would be expected. After the specimen with the preformed Fe$_3$O$_4$ was transferred to the H$_2$S environment at the 1-day mark, the LPR corrosion rate in the experiment “with H$_2$S” started at 3.5 mm/yr, which is lower than the initial LPR rate obtained the experiment “with H$_2$S” (5.5 mm/yr). This result demonstrates that the Fe$_3$O$_4$ layer alone offers additional protection in an H$_2$S environment. The relatively high initial corrosion rate (3.5 mm/yr) value could be due to some cracking and/or spalling, created when the specimen was transferred, as the Fe$_3$O$_4$ layer was expected to provide higher initial corrosion protection in the H$_2$S environment.

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environment. The corrosion rate did decrease sharply in the next few hours of exposure but stabilized at 1.8 mm/yr, similarly to the final rate in the experiment “with H2S”. In comparison, a higher protectiveness by the Fe3O4 layer was clearly demonstrated in an environment without H2S at the same high temperature.\(^{19}\)

![Graph showing LPR corrosion rate](image)

Figure 5. LPR corrosion rate in experiments without H2S (green), with 0.1 bar H2S (blue), and with preformed Fe3O4 layer for one-day, T=120°C, initial pH=4.0, B=23 mV/decade.

The corrosion products from the experiment “without H2S” at high temperature were characterized by X-ray diffraction (XRD) after different test durations, as shown in Figure 6. All the corrosion products were identified as pure magnetite (Fe3O4) regardless of the exposure time. The EDS mapping scan, Figure 7, also confirms that the layer was comprised of iron (Fe) and oxygen (O). The intensity of the peaks also did not increase with time and the \(\alpha\)-Fe matrix was already undetectable after the 1 day experiment. This means that the Fe3O4 became very thick and compact rapidly, implying good corrosion protection properties. The thickness after 1 day of exposure was approximately 25 µm, which is appropriately the same value as the thickness of the oxide layer obtained from experiment “with H2S” for 1 day, as shown in Figure 1 and Figure 7. The fact that the two Fe3O4 layer thicknesses are the same seems to indicate that the Fe3O4 growth during the first day of testing occurs with little interference from H2S. Consequently, it is proposed that the Fe3O4 formation dominated the first few hours of testing at high temperature and that the Fe3O4 layer rapidly reached its steady state thickness, even with H2S. This is discussed in more details below.
The cross-sections of specimens from the experiment “without H₂S” are shown in Figure 8. It can be seen that the overall layer thickness increased from 25 µm after 1 day to 80 µm after 21 days. Figure 9 shows that, the Fe₃O₄ layer growth in experiment “without H₂S” follows almost the same trend as the mixed FeS/Fe₃O₄ corrosion product layer growth in the experiment “with H₂S” displayed in Figure 1. This could be a coincidence, especially since the thickness of the Fe₃O₄ layer alone stayed at ~25 µm in the experiment “with H₂S” and did not increase further with exposure time. However, this could also...
indicate that the FeS and the Fe₃O₄ formation rates are inherently linked. This, again, highlights the complexity of the growth mechanism of iron sulfide in the presence of a Fe₃O₄ layer, which will be discussed later.

Figure 8. The growth of Fe₃O₄ layer with time, shown by cross-sections of X65 specimen in the experiment without H₂S after different test durations (obtained in separate experiments), T=120°C, initial pH=4.0.

Figure 9. The thickness of Fe₃O₄ layer with time in the experiment without H₂S, T=120°C, initial pH=4.0.

