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ELECTROCHEMICAL CORROSION OF CARBON STEELS
IN H₂S-CONTAINING BRINES

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ABSTRACT

The electrochemical corrosion behaviors of high strength low alloy carbon steel, Grade S-135, and ultra-high strength low alloy carbon steel, Grade UD-165, were investigated in alkaline brines at pH of 7.9, 10.7, and 12.4 and four H$_2$S partial pressures ($P_{\text{H}_2\text{S}}$) from 0 to 69 kPa at 85 °C using in situ electrochemical measurements, ex situ surface analyses, and software modeling. HS (aq) was calculated to be the dominant sulfide species from pH 7.9 to 12.4. After 60 hours, polarization resistance ($R_{\text{pol}}$) of S-135 and UD-165 generally increased as pH increased at lower $P_{\text{H}_2\text{S}}$ (0 and 0.83 kPa), whereas $R_{\text{pol}}$ decreased and then increased as pH increased at higher $P_{\text{H}_2\text{S}}$ (8.3 and 69 kPa). At each pH, the lower $P_{\text{H}_2\text{S}}$ increased $R_{\text{pol}}$ or did not significantly change $R_{\text{pol}}$, whereas the higher $P_{\text{H}_2\text{S}}$ decreased $R_{\text{pol}}$. Two opposite effects from H$_2$S were proposed, an accelerating effect due to H$_2$S(aq) and HS (aq) facilitating the Faradaic reactions and the localized corrosion, and an inhibiting effect due to the protectiveness of the corrosion products. The inhibiting effect was often observed at relatively low H$_2$S concentrations at pH 7.9 and 12.4.

The electrochemical impedance did not change significantly at different stir rates for both S-135 and UD-165, indicating that mass transport in the bulk solution was not the rate determining step. The corrosion products generally changed from iron carbonate and sulfides to iron oxide as pH increased, which agreed with the Pourbaix diagrams.

Solution pH in the three solutions were calculated to be 8.1, 9.8, and 10.8 at 200 °C, respectively. Polarization resistance values of UD-165 at 200 °C were consistently one to two orders of magnitude lower than at 85 °C, which corresponded to a drastic increase in corrosion rate at elevated temperature. At 200 °C, $R_{\text{pol}}$ at 9.8 was the smallest after 60 hours among the three solutions. The modeled results were in reasonable agreement with the experimental CR values within a factor of 4.
A new method derived from the generalized Butler-Volmer equation allowed to obtain anodic Tafel slopes from LSV even with the effect of limiting current. At 200 °C, the $b_2$ values indicated that the anodic reactions followed the Bockris mechanism at pH 8.1 and a two-electron mechanism at pH 9.8 and 10.8. As pH increased, the major corrosion products changed from pyrrhotite/siderite to magnetite although the corrosion products were a mixture of iron carbonate, sulfide and oxide.

At 4 °C and 10 MPa total pressure, experimental results for two drill steels, Grade S-135 and Grade UD-165, showed a distinct drop in corrosion rate when transitioning from sweet (CO$_2$) corrosion to sour (H$_2$S) corrosion in 5% wt. NaCl brine. It was found that a CO$_2$:H$_2$S ratio as high as 1000 was still enough for sour corrosion to dominate the conditions tested. The CO$_2$+H$_2$S condition and H$_2$S condition had the similar anodic and cathodic Tafel slopes, which were smaller than the CO$_2$ condition. The presence of H$_2$S could have caused the formation of FeS(s) at the steel surface where the pH and Fe$^{2+}$(aq) concentration might be higher than in the bulk solution.
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Chapter 1
Introduction

1.1 Research background

Energy demand is predicted to increase by 50-60% by 2030 with the industry development and the population growth.\textsuperscript{1} The primary energy source will still be crude oil and natural gas for the coming decades although the renewable energy alternatives have been developed. Since the drilling from relatively shallow wells is reaching the peak, the exploration to deep wells (below 4572 m or 15000 ft) and ultra-deep wells (below 7620 m or 25000 ft) is quite important for the petroleum and natural gas industry.

High-strength low-alloy carbon steels are commonly used for drill pipes in the natural gas and oil industry due to their high strength/weight ratio and economical cost. With the oil and natural gas exploration going deeper, the environment in deep wells or ultra-deep wells becomes more aggressive, which includes high-pressure, high-temperature, and high H\textsubscript{2}S and CO\textsubscript{2} concentrations as shown in Figures 1-1 and 1-2.\textsuperscript{2} Figure 1-1 generally describes the temperature and pressure range for deep and ultra-deep wells, where the temperature is usually above ~85 °C and up to 250 °C and the total pressure is above ~70 MPa. It can be seen in Figure 1-2 that the concentrations of acid gases CO\textsubscript{2} and H\textsubscript{2}S increase exponentially with increasing well depth.

H\textsubscript{2}S has been found to make carbon steels more susceptible to hydrogen induced cracking (HIC) / sulfide stress cracking (SSC), stress corrosion cracking (SCC), and corrosion fatigue (CF).\textsuperscript{2-5} The presence of H\textsubscript{2}S is detrimental to the carbon steels and could cause catastrophic failure of the drill pipes and drastically increase the exploration and operation cost.
Figure 1-1. The general temperature and pressure ranges for deep and ultra-deep wells. (Adopted from Reference 2)

Figure 1-2. CO₂ and H₂S contents in some oil and natural gas wells. ²

1.2 Corrosion reactions and cracking

Corrosion reactions between H₂S and carbon steels play an important role on the initiation and propagation of cracking and failure. The cathodic reaction is the hydrogen evolution
reaction (HER). Hydrogen could be produced through the reduction reaction of H$_2$S on the steel surface as expressed in Equations [1-1] to [1-3]. The produced hydrogen atom can penetrate into the metallic lattice and diminish the mechanical properties of carbon steels, causing HIC/SSC. The diffused hydrogen atoms can recombine to form hydrogen molecule inside the steel, causing hydrogen blistering.$^{5,6}$

$$
H_2S(aq) = H_2S(ad) \quad [1-1]
$$

$$
H_2S(ad) + e^- = H(ad) + HS^{-}(ad) \quad [1-2]
$$

$$
H_2S(ad) + H(ad) + e^- = H_2(g) + HS^{-}(ad) \quad [1-3]
$$

The anodic reaction is the oxidation reaction of Fe. Shoesmith et al.$^{7}$ proposed a solid-state reaction mechanism for the reaction between H$_2$S and Fe, which is expressed in Reaction [1-4]. The mass loss of Fe damages the steel integrity and weaken the strength. Meanwhile, the formation of iron sulfide can cover the reactive sites on the steel surface. Depending on the morphology and mechanical features of iron sulfides$^{8}$, the corrosion product layers could be protective or non-protective in different conditions$^{9,10}$. Moreover, iron sulfide products could also cover or plug the cracks, which further influence the propagation of cracking$^{11,12}$.

$$
Fe(s) + H_2S(aq) = FeS(s) + 2 H^+(aq) + 2 e^- \quad [1-4]
$$

Thus, studying on the electrochemical corrosion reactions between H$_2$S and Fe can help to better understand the initiation and propagation of cracking. Higher corrosion rate tends to correlate with higher susceptibility of carbon steel to cracking and mechanical failure. This research focused on the electrochemical corrosion rate measurement and mechanism analysis in the brines containing H$_2$S.
1.3 Factors influencing H₂S corrosion

The H₂S corrosion has been studied intensively due to the relevance to oil and natural gas industry.\textsuperscript{5,7,8,13–33} The main factors influencing H₂S corrosion include pH, H₂S concentration, and temperature.