The X65 steel specimen with preformed with Fe₃O₄ was exposed to a 0.1 bar H₂S under otherwise same conditions (Table 2) for another day. The EDS mapping results for the cross-sections are shown in Figure 10; all images are at the same magnification for ease of comparison. However, the data related to the experiment "with H₂S" were obtained using a different EDS detector than for the other two conditions and the display of the results can be more difficult to interpret. In the first row of Figure 10, the highest magnitude concentration of elements is indicated by white pixels and lowest magnitude by blue pixels; in the other two rows, the brightness intensity of the same-color pixels is related to the concentration. The level of color brightness can only be used in a qualitative way and can be compared from image to image. In terms of Fe₃O₄ layer thickness for the specimen with, without H₂S, and with preformed Fe₃O₄ layer, no significant difference can be found. However, the thickness of the outer iron
sulfide layer, represented by sulfur (S) content, greatly increased from less than 5 µm without the preformed Fe₃O₄ layer to 30 µm with the preformed Fe₃O₄ layer.

These experimental results infer that the formation rate of Fe₃O₄ is faster than that of iron sulfide at the tested temperatures. This explains why Fe₃O₄ is persistently detected while not being thermodynamically favored. In comparison, the presence of Fe₃O₄ was not reported at lower temperature in similar environments. A deeper look into the solubility limit of each corrosion product can help explain this behavior.

The solubility equilibria for Fe₃O₄ and mackinawite are given by Reactions (1) and (5) with the corresponding solubility limit expressions given by Equations (4) and (6). The effect of temperature on the solubility limit is shown in Figure 11. The solubility limit for Fe₃O₄ experiences a significant drop with the increase of temperature, while in comparison, for mackinawite, the decrease in solubility limit is only moderate.

\[
Fe₃O₄ + 8H^+ \leftrightarrow 2Fe^{3+} + Fe^{2+} + 4H₂O
\]

\[
K_{sp,Fe₃O₄} = e^{\frac{\Delta G}{RT}}
\]

(4)

\[
FeS + H^+ \leftrightarrow Fe^{2+} + HS^-
\]

\[
K_{sp,2} = 10^{\frac{2848779}{T_K} - 6.347 + \log(K_{a,1})}
\]

(6)
The level of saturation value governs the precipitation rate and consequently the layer formation/dissolution rate. The expressions for saturation value of Fe$_3$O$_4$ ($S_{Fe_3O_4}$) and mackinawite ($S_{mackinawite}$) are given in Equations (7) and (8). In this work, the ferric ion concentration [Fe$^{3+}$] was assumed to be $1.0 \times 10^{-10}$ M, which means the calculated $S_{Fe_3O_4}$ may be underestimated compared to earlier similar studies$^{13}$.

$$S_{Fe_3O_4} = \frac{[Fe^{3+}]^2[Fe^{2+}]}{[H^+]^8} \frac{1}{K_{sp,Fe_3O_4}}$$

$$S_{mackinawite} = \frac{[Fe^{2+}][HS^-]}{[H^+]} \frac{1}{K_{sp,2}}$$

As soon as the steel specimen is inserted into an aqueous H$_2$S environment, iron starts to dissolve and release Fe$^{2+}$, resulting in an increase in pH (considering a closed system such as an autoclave). Figure 12 shows the changes in $S_{Fe_3O_4}$, bulk solution pH, and $S_{mackinawite}$ with an increase in [Fe$^{2+}$] from 0 to 10 ppm in a closed system. At 120$^\circ$C with an initial pH 4.0, Fe$_3$O$_4$ is strongly supersaturated ($S_{Fe_3O_4}=10^6$) almost immediately after Fe$^{2+}$ ions are generated in the solution. In contrast, $S_{mackinawite}$ requires at least 0.8 ppm of Fe$^{2+}$ to reach a saturation of 1. Obviously, Fe$_3$O$_4$ is expected to precipitate faster and dominate the layer growth during the initial stage, because $S_{Fe_3O_4}$ is at least six orders of magnitude greater than $S_{mackinawite}$ and highly supersaturated. However, the solution pH will increase with time and this could change the ratio of saturation levels. Figure 12 also presents the saturation values at initial pH 5.0. However, the difference between initial $S_{Fe_3O_4}$ and $S_{mackinawite}$ is even higher at pH 5.0, so mildly acidic environments (pH 4 and pH 5) are not expected to largely affect the sequence and rate of layer growth at the tested temperature.
Figure 12. Saturation value for Fe$_3$O$_4$ and mackinawite at initial pH 4.0 and 5.0, [Fe$^{3+}$]=1×10$^{-10}$ M, T=120°C, pH$_{2S}$=0.1 bar.

Figure 13 presents the trend of $S_{Fe_3O_4}$ and $S_{mackinawite}$ at 25°C and 120°C. It is important to notice that at 25°C and for very low ferrous ion concentrations, $S_{Fe_3O_4}$ is of the same magnitude as $S_{mackinawite}$. Considering that Fe$_3$O$_4$ is more soluble at lower temperatures (see Figure 11), this explains why Fe$_3$O$_4$ is not found at temperatures below 80°C while it forms very quickly and actually dominates during the initial stages of corrosion at temperatures above 80°C in an H$_2$S corrosion environment. Temperature is the key influential factor.

Figure 13. Saturation value for Fe$_3$O$_4$ and mackinawite at 25°C and 120°C, [Fe$^{3+}$]=1×10$^{-10}$ M, pH$_{2S}$=0.1 bar, initial pH=4.0. (pH lines for 25°C and 120°C overlap in the graph)

In summary, due to a much higher saturation value, Fe$_3$O$_4$ is likely to form very quickly, faster than mackinawite, during the initial stages of corrosion at temperatures above 80°C in aqueous H$_2$S corrosion environments. It is hypothesized that Fe$_3$O$_4$ is responsible for the initial decrease in corrosion rate. A thin mackinawite layer is expected to immediately form as well when the steel is exposed to [H$_2$S]$_{aq}$. Simultaneous growth of Fe$_3$O$_4$ and mackinawite is then expected to occur, but initially the kinetics for Fe$_3$O$_4$ precipitation dominates at high temperatures.

**Iron Sulfide Formation Mechanism**

After the initial stages of formation, the iron sulfide growth mechanism was investigated in Experimental Set #2 in order to test the 2$^{nd}$ hypothesis. The experimental design is shown in Figure 3. The Fe$_3$O$_4$
precipitation was performed on Ni specimens using Fe$^{2+}$ ions generated by an independently corroding X65 steel specimens immersed in the same solution at 120°C, with an initial pH 4.0 and for 21 days. The Fe$_3$O$_4$ did indeed precipitate on the Ni surface, as identified by XRD in Figure 14. A precipitated Fe$_3$O$_4$ layer (~10 µm) can also be observed from the cross-section analysis in Figure 15 and is confirmed by the EDS mapping scan. This Ni specimen with the preformed Fe$_3$O$_4$ layer was then exposed for one day in a 0.1 bar H$_2$S environment under otherwise same conditions (120°C, initial pH 4.0) to verify the 2nd hypothesis.

After 1 day of exposure, the Ni specimen was retrieved and again characterized by XRD and SEM/EDS, as shown in Figure 14 and Figure 15. The Fe$_3$O$_4$ layer disappeared and was totally replaced by a mackinawite layer as confirmed by both XRD and EDS. The EDS mapping results show an iron sulfide layer on the Ni surface with no obvious oxygen (O) detected.

![XRD patterns of preformed Fe$_3$O$_4$ layer on Ni specimen before and after H$_2$S was introduced, T=120°C, initial pH=4.0.](image)