1.3.1 pH

The pH influences the dissociation of H₂S and the solubility and stability of the corrosion products. The dissolved H₂S could dissociate into H\textsuperscript{+}(aq), HS\textsuperscript{−}(aq), and S\textsuperscript{2−}(aq) ions through Reactions [1-5] and [1-6], which could in turn decrease the environment pH. Meanwhile, H₂S could regenerate at the acidic conditions following the reverse direction of Reaction [1-5].

\[
\begin{align*}
\text{H}_2\text{S}(aq) &= \text{H}^+(aq) + \text{HS}^{−}(aq), \quad \text{pK}_a=7.05 \text{ at } 25 \degree C^{34} \quad [1-5] \\
\text{HS}^{−}(aq) &= \text{H}^+(aq) + \text{S}^{2−}(aq), \quad \text{pK}_a=19 \text{ at } 25 \degree C^{34} \quad [1-6]
\end{align*}
\]

Ma et al\textsuperscript{20} concluded the pH dependence based on the electrochemical experiments of iron at 22 °C. At very low pH ( < 2), there was little iron sulfide formed on the carbon steel due to the relatively high solubility at low pH, which resulted in the acceleration effect of H₂S on active corrosion. As the pH increased into the range of 3 to 5 with relatively low H₂S concentration, the addition of H₂S was found to result in an initial increase and then inhibiting effect on corrosion rate as the initially formed mackinawite converted into more protective iron sulfide layer on steel surface over time. At the pH higher than 5, only mackinawite was observed, resulting in the decreased inhibiting effect, because it was less protective than other forms of iron sulfide like troilite and pyrite. It was consistent with what Sardisco and Pitts\textsuperscript{9} found in 1965 using weight loss
method. They found that at 24 °C the sulfide film formed at pH of 6.5 to 8.8 was the least protective which contained essentially mackinawite.

1.3.2 H₂S concentration

The introduction of H₂S is expected to increase the corrosion rate, according to Reaction [1-4], which was confirmed in the systems without CO₂. Tang et al. reported that the increase of H₂S concentration from zero significantly increased the corrosion rate of carbon steels in Na₂SO₄(aq) base solution at 90 °C, which was attributed to a promoted hydrogen evolution reaction.³⁵

However, many researchers found that, in the system with CO₂, low H₂S concentration decreased the corrosion rate of carbon steels compared to the case without H₂S, and then the corrosion rate increased gradually with the increase of H₂S concentration. Videm et al reported that the addition of low H₂S concentration, corresponding to 45 Pa H₂S partial pressure (P₁₂₅), decreased the anodic dissolution rate by two decades in brine solutions with CO₂ at 70 °C, which was attributed to the rapid formation of protective films.²⁹ Abelev et al reported similar inhibiting effect of low H₂S concentration on corrosion in the presence of CO₂ in NaCl solutions at room temperature, and the corrosion rate increased at higher H₂S concentration but still below the H₂S-free case.¹³ The film formed on the steel surface was thin and protective at low H₂S concentration and thicker and more porous at higher H₂S concentration.

Sardisco et al ⁹,¹⁰ reported that in the H₂S-CO₂-H₂O system at 30°C, when P₁₂₅ was lower than 0.69 kPa, the corrosion rate was relatively low due to a protective sulfide film consisting of pyrite (FeS₂), troilite (hexagonal FeS), and some mackinawite (Fe₁₊₅S). When P₁₂₅ was increased to 0.69-28 kPa, the corrosion rate increased rapidly with an increase in H₂S concentration, which was attributed to the formation of a non-protective porous film composed of mainly mackinawite.
The inhibiting effect of low H$_2$S concentration was also attributed to the decrease in active surface by sulfur coverage and mackinawite coverage by some researchers.$^{13,18}$ It’s worth noting that H$_2$S still can be a hazard for pitting corrosion and cracking even when it is decreasing the general corrosion rate.$^{23}$

1.3.3 Temperature

Temperature could impact H$_2$S corrosion through affecting many thermodynamic and kinetic factors, like the solubility of H$_2$S, the speciation in the solution, the solubility and stability of corrosion products, reaction rate constants, and diffusion coefficients of reactive ions.

Zhang et al $^{31}$ reported that the corrosion rate increased with increasing temperature from 30 °C to 60 °C and then gradually decreased up to 120 °C with $P_{H2S}$ = 1.2 MPa. Qi et al $^{36}$ reported a similar trend that the corrosion rate increased from 25 °C to 40 °C and then decreased up to 80 °C in 5%wt NaCl solution saturated with H$_2$S. They further concluded that the increase of corrosion rate at moderately elevated temperature was mainly attributed to the increased diffusion of corrosive species, higher concentration of H$^+$, and the greater reaction rate constant. The decrease of corrosion rate at further increased temperature was mainly due to higher transport resistance or the protectiveness of corrosion product film, and, less significantly due to lower H$^+$ concentration. The corrosion product film was more compact and protective at higher temperature, and the film morphology played a major role above the transition temperature. At even higher temperature of 204 °C, Ramanarayanan and Smith reported that diffusion of Fe$^{2+}$ through a growing pyrrhotite film was the rate-limiting step in H$_2$S-saturated, brine condition.$^{37}$

High pressure and high temperature (HPHT) conditions pose great challenge on the drilling and operation materials (Figure 1-1). Meanwhile, these conditions are also relatively
difficult to simulate in the laboratory level with respect to reliability and safety, and therefore the studies of \( \text{H}_2\text{S} \) corrosion at HPHT conditions (> 150 °C) are not common.

### 1.3.4 Other factors

Besides the factors discussed above, there are some other factors affecting \( \text{H}_2\text{S} \) corrosion found by some researchers. Corrosion rate is reported to decrease over time before the steady state in a \( \text{H}_2\text{S} \)-containing brine solution at 20 °C, which is indicated by the electrochemical impedance measurements over time.\(^{18}\) It was attributed to the formation of a protective film on the steel surface before the formation and dissolution of the film reached the steady state. Ma et al \(^{20}\) also reported the inhibiting effect of \( \text{H}_2\text{S} \) after two hours, which was explained by the conversion of initially formed metastable mackinawite to more stable and more protective troilite and pyrite. Thus, time scale was one factor influencing \( \text{H}_2\text{S} \) corrosion rate, and a relative steady state of corrosion rate can be reached after sufficient time.

The flow in the corrosion system can also influence the corrosion of carbon steel. The effect of flow on corrosion depends on the absence / presence of protective film on the surface.\(^{38}\) Without the protective film, the enhanced flow could increase the corrosion rate by facilitating the transport of reactive species. In contrast, the transport effect of the flow becomes insignificant when the corrosion was limited by the protective film. If the flow causes the removal of the protective film, the corrosion rate tends to increase.
1.4 Objectives and study scope

1.4.1 Objectives

Sour corrosion has been studied mainly in acidic to neutral conditions with varying H$_2$S concentrations and sometimes with CO$_2$. However, in the drilling practice, a drilling fluid treated to an elevated pH between 10 and 12 is used to flow through the drill pipes to mitigate the corrosion, as shown in Figure 1-3. The functions of drilling fluid / mud include many, from the initial use to remove cuttings from wells to cooling and cleaning the bit, controlling the subsurface pressures, sealing permeable formations, controlling corrosion and so on. To fulfill the various purpose, the compositions of drilling fluid / mud can be complicated. The drilling fluid / mud are generally divided to water-based muds and oil-based muds, and the former is the most commonly used muds. In the aqueous phase, caustic soda (NaOH) and soda ash (Na$_2$CO$_3$) are typically used to adjust the pH in water based mud. Therefore, the corrosion environment during drilling is in alkaline conditions, where the data and study is not as much as for acidic conditions.

![Diagram of drilling fluid](image)

Figure 1-3. The drilling fluid used in the deep drilling. (Source: Air Drilling Associates)
The overall goal of this research was focused on the electrochemical corrosion behavior of high strength low alloy carbon steels in the presence of H$_2$S in neutral to alkaline brines. The effects of pH and H$_2$S concentration was investigated using in-situ electrochemical measurements, ex-situ surface analyses, and software modeling in alkaline brines. The corrosion mechanisms were studied in terms of the role of H$_2$S on Faradaic reactions and the corrosion products. The corrosion behavior was also studied at elevated temperature in alkaline brines and when H$_2$S was mixed with high pressure CO$_2$.

1.4.2 Study scope

To fulfill the objectives, the study scope for this research is defined in terms of pH, H$_2$S concentration, and temperature.

The pH in this study was chosen from 7 to 12 for two main reasons. Firstly, this pH range is representative of drilling fluid / mud as discussed in the previous section. Secondly, the mechanical tests of the carbon steels used in this study have been carried out at the pH range of 7 to 12 by M. Ziomek-Moroz et al. They found that at ambient temperature fatigue crack growth rate was controlled by hydrogen diffusion at pH = 7, whereas the cracks seemed to be plugged by corrosion products at pH = 12 and showed the characteristic for SCC. The electrochemical corrosion study in the same pH range could help combine the reaction with the cracking mechanism. The pH was achieved by adding NaHCO$_3$/Na$_2$CO$_3$/NaOH buffer substances into 5%wt. NaCl(aq) based on the drilling fluid components and ASTM test standard. The solutions were designed to represent the pH of drilling fluid but not to simulate its composition in reality because pH was the factor of interest in this study rather than its composition.
The H₂S concentration tested in the study was in a range equivalent to $P_{\text{H}_2\text{S}}$ in deep and ultra-deep wells. According to Figures 1-1 and 1-2, H₂S partial pressures equal 0.83 kPa, 8.3 kPa and 69 kPa were representative of the H₂S concentrations at the depth below 5000 m if using the total pressure as 83 MPa. These three H₂S partial pressures spanned over three orders of magnitude, which was a wide range for investigation on H₂S corrosion in deep and ultra-deep wells.

Two temperatures were used for the corrosion study for high temperature tests: 85 °C and 200 °C. As shown in Figure 1-1, 85 °C is roughly the high temperature end of the current industry capability, which would make a good starting point for corrosion when it goes to deep wells. 200 °C can be representative of the temperature in the ultra-deep wells. Due to the challenges to conduct tests at higher temperature, the corrosion data at 200 °C could provide valuable information in H₂S corrosion. Considering Arctic drilling and the temperature in deep water, 4 °C was chosen as the test temperature.

The corrosion rate at steady state was compared among different conditions to control the time scale effect. The flow effect was comparable between tests because of the consistent system setup design, and the mass transport effect was studied by changing the stir rate.

### 1.5 Content of each chapter

In Chapter 2, the electrochemical corrosion behavior of grade S-135 steel at 85 °C was investigated in alkaline brines at pH of 7.9, 10.7, and 12.4 with four H₂S partial pressure ($P_{\text{H}_2\text{S}}$) ranging from 0 to 69 kPa. Grade S-135 was a high-strength low-alloy carbon steel which is commonly used as drill pipe in the oil and natural gas industry. The corrosion rate was determined using electrochemical methods and was compared with modeling results. The primary reactive species, Pourbaix diagram, and surface analysis were studied to understand the reactions
and the formation of the corrosion products. This study on a wide range of pH and \( P_{\text{H}_{2}\text{S}} \) provided an encompassing view of corrosion behavior of carbon steel in alkaline brines.

Chapters 3 and 4 covered the electrochemical corrosion behavior of grade UD-165 steel at 85 °C in the same conditions as grade S-135, which was in a pH range of 7.9, 10.7, and 12.4 with \( P_{\text{H}_{2}\text{S}} \) of 0, 0.83, 8.3 and 69 kPa. Grade UD-165 is a newly designed ultra-high-strength low-alloy carbon steel specially for ultra-deep drilling. Beyond the corrosion rate and corrosion products analyses, the reaction mechanisms were further studied through Tafel analysis and electrochemical impedance spectroscopy. The effect of H\(_2\)S was first determined by comparison between \( P_{\text{H}_{2}\text{S}} \) 0 and 8.3 kPa in Chapter 3, and then the \( P_{\text{H}_{2}\text{S}} \) range was extended to 0.83 and 69 kPa in Chapter 4.

In Chapter 5, electrochemical corrosion of UD-165 was studied at higher temperature, 200 °C, which was simulating the drilling condition at Gulf of Mexico. The solution compositions were the same as at 85 °C in the previous chapters, and the pH was calculated to be pH 8 to 11 in the presence of \( P_{\text{H}_{2}\text{S}} \) 69 kPa. The effects of high pH and high temperature were determined on the corrosion rate and corrosion products to understand the H\(_2\)S corrosion mechanism in drilling fluid conditions. The solution speciation, Pourbaix diagram, and the corrosion rate were calculated with commercial software at 200 °C. The generalized Butler-Volmer equation was employed to analyze LSV data to study the reaction mechanisms.

In Chapter 6, the corrosion behaviors of S-135 and UD-165 were studied at lower temperature, 4 °C, representative of Arctic drilling environments. The tests investigated corrosion in 5%wt. NaCl(aq) at equilibrium with CO\(_2\) only, H\(_2\)S only, or a mixed gas with a CO\(_2\):H\(_2\)S ratio of 1000 at 4 °C and 10 MPa total pressure. Without the pH buffers, the dissolution of acidic gases put the solution pH into acidic region. Besides the corrosion results, the emphasis was put on the transition from sweet (CO\(_2\)) corrosion to sour (H\(_2\)S) corrosion, which had the industrial value to illuminate material selection and corrosion mitigation strategy.
Chapter 7 is the summary of the principal conclusions in this dissertation. The suggestions on future work are also included.

In order to maintain the integrity, each chapter is included in this dissertation with the same content as a paper. Some repetition may be found in the experimental and theoretical sections and modeling results in Chapters 2 to 4 due to the consistency in experimental setup and test conditions.

References

Chapter 2

Electrochemical Corrosion Behavior of High Strength Carbon Steel S-135 in H$_2$S-Containing Alkaline Brines

This chapter presents the research results on corrosion of S-135 at pH 7.9, 10.7, and 12.4 at 85 °C with $P_{H_2S}$ from 0 to 69 kPa. The effects of pH and $P_{H_2S}$ were investigated through a wide range of pH and $P_{H_2S}$. The corrosion rate was determined using in situ electrochemical methods and was compared with modeling results. The primary reactive species, Pourbaix diagram, and surface analysis were studied to understand the corrosion process.

Abstract

The electrochemical corrosion behavior of high-strength low-alloy (HSLA) carbon steel, Grade S-135 was investigated using electrochemical measurements, surface analyses, and software modeling in alkaline brines at pH of 7.9, 10.7, and 12.4 and four $H_2S$ partial pressures ($P_{H_2S}$) from 0 to 69 kPa at 85 °C. HS (aq) was calculated to be the dominant sulfide species from pH 7.9 to 12.4. After 60 hours, polarization resistance ($R_{pol}$) increased as pH increased at $P_{H_2S}$ 0 and 0.83 kPa, whereas $R_{pol}$ decreased and then increased as pH increased at $P_{H_2S}$ 8.3 and 69 kPa. At each pH, the lower $P_{H_2S}$ increased $R_{pol}$ or did not significantly change $R_{pol}$ and the higher $P_{H_2S}$ decreased $R_{pol}$. The highest corrosion rate (CR) was 0.26 mm y$^{-1}$ at pH = 10.7 with $P_{H_2S}$ 69 kPa, and the lowest CR was 0.0053 mm y$^{-1}$ at pH 12.4 with $P_{H_2S}$ 0.83 kPa. The electrochemical

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1 The text in this chapter was originally prepared for the publication as “Ruishu Feng, Justin Beck, Aysel Buyuksagis, Ian Wolfe, Rosemary Cianni, Margaret Ziomek-Moroz, and Serguei Lvov. Electrochemical Corrosion Behavior of High Strength Carbon Steel in $H_2S$-Containing Alkaline Brines. Journal of The Electrochemical Society, in review.”
impedance did not change significantly at different stir rates, indicating that mass transport of reactive species in the bulk solution was not the rate determining step. The corrosion products generally changed from iron carbonate and sulfides to iron oxide as pH increased, which agreed with the Pourbaix diagrams.

2.1 Introduction

High-strength low-alloy (HSLA) carbon steel, Grade S-135, is commonly used for drill pipes in the natural gas and oil industry due to its high strength/weight ratio and economical cost. Acid gas H$_2$S has been found to make carbon steels more susceptible to hydrogen induced cracking (HIC) / sulfide stress cracking (SSC) in addition to accelerating general and localized corrosion\textsuperscript{1–4}. With the offshore exploration going deeper, the environment in deep and ultra-deep wells become more aggressive, which includes high-pressure, high-temperature, and high H$_2$S and CO$_2$ concentrations. Literature data indicate that the concentration of H$_2$S(aq) increases exponentially with depth\textsuperscript{1}. Corrosion caused by H$_2$S, called sour corrosion, could cause catastrophic failure of the drill pipes and increase the cost drastically.