Figure 14. XRD patterns of preformed Fe$_3$O$_4$ layer on Ni specimen before and after H$_2$S was introduced, T=120°C, initial pH=4.0.
The above results seem to validate the 2nd hypothesis, stating that the FeS layer grows through Fe₃O₄ conversion. Without H₂S present, the Fe₃O₄ layer increased in thickness over time (Figure 9). With H₂S present, the Fe₃O₄ layer stabilized at a specific thickness while the iron sulfide layer increased in thickness with time due to the conversion reaction (Figure 1). Coincidentally, the FeS growth rate is similar to the rate of formation of the Fe₃O₄ layer observed in Figure 9. However, FeS precipitation via Reaction (5) cannot be entirely excluded since $S_{mackinaw}$ did exceed 1. However, previous results show that the Fe²⁺ concentration was around 3 ppm, which gives a $S_{mackinaw}$ value around 10 (Figure 12). This value of saturation is not extremely high and would not constitute a high driving force to produce a significant amount of precipitated iron sulfide. A recent corrosion prediction model developed by Zheng, et al., which includes iron sulfide precipitation, predicts the iron sulfide layer thickness to be below 14 µm after 7 days. Compared with the result in Figure 1, the thickness of iron sulfide was above 45 µm after 7 days. This further demonstrates that the main contribution to iron sulfide growth at higher temperatures was through the Fe₃O₄ conversion mechanism rather than the precipitation mechanism.

**Descriptive Model for the Fe₃O₄/FeS Formation Mechanisms at High Temperature**

Based on the experimental results, a descriptive model for Fe₃O₄ and FeS formation mechanisms at high temperature is presented in Table 3.
Table 3. Schematic diagrams for Fe$_3$O$_4$/FeS formation mechanisms at higher temperatures in a sour environment.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Schematic Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>X65 carbon steel is exposed to H$_2$S corrosion environment at high temperature. Fe starts to dissolve and releases Fe$^{2+}$ ions in the solution.</td>
<td><img src="image" alt="Diagram (a)" /></td>
</tr>
<tr>
<td>(b)</td>
<td>Fe$^{2+}$ reacts with its surrounding H$_2$O molecules and Fe$_3$O$_4$ forms quickly via reaction (1). Fe$_3$O$_4$ layer is protective and the corrosion rate (i.e. the rate of Fe$^{2+}$ ions release) decreases. Consequently, the formation rate of Fe$_3$O$_4$ also decreases which slows down the layer growth rate. Simultaneously, the aqueous H$_2$S reacts with the Fe$_3$O$_4$ layer, on the solution side, which transforms it to iron sulfide via Reaction (2) but initially at a much lower rate than Fe$_3$O$_4$ formation.</td>
<td><img src="image" alt="Diagram (b)" /></td>
</tr>
<tr>
<td>(c)</td>
<td>Iron sulfide formation through Fe$_3$O$_4$ conversion catches up as the formation of Fe$_3$O$_4$ slows down. Fe$_3$O$_4$ continuously forms at the metal surface and converts to iron sulfide at the Fe$_3$O$_4$/FeS interface; these two reactions occur at a similar rate which stabilizes the thickness of the Fe$_3$O$_4$ layer.</td>
<td><img src="image" alt="Diagram (c)" /></td>
</tr>
<tr>
<td>(d)</td>
<td>If the saturation value exceeds the solubility limit of iron sulfide, iron sulfide will precipitate at the FeS/solution interface and the FeS layer will grow even further.</td>
<td><img src="image" alt="Diagram (d)" /></td>
</tr>
</tbody>
</table>

Other research studies$^{25-27}$ suggested alternative pathways for the layer growth mechanism, either stating that both Fe$_3$O$_4$ and FeS layers grow solely through precipitation (the present work suggests that precipitation is only a minor contributor) or postulating that the layer growth is linked to Fe solid state outward diffusion through the Fe$_3$O$_4$ lattice. However, the experimental results presented here do not seem to validate either of these mechanisms.
CONCLUSIONS

- Due to the faster kinetics at high temperature, a Fe₃O₄ layer is the dominant corrosion product forming at the steel surface in the initial stages of experiments where steel is exposed to an aqueous H₂S environment.
- Fe₃O₄ is responsible for the initial rapid decrease of the corrosion rate observed in sour environment at high temperature.
- Fe₃O₄ converts to mackinawite since it is thermodynamically less stable than iron sulfide. Fe₃O₄ experienced a simultaneous and continuous process of formation, at the steel/Fe₃O₄ interface, and transformation to FeS, at the Fe₃O₄/FeS interface.

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