Sour corrosion of oil country tubular goods (OCTGs) has been intensively studied mainly in acidic to neutral conditions\textsuperscript{5–15}. In practice, a drilling fluid treated to a pH between 10 and 12 is used to flow through the drill pipe to inhibit corrosion. Therefore, the corrosive environment during the drilling operation can be in alkaline conditions, in which corrosion behaviors of materials need to be studied.

H$_2$S could impact the Faradaic reactions and the corrosion products. For the cathodic reaction, H$_2$S could decrease the pH through dissociation and provide an additional reaction path\textsuperscript{14,16}. For anodic reaction, it has been proposed that HS (aq) could specifically adsorb on the steel surface and react with Fe\textsuperscript{16}. In the presence of H$^+$ (aq), H$_2$S(aq) could be regenerated and have a
catalytic effect on corrosion. In other cases, H$_2$S(aq) could be consumed directly by producing iron sulfides as the corrosion products. The protectiveness of corrosion products was found to influence the corrosion rate $^7$. Thus, the presence of H$_2$S could have an accelerating or inhibiting effect on the corrosion rate, depending on $P_{\text{H}_2\text{S}}$, pH, and temperature. In this work, a wide range of $P_{\text{H}_2\text{S}}$ was investigated from 0 to 69 kPa to better understand the corrosion in alkaline conditions.

The effects of $P_{\text{H}_2\text{S}}$, pH, and formation of corrosion products were investigated using in-situ electrochemical measurements, ex-situ surface analyses, and software modeling in alkaline brines at pH of 7.9, 10.7, and 12.4 with four $P_{\text{H}_2\text{S}}$ from 0 to 69 kPa at 85 °C. The primary species, CR, and Pourbaix diagrams were calculated with OLI Analyzer software for comparison with the experimental data.

2.2 Experimental

2.2.1 Materials and preparation

The steel investigated in this study was Grade S-135, a high-strength low-alloy carbon steel, which is used for drilling in the oil and natural gas industry. The chemical composition of the S-135 steel is given in Table 2-1. $^{18}$

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Al</th>
<th>Ni</th>
<th>Cu</th>
<th>Nb</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal</td>
<td>1.39</td>
<td>0.78</td>
<td>0.68</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-1. Chemical composition (%wt.) of S-135. $^{18}$
The steel was machined to plate samples with the dimensions of 10×20×5 mm. The plate samples were coated with an epoxy over all the surfaces except for one of the 10×20 mm faces, which was exposed to the test solutions and faced the counter electrode. The exposed surface was ground with 600, 800, and 1200 grit SiC papers and then polished by 0.1 and 0.05 microns alumina polishing slurries until a mirror finish was observed so that the surface defects were minimized and the surface area was kept consistent. The steel electrode was cleaned with propanol and distilled water and then wiped dry with lint-free wipes. The wire attached to the steel samples were coated with shrinkable polytetrafluoroethylene (PTFE) tubing to protect the leads and to avoid short circuit with the autoclave vessel.

2.2.2 System setup

The electrochemical measurements were performed using a three-electrode setup in the autoclave vessel. The working electrode was the prepared steel sample as described earlier, and the counter electrode was a platinum plate with the dimensions of 10×20×1 mm, which was coated with epoxy similarly to working electrodes. All of the wires attached to the electrodes were covered with PTFE shrinkable tubing. The two electrodes were held in parallel between two PTFE plates, and the polished surfaces were facing each other with the spacing of 10 mm. Two PTFE-coated screws were used to tighten the PTFE plates.

A double junction Ag/AgCl electrode was used as the reference electrode to minimize contamination from the corrosive test solutions. The fill solution for the outer junction was 5 \%wt. NaCl(aq) solution to minimize the junction potential difference from the concentration gradient between the reference electrode and the test solutions. The diffusion potential between the reference electrode and the test solutions were calculated according to the Henderson
equation\textsuperscript{19}, and the values were within 1.5 mV. More details about the reference electrode can be found in Reference 20.

The autoclave was Parr 4560, which consisted of a 600 mL stainless steel reactor vessel, a PTFE liner which was used to contain the corrosive test solution, and the autoclave lid. Mounted in the lid were a thermocouple, a pressure transducer, and a plastic tube for the injections of gas and solution. The thermocouple was protected from corrosion with a polymer coating. A heating mantle connected to a controller was used to control the temperature. The stainless steel stir rod and impeller inside the vessel were coated with epoxy to prevent undesired corrosion. PTFE compression glands were used to seal the wires coming out from the vessel. A schematic diagram of the autoclave is shown in Figure 2-1\textsuperscript{20}. The system temperature and pressure were recorded over the corrosion test using a computer. Electrochemical measurements were performed using Gamry Reference 600 potentiostat.

Figure 2-1. Schematic diagram of the autoclave system. 1- Connection to pressure transducer; 2- Heating mantle; 3- Autoclave stainless steel vessel; 4- PTFE liner; 5- Polymer-coated thermocouple; 6- Plastic tubing; 7- Epoxy-coated stirrer; 8- PTFE-coated lead wires; 9- Ag/AgCl reference electrode; 10- PTFE assembly; 11- working electrode; 12- Pt counter electrode; 13- H\textsubscript{2}S/N\textsubscript{2} cylinder.
2.2.3 Test solutions and experimental procedure

The system temperature was held at 85 °C. The test solutions were 5 %wt. (0.9 mol kg\(^{-1}\)) NaCl solutions buffered with NaHCO\(_3\)/Na\(_2\)CO\(_3\)/NaOH. The compositions of test solutions are given in Table 2-2, and the solution pH in different conditions were calculated with OLI Analyzer software.\(^{21}\) From Solution #1 to #3 at \(P_{\text{H}_2\text{S}} = 0\) kPa, pH increased from 7.9 to 12.4. The dissociation of H\(_2\)S would decrease the pH slightly, but the pH was not predicted to change significantly until \(P_{\text{H}_2\text{S}}\) was increased to 69 kPa. Note that when discussing the pH dependence, the pH at \(P_{\text{H}_2\text{S}} = 0\) kPa was used to represent each solution.

<table>
<thead>
<tr>
<th>Soln.</th>
<th>NaCl</th>
<th>NaHCO(_3)</th>
<th>Na(_2)CO(_3)</th>
<th>NaOH</th>
<th>pH, (P_{\text{H}_2\text{S}} = 0)</th>
<th>pH, (P_{\text{H}_2\text{S}} = 0.83)</th>
<th>pH, (P_{\text{H}_2\text{S}} = 8.3)</th>
<th>pH, (P_{\text{H}_2\text{S}} = 69)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.9</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>7.9</td>
<td>7.9</td>
<td>7.9</td>
<td>7.7</td>
</tr>
<tr>
<td>#2</td>
<td>0.9</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>10.7</td>
<td>10.7</td>
<td>10.7</td>
<td>10.5</td>
</tr>
<tr>
<td>#3</td>
<td>0.9</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
</tr>
</tbody>
</table>

All of the solutions were prepared with 250 g deionized water, and then were deaerated by bubbling with N\(_2\) or Ar for at least one hour. The deaerated solution was injected into the deaerated autoclave vessel through the plastic tubing (No. 6 in Figure 2-1). When the system was heated up to 85 °C, a H\(_2\)S/N\(_2\) mixture gas (10%vol. H\(_2\)S) was slowly added into the solution through the plastic tubing. The autoclave was well-sealed when \(P_{\text{H}_2\text{S}}\) achieved the target partial pressure (0.83 kPa, 8.3 kPa, and 69 kPa). The amount of H\(_2\)S in the closed autoclave was estimated by the ideal gas law. The available volume in the reactor vessel was measured to be 236.3 mL after the solution injection. Thus, the total H\(_2\)S concentrations were calculated to be \(2.63\times10^{-4}\) mol kg\(^{-1}\), \(2.63\times10^{-3}\) mol kg\(^{-1}\), and \(2.19\times10^{-2}\) mol kg\(^{-1}\), respectively.
The in situ electrochemical measurements were performed every two hours over the corrosion test, which included linear polarization resistance (LPR), electrochemical frequency modulation (EFM), and electrochemical impedance spectroscopy (EIS). LPR was measured with the sweep rate of 1 mV s$^{-1}$ over the potential range of ± 20 mV around the measured open circuit potential (OCP). EFM was measured with 25 mV as the amplitude around the OCP at the base frequency of 0.01 Hz with multipliers of 2 and 5. EIS was measured within ±10 mV around the OCP at least over the frequency from 300 kHz to 5 mHz. After 60 hours, the same measurements were performed at reduced stir rates. After the corrosion tests, the corroded surfaces were examined using scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS).

### 2.2.4 Calculation of corrosion rate

In a three-electrode cell, when the corrosion is under activation control and a small polarization is applied, the corrosion current density, $j_{\text{corr}}$, can be calculated according to Stern-Geary equation shown in Equations [2-1] and [2-2].

$$j_{\text{corr}} = \frac{1}{(R_{\text{pol}} B')}$$  \hspace{1cm} [2-1]

$$B' = (\ln 10) \left( \frac{b_c + b_a}{b_c b_a} \right)$$  \hspace{1cm} [2-2]

where $R_{\text{pol}}$ is the area specific polarization resistance and $B'$ is a combination of the cathodic, $b_c$, and anodic, $b_a$, Tafel slopes. $R_{\text{pol}}$ was measured from LPR and corrected for the area-specific solution resistance ($R_{\text{sol}}$) obtained from EIS, and the Tafel slopes were obtained from EFM.

The corrosion rate (CR), defined as the depth of uniform corrosion penetration per time, can be calculated following Equation [2-3].
\[ CR = \frac{j_{\text{corr}} M}{n F \rho} \]  \[2-3\]

where \( M \) is the molecular mass of the corroding metal, \( n \) is the electron number being transferred, \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), and \( \rho \) is the metal density.

### 2.3 Results and Discussion

#### 2.3.1 Primary carbonate and sulfide species

The speciation of carbonate and sulfide species in the NaCl(aq)-based solutions given in Table 2-2 were calculated using OLI Analyzer software.\(^{21}\) Figure 2-2 shows the concentrations of primary carbonate species in the three solutions at \( P_{\text{H}_{2}\text{S}} = 0 \) kPa and 69 kPa at 85 °C. As pH increased, the concentrations of \( \text{CO}_2^{\text{aq}} \) and \( \text{HCO}_3^{-}\text{(aq)} \) decreased whereas \( \text{CO}_3^{2-}\text{(aq)} \) increased at \( P_{\text{H}_{2}\text{S}} = 0 \) kPa and 69 kPa. The addition of the largest \( P_{\text{H}_{2}\text{S}} \) (69 kPa) only slightly influenced the concentrations of carbonate species due to the effect on the pH, and the effects of the other two lower \( P_{\text{H}_{2}\text{S}} \) (0.83 and 8.3 kPa) were even smaller. Therefore, the primary carbonate species were similar at different \( P_{\text{H}_{2}\text{S}} \).

Figure 2-3 shows the concentrations of primary sulfide species in the three solutions at \( P_{\text{H}_{2}\text{S}} = 0.83 \) kPa and 69 kPa at 85 °C. For both \( P_{\text{H}_{2}\text{S}} = 0.83 \) kPa and 69 kPa, the concentration of \( \text{H}_2\text{S}^{\text{aq}} \) decreased whereas \( \text{S}^{2-}\text{(aq)} \) increased as pH increased. \( \text{HS}^{\text{aq}} \) was the dominant sulfide species from pH 7.9 to 12.4, and its concentration was comparable among different pH. The dissociation of sulfide species was similar at different \( P_{\text{H}_{2}\text{S}} \), but the total \( \text{H}_2\text{S} \) concentration was different. For example, all of the sulfide species were roughly two orders of magnitude higher at \( P_{\text{H}_{2}\text{S}} = 69 \) kPa than at \( P_{\text{H}_{2}\text{S}} = 0.83 \) kPa.
Figure 2-2. The primary carbonate species in the three solutions at $P_{H_2S} = 0$ kPa and 69 kPa at 85 °C. (Soln. #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Soln. #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).

Figure 2-3. The primary sulfide species in the three solutions at $P_{H_2S} = 0.83$ kPa and 69 kPa at 85 °C. (Soln. #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Soln. #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).
It has been proposed that OH\(^{-}\)(aq), HCO\(_3\)^{-}(aq), and HS\(^{-}\)(aq) could react with Fe(s) for the anodic reactions\(^{16,24-26}\). The dominant reaction paths depended on the concentrations and surface coverage of the reactive species. The calculated concentrations of OH\(^{-}\)(aq), HCO\(_3\)^{-}(aq), and HS\(^{-}\)(aq) are listed in Table 2-3, and the dominant reactive ions in each condition are highlighted in bold and italicized. The ratios of HS\(^{-}\)(aq) over the total amount of OH\(^{-}\)(aq), HCO\(_3\)^{-}(aq), and HS\(^{-}\)(aq) are also listed in Table 2-3. The dominant reactive species generally changed from HCO\(_3\)^{-}(aq) to OH\(^{-}\)(aq) as pH increased while the concentrations of HS\(^{-}\)(aq) were comparable among the three solutions. In Solution #2, the reactive ions were most diverse among the three solutions with at least two dominant reactive ions of comparable concentrations. For example, OH\(^{-}\)(aq) and HCO\(_3\)^{-}(aq) were the dominant reactive ions at \(P_{H2S} = 0\) kPa and 0.83 kPa, and OH\(^{-}\)(aq), HCO\(_3\)^{-}(aq), and HS\(^{-}\)(aq) at \(P_{H2S} = 8.3\) kPa and 69 kPa. The ratio of HS\(^{-}\)(aq) was the largest in Solution #2 at each \(P_{H2S}\).

Table 2-3. The concentrations (mol kg\(^{-1}\)) of reactive ions calculated with OLI Analyzer software.

<table>
<thead>
<tr>
<th>(P_{H2S})</th>
<th>Solution</th>
<th>OH(^{-})(aq)</th>
<th>HCO(_3)^{-}(aq)</th>
<th>HS(^{-})(aq)</th>
<th>HS(^{-})(aq) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 kPa</td>
<td>#1</td>
<td>4.20×10(^{-5})</td>
<td>4.57×10(^{-1})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>2.35×10(^{-2})</td>
<td>2.43×10(^{-2})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>9.63×10(^{-1})</td>
<td>5.16×10(^{-4})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.83 kPa</td>
<td>#1</td>
<td>4.18×10(^{-5})</td>
<td>4.57×10(^{-1})</td>
<td>2.48×10(^{-4})</td>
<td>0.00054</td>
</tr>
<tr>
<td></td>
<td>#2</td>
<td>2.33×10(^{-2})</td>
<td>2.44×10(^{-2})</td>
<td>2.62×10(^{-4})</td>
<td>0.0055</td>
</tr>
<tr>
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2.3.2 Corrosion potential \( (E_{\text{corr}}) \)

The anodic reaction for corrosion is the oxidation of \( \text{Fe}(s) \), and the cathodic reactions are HER and its variations with different hydrogen sources. Reactions [2-4] - [2-7] show the examples of the relevant reactions in the reduction direction. The standard electrode potential, \( E^0 \), at 85 °C was calculated using the Gibbs free energy values from HCh simulation software and OLI Analyzer software\textsuperscript{27,28}. The Nernst equations for each reaction are shown in Equations [2-8] - [2-11]. The symbol \( a \) represents the activity of ionic species, \( P_{\text{H}_2(g)} \) represents the partial pressure of \( \text{H}_2(g) \) and the fugacity coefficient is assumed to be unity.

\[
\text{Fe}^{2+}(\text{aq}) + 2 \, \text{e}^- = \text{Fe}(s) \quad E^0 = -0.473 \text{ V vs SHE, 85 °C} \quad [2-4]
\]

\[
2 \, \text{H}^+(\text{aq}) + 2 \, \text{e}^- = \text{H}_2(\text{g}) \quad E^0 = 0 \text{ V vs SHE, 85 °C} \quad [2-5]
\]

\[
2 \, \text{H}_2\text{O}(l) + 2 \, \text{e}^- = \text{H}_2(\text{g}) + 2 \, \text{OH}^-(\text{aq}) \quad E^0 = -0.890 \text{ V vs SHE, 85 °C} \quad [2-6]
\]

\[
2 \, \text{H}_2\text{S}(\text{aq}) + 2 \, \text{e}^- = \text{H}_2(\text{g}) + 2 \, \text{HS}^-(\text{aq}) \quad E^0 = -0.463 \text{ V vs SHE, 85 °C} \quad [2-7]
\]

\[
E_{\text{Fe}^{2+}|\text{Fe}} = E^0_{\text{Fe}^{2+}|\text{Fe}} + \frac{RT}{2F} \ln a_{\text{Fe}^{2+}(\text{aq})} \quad [2-8]
\]

\[
E_{\text{H}^+|\text{H}_2} = E^0_{\text{H}^+|\text{H}_2} + \frac{RT}{2F} \ln \frac{a_{\text{H}^+(\text{aq})}}{P_{\text{H}_2(\text{g})}} \quad [2-9]
\]

\[
E_{\text{H}_2\text{O}|\text{H}_2} = E^0_{\text{H}_2\text{O}|\text{H}_2} + \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}(l)}}{a_{\text{OH}^-(\text{aq})} P_{\text{H}_2(\text{g})}} \quad [2-10]
\]

\[
E_{\text{H}_2\text{S}|\text{H}_2} = E^0_{\text{H}_2\text{S}|\text{H}_2} + \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{S}(\text{aq})}}{a_{\text{HS}^-(\text{aq})} P_{\text{H}_2(\text{g})}} \quad [2-11]
\]

\( E_{\text{corr}} \) is the mixed potential on the corroding steel which was measured as the open circuit potential (OCP) during the corrosion tests. The OCP was measured with respect to the Ag/AgCl reference electrode and converted to the standard hydrogen electrode (SHE) scale at 85 °C. \( E_{\text{corr}} \)
changing with time for $P_{\text{H}_2\text{S}} = 0 \text{ kPa}$ and 69 kPa are shown as examples in Figure 2-4. $E_{\text{corr}}$ generally increased with time and then was approaching or achieved the steady state by 60 hours. Due to the Fe dissolution during corrosion, the increasing concentration of Fe$^{2+}$ (aq) increased the potential in Equation [2-8]. $E_{\text{corr}}$ in the three solutions at $P_{\text{H}_2\text{S}} = 0 \text{ kPa}$ were more positive than those at $P_{\text{H}_2\text{S}} = 69 \text{ kPa}$. At $P_{\text{H}_2\text{S}} = 69 \text{ kPa}$, $E_{\text{corr}}$ became more negative as pH increased, which was due to the increasing OH$^-$ (aq) concentration and decreasing H$_2$S(aq) and H$^+$ (aq) concentrations in Equations [2-9] - [2-11].

Figure 2-4. $E_{\text{corr}}$ changing with time in the three solutions at $P_{\text{H}_2\text{S}} = 0 \text{ kPa}$ and 69 kPa at 85 °C. (Soln. #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Soln. #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).

2.3.3 Polarization resistance and corrosion rate

$R_{\text{pol}}$ was measured over time using LPR and corrected for $R_{\text{sol}}$. Figures 2-5 to 2-7 depict $R_{\text{pol}}$ changing with time in the three solutions, respectively. $R_{\text{pol}}$ generally increased with time and was approaching or achieved the steady state by 60 hours in Solutions #1 and #3, except that $R_{\text{pol}}$
in Solution #1 at $P_{\text{H}_2\text{S}} = 69$ kPa slightly decreased. The increase of $R_{\text{pol}}$ could be attributed to the formation of corrosion products causing a decrease in active steel surface area. Once the formation and the dissolution of the corrosion product layers became balanced, $R_{\text{pol}}$ approached the steady state. Inversely, the corrosion rate generally decreased over time by 60 hours. Different from the general trend in Solutions #1 and #3, in Solution #2 $R_{\text{pol}}$ decreased in varying degrees at different $P_{\text{H}_2\text{S}}$ after the initial increase during the early 12 to 24 hours. A similar trend was also observed in Solution #1 at $P_{\text{H}_2\text{S}} = 69$ kPa. The decrease of $R_{\text{pol}}$ after an initial increase could be related to the occurrence of localized corrosion due to the defects in the non-homogeneous corrosion product layers formed during the early stage. The diverse reactive species present in Solution #2 participated in the multiple reaction paths and formation of different corrosion products. The non-homogeneity of corrosion products and the high HS$^-$ (aq) ratio were prone to trigger localized corrosion on the steel$^{29}$. After all of the fluctuations, $R_{\text{pol}}$ was approaching the steady state by 60 hours.

![Figure 2-5. $R_{\text{pol}}$ changing with time in Solution #1 at $P_{\text{H}_2\text{S}}$ = 0 kPa, 0.83 kPa, 8.3 kPa, and 69 kPa at 85 °C. (Soln. #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9).](image-url)
Figure 2-6. $R_{pol}$ changing with time in Solution #2 at $P_{H2S} = 0$ kPa, 0.83 kPa, 8.3 kPa, and 69 kPa at 85 °C. (Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7).

Figure 2-7. $R_{pol}$ changing with time in Solution #3 at $P_{H2S} = 0$ kPa, 0.83 kPa, 8.3 kPa, and 69 kPa at 85 °C. (Soln. #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).

$R_{pol}$ and the experimental CR after 60 hours were compared in all the conditions and are shown in Figures 2-8 and 2-9, respectively. At $P_{H2S} = 0$ kPa and 0.83 kPa, $R_{pol}$ increased as pH increased from 7.9 to 12.4. This trend could be related to the suppressed HER reactions at high
pH and presumably more protective corrosion product layers. At $P_{\text{H}_2\text{S}} = 8.3$ kPa and 69 kPa, $R_{\text{pol}}$ first decreased and then increased as pH increased. The pH dependence of $R_{\text{pol}}$ changed at relatively high $P_{\text{H}_2\text{S}}$. The divergence was attributed to the decrease of $R_{\text{pol}}$ in Solution #2 at $P_{\text{H}_2\text{S}} = 8.3$ kPa and 69 kPa, which might be due to the localized corrosion at higher $P_{\text{H}_2\text{S}}$. This corresponded to the decrease of $R_{\text{pol}}$ after an initial increase at higher $P_{\text{H}_2\text{S}}$ in Figure 2-6, which was considered as a characteristic of localized corrosion as discussed earlier. Besides the non-homogeneity on the steel surface, the ratio of HS (aq) was another factor which correlated with localized corrosion and small $R_{\text{pol}}$. Although the aqueous species were diverse and the corrosion products were non-homogeneous in Solution #2 for all of the $P_{\text{H}_2\text{S}}$, the ratio of HS (aq) did not become significant (>5%) until $P_{\text{H}_2\text{S}}$ increased to 8.3 kPa. The higher ratio of HS (aq) at higher $P_{\text{H}_2\text{S}}$ could have facilitated localized corrosion and might have led to a smaller $R_{\text{pol}}$ when the HS$^-$(aq) reaction path became more significant. $R_{\text{pol}}$ for HS (aq) reaction path may be smaller than $R_{\text{pol}}$ for the HCO$_3$ (aq) or OH (aq) reaction path.

![Graph showing $R_{\text{pol}}$ vs pH](image-url)  

Figure 2-8. $R_{\text{pol}}$ in the three solutions after 60 hours at $P_{\text{H}_2\text{S}} = 0$ kPa, 0.83 kPa, 8.3 kPa, and 69 kPa at 85 °C. (Soln. #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Soln. #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).
Figure 2-9. Experimental corrosion rates in the three solutions after 60 hours at $P_{\text{H}_2\text{S}} = 0$ kPa, 0.83 kPa, 8.3 kPa, and 69 kPa at 85 °C. (Soln. #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Soln. #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).

A pH dependence was observed for the effect of $P_{\text{H}_2\text{S}}$ on $R_{\text{pol}}$ after 60 hours. In Solution #1 with pH = 7.9, $R_{\text{pol}}$ increased as $P_{\text{H}_2\text{S}}$ increased from 0 to 8.3 kPa and then decreased at $P_{\text{H}_2\text{S}} = 69$ kPa. In Solution #2 with pH = 10.7, $R_{\text{pol}}$ slightly decreased as $P_{\text{H}_2\text{S}}$ increased from 0 to 8.3 kPa and then largely decreased by a factor of four at $P_{\text{H}_2\text{S}} = 69$ kPa. In Solution #3 with pH = 12.4, $R_{\text{pol}}$ increased at $P_{\text{H}_2\text{S}} = 0.83$ kPa and then decreased as $P_{\text{H}_2\text{S}}$ increased to 8.3 and 69 kPa. There were two opposite effects expected from H$_2$S, an accelerating effect due to H$_2$S(aq) and HS$^-$ (aq) facilitating the Faradaic reactions and localized corrosion$^{29,30}$, and an inhibiting effect due to the surface coverage and protectiveness of iron sulfides on the steel surface. In Solutions #1 and #3, the inhibiting effect was greater at lower $P_{\text{H}_2\text{S}}$ and the accelerating effect greater at higher $P_{\text{H}_2\text{S}}$. In Solution #2, the accelerating effect was more pronounced although to different extents, almost negligible at lower $P_{\text{H}_2\text{S}}$ and quite significant at the highest $P_{\text{H}_2\text{S}}$. 
It is worth noting that $R_{\text{pol}}$ after 60 hours in Solutions #2 and #3 did not significantly change when $P_{\text{H}_2\text{S}}$ increased from 0 to 8.3 kPa but decreased significantly at $P_{\text{H}_2\text{S}} = 69$ kPa. As a comprehensive result from both accelerating and inhibiting effects, the effect of $P_{\text{H}_2\text{S}}$ on $R_{\text{pol}}$ did not become significant until $P_{\text{H}_2\text{S}}$ increased to 69 kPa in Solutions #2 and #3. This trend was also observed in Figures 2-6 and 2-7. It appears that the high pH in Solutions #2 and #3 overwhelmed the effects of lower $P_{\text{H}_2\text{S}}$ (< 8.3 kPa) on the corrosion process. The experimental CRs shown in Figure 2-9 followed the inverse trend of $R_{\text{pol}}$, and the slight deviation was due to the Tafel slopes obtained from EFM. The fastest CR was 0.26 mm y$^{-1}$ in Solution #2 with $P_{\text{H}_2\text{S}} = 69$ kPa, and the slowest CR was 0.0053 mm y$^{-1}$ in Solution #3 with $P_{\text{H}_2\text{S}} = 0.83$ kPa.

Figure 2-10 shows the corrosion rates of generic carbon steel (G10100) calculated as a rotating disk electrode with OLI Analyzer. At each $P_{\text{H}_2\text{S}}$, the fastest CR was predicted to be in Solution #1 within 0.25 and 0.95 mm y$^{-1}$. At $P_{\text{H}_2\text{S}} = 0$ kPa and 0.83 kPa, the slowest CRs were in Solution #2 with the values of 0.003 mm y$^{-1}$ and 0.006 mm y$^{-1}$, respectively. At $P_{\text{H}_2\text{S}} = 8.3$ kPa and 69 kPa, the slowest CRs were in Solution #3 with the values of 0.012 mm y$^{-1}$ and 0.030 mm y$^{-1}$. According to the modeling, CR should have increased when $P_{\text{H}_2\text{S}}$ increased from 0 to 69 kPa in Solutions #1 and #2. In Solution #3, CR without H$_2$S was faster than those with H$_2$S, and CR still increased when $P_{\text{H}_2\text{S}}$ increased from 0.83 to 69 kPa. All of the trends were reasonable considering the accelerating effect of H$_2$S and the dominant corrosion products predicted from Pourbaix diagrams, which will be discussed later in detail. The modeled CR was generally higher than the experimental CR in Solution #1, lower in Solution #2, and in better agreement in Solution #3. The divergence could be attributed to the significance of kinetic factors over thermodynamic calculations. The kinetically favorable species could have formed on the steel surface before the most thermodynamically stable products were finally achieved. In Solution #1, iron carbonate and sulfide could have precipitated out on the steel surface due to oversaturation near the corroding surface, and these corrosion products could have lowered the corrosion rate
although only soluble species were predicted in the Pourbaix diagrams. In Solution #2, the non-
uniform corrosion products initially formed on the surface might not be inhibiting the corrosion;
on the contrary, the non-homogeneity on the surface could have facilitated the localized corrosion
and, therefore, accelerated CR.

![Graph showing modeled corrosion rates for solutions with different pH levels and H2S pressures.]

Figure 2-10. Modeled corrosion rates of generic carbon steel calculated with OLI Analyzer in the
three solutions at $P_{\text{H2S}} = 0$ kPa, 0.83 kPa, 8.3 kPa, and 69 kPa at 85 °C. (Soln. #1: 0.9 mol kg$^{-1}$ NaCl,
0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Soln.
#3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).

2.3.4 The effect of stir rate

After 60 hours, the Nyquist plots at different stir rates in Solution #2 at $P_{\text{H2S}} = 69$ kPa are
shown in Figure 2-11. The plots were nearly identical at different stir rates, indicating that mass
transport in the bulk solution did not influence the rate determining step for the overall corrosion
process. This also means that the corrosion process was not limited by concentration polarization.
Similar results were found in the other conditions.
Figure 2-11. The Nyquist plots of S-135 after 60 hours at different stir rates in Solution #2 at $P_{\text{H}_2\text{S}} = 69$ kPa at 85 °C. (Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.5).

2.3.5 EIS behavior

Phase angles of electrochemical impedance in all the conditions were compared after 60 hours and are shown in Figure 2-12. In Solution #2, there were two separated time constants for all of the $P_{\text{H}_2\text{S}}$. In Solutions #1 and #3, two time constants appeared at higher $P_{\text{H}_2\text{S}}$ (8.3 kPa and 69 kPa). Correlating the EIS behavior with the speciation in Table 2-3, when there were two or three dominant reactive species predicted in the solutions, two separated time constants tended to appear in the corresponding phase angle plots. The correlation may be attributed to multiple reaction paths and higher HS (aq) ratio. The maximum phase angle at low frequency was beyond -45 ° which was corresponding to the Warburg element, confirming that diffusion was not affecting the corrosion process$^{31}$. 
Figure 2-12. Phase angles of Bode plots for S-135 after 60 hours in the three solutions at $P_{\text{H}_2\text{S}} = 0$ kPa, 0.83 kPa, 8.3 kPa, and 69 kPa at 85 °C. (Soln. #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Soln. #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).
2.3.6 Corrosion products

The corrosion products were predicted in Pourbaix diagrams obtained using OLI Analyzer software\textsuperscript{32–34}. Figures 2-13 to 2-15 show the Pourbaix diagrams in Solution #2 with $P_{\text{H}_2\text{S}}$ = 0 kPa, 8.3 kPa, and 69 kPa, respectively. The Pourbaix diagrams in Solutions #1 and #3 were similar. With the increase of $P_{\text{H}_2\text{S}}$, the stable regions of iron sulfides became larger. The Pourbaix diagram at $P_{\text{H}_2\text{S}}$ = 0.83 kPa was in the transition between Figures 2-13 and 2-14 and can be found in the authors’ previous work\textsuperscript{35}.

In the Fe-H$_2$O-H$_2$CO$_3$ system without H$_2$S, the thermodynamically dominant species changed from soluble FeH(CO$_3$)$_2$(aq) to FeCO$_3$(s)/Fe$_3$O$_4$(s) to HFeO$_2$(aq)/Fe$_3$O$_4$(s) when pH increased from 7.9 to 12.4. The trend of changing from carbonate-containing species to hydroxide/oxide was in accordance to the Pourbaix diagram calculation from other researchers.\textsuperscript{36,37} In the Fe-H$_2$O-H$_2$CO$_3$-H$_2$S system at $P_{\text{H}_2\text{S}}$=8.3 kPa, the thermodynamically dominant species changed from FeS(s)/FeS$_2$(s)/FeH(CO$_3$)$_2$(aq) to FeS(s)/FeS$_2$(s)/Fe$_3$O$_4$(s) to HFeO$_2$(aq)/Fe$_3$O$_4$(s) when pH increased from 7.9 to 12.4. It was similar at $P_{\text{H}_2\text{S}}$ = 69 kPa only with FeS(s)/Fe$_3$O$_4$(s) being stable at pH = 12.4 due to the expansion of FeS(s) region. The thermodynamically dominant species corresponded to the dominant reactive species in Table 2-3, which changed from HCO$_3^-$(aq) and HS$^-$(aq) to OH$^-$(aq) as pH increased. The Pourbaix diagrams of Fe-H$_2$O-H$_2$CO$_3$-H$_2$S system constructed by other researchers showed similar trends with potential and pH although the specific conditions like pH or concentrations were different, and the stable phases of iron sulfides were also studied by some researchers using Pourbaix diagrams.\textsuperscript{32,38,39} As discussed earlier, the modeled CR was lower in the region where solid species were predicted to be dominant than where soluble species were dominant. However, the complex kinetic factors should also be taken into account, like localized corrosion, metastable species, and the divergence between the surface and bulk concentrations of reactive species.
Figure 2-13. Pourbaix diagram of Fe-H$_2$O-H$_2$CO$_3$ system in Soln. #2 without H$_2$S at 85 °C. (Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Titrants: NaOH/HCl).

Figure 2-14. Pourbaix diagram of Fe-H$_2$O-H$_2$CO$_3$-H$_2$S system in Soln. #2 at $P_{H_2S} = 8.3$ kPa at 85 °C. (Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Titrants: NaOH/HCl).
The corroded surfaces after the tests at $P_{\text{H}_2\text{S}} = 8.3$ kPa and 69 kPa were analyzed with SEM and EDS. The back-scattered electron images are shown in Figures 2-16 and 2-17, respectively. EDS spot analyses were performed at representative spots which are marked in the images, and the results are given in Table 2-4. The accelerating voltage was 7 kV for the EDS analysis to avoid penetrating too deep into the substrate and stimulating undesired signals from the underlying steel.
Figure 2-16. The back-scattered electron images of the corroded surfaces of S-135 at $P_{\text{H}_2\text{S}} = 8.3$ kPa at 85 °C. (a1, a2: Soln. #1, 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; b: Soln. #2, 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; c: Soln. #3, 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).
At $P_{\text{H}_2\text{S}} = 8.3$ kPa, the amount of S was detectable but was quite low. Fe, C, O, and S were detected in all of the three solutions, indicating that a mixture of iron carbonate, iron sulfides, and iron oxides were probably formed on the steel surfaces. However, the morphology and the dominant corrosion products varied among the three solutions.
Table 2-4. EDS chemical analyses (%at.) on the corroded S-135 surfaces.

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<tr>
<td></td>
<td></td>
<td>1</td>
<td>19.71</td>
<td>9.13</td>
<td>64.58</td>
<td>5.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td># 1</td>
<td>a 2</td>
<td>11.12</td>
<td>3.33</td>
<td>55.42</td>
<td>30.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>25.34</td>
<td>15.20</td>
<td>54.35</td>
<td>2.54</td>
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<td></td>
<td></td>
<td>4</td>
<td>33.09</td>
<td>6.76</td>
<td>48.98</td>
<td>6.38</td>
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<tr>
<td>2-17</td>
<td>69</td>
<td>1</td>
<td>30.61</td>
<td>10.24</td>
<td>41.10</td>
<td>16.26</td>
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<tr>
<td></td>
<td></td>
<td># 2</td>
<td>2</td>
<td>42.72</td>
<td>3.26</td>
<td>44.02</td>
<td>5.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>b 3</td>
<td>61.97</td>
<td>3.18</td>
<td>27.69</td>
<td>3.10</td>
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<tr>
<td></td>
<td></td>
<td>4</td>
<td>25.50</td>
<td>5.73</td>
<td>55.62</td>
<td>8.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>32.33</td>
<td>1.94</td>
<td>48.49</td>
<td>9.08</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td># 3</td>
<td>c 2</td>
<td>54.94</td>
<td>3.35</td>
<td>36.63</td>
<td>4.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>27.27</td>
<td>10.63</td>
<td>43.91</td>
<td>8.69</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Solution #1, the corrosion product layers were thick and porous, which was probably due to comparatively fast corrosion and formation of corrosion products through direct reaction.
and precipitation. The corrosion products decreased the reactive surface area and served as a barrier for corrosion, which correlated to a comparatively large $R_{pol}$. Location 1 in Figure 2-16(a1) was a ball-like structure consisting of cubic crystals, which had a chemical composition similar to FeCO$_3$(s). Similar structure of different sizes were observed over the steel surface in Solution #1. Between the FeCO$_3$(s)-like crystalline structures, there were other structures with a composition of lower C, higher O, and a small amount of S (0.5-3.6 %at.). They appeared as amorphous structures, thin plate-like structures, and star-like structures as shown in Images a1 and a2 in Figure 2-16.

In Solution #2, there was a non-homogenous thin film of corrosion products on the steel surface. According to Figure 2-6, $R_{pol}$ in Solution #2 at $P_{H2S} = 8.3$ kPa increased and stayed at a quite large value during the first 24 hours, which corresponded to a slow CR and resulted in this thin film. Multiple reactive species in Solution #2 are believed to have resulted in the non-homogeneity of the film and have triggered localized corrosion, which correlated to the decrease of $R_{pol}$ after 24 hours. Without thick layers of corrosion products and with the possibility of localized corrosion, $R_{pol}$ in Solution #2 was the smallest among the three solutions after 60 hours.

In Solution #3, the chemical composition on the surface was very close to Fe$_3$O$_4$(s). There were mainly two regions on the surface as shown in Figure 2-16(c), the flat region and the outstanding region. The corrosion products in the flat region were relatively uniform and dense, which might be more protective. The outstanding region seemed to be a localized corrosion region with more corrosion products than the flat region. According to Figure 2-8, $R_{pol}$ was the largest in Solution #3 for $P_{H2S} = 8.3$ kPa, which was probably due to the protective film and the localized corrosion being blocked. The Fe$_3$O$_4$(s)-like products in Solution #3 agreed with the prediction from Pourbaix diagram at pH = 12.4.

At $P_{H2S} = 69$ kPa, the amount of S was larger than that at $P_{H2S} = 8.3$ kPa according to the EDS analysis results in Table 2-4. The chemical compositions also indicated a combination of
iron carbonate, iron sulfide, and iron oxide in the three solutions. As shown in Figure 2-8, the pH
dependence of $R_{\text{pol}}$ at $P_{\text{H}_2\text{S}} = 69$ kPa was similar to $P_{\text{H}_2\text{S}} = 8.3$ kPa, and the corroded surfaces
followed a similar trend as pH increased. In Solution #1, a relatively thick layer of corrosion
products was observed on the corroded steel surface. There were some ball-like structures
aggregated from cubic crystals with the chemical composition similar to FeCO$_3$(s), like Location
3 in Figure 2-17(a). There were other locations with higher concentrations of O or S in the layer.
The thick layer in Solution #1 could have been protective, which corresponded to a high value of
$R_{\text{pol}}$.

Compared with Solution #1, the corrosion product layers in Solutions #2 and #3 were
quite thin. The collapse of corrosion product layers and pits were observed at some spots on the
corroded steel in Solution #2, which were the obvious characteristics of localized corrosion. In
the localized corrosion regions, the amount of S was a little higher, like Locations 1 and 4, and
the amount of corrosion products were more than the other flat regions. There was more of Fe
(62 %at.) detected in the flat regions like Location 3, which may come from the steel substrate
through the thin film. The thin corrosion product film and localized corrosion could explain the
smallest $R_{\text{pol}}$ in Solution #2. The corrosion products in Solution #3 were intact in some regions
and loose others, and the cracks in the layer could have taken place during the corrosion exposure
or have been due to drying out after taking the sample out of the solution. The chemical
compositions in the intact regions were very close to Fe$_3$O$_4$(s), like Locations 1 and 2 in Figure 2-
17(c). The chemical composition in the loose region was more like a combination of iron
carbonate and iron sulfide, like Location 3 in Figure 2-17(c). According to the EDS analyses, the
chemical compositions of the corrosion products generally followed the trend of changing from
iron carbonate and sulfides to iron oxide as pH increased, which agreed with the Pourbaix
diagram in Figure 2-15. The thickest layer of the corrosion products in Solution #1 and the
localized corrosion in Solution #2 explained the slowest CR in Solution #1 and the fastest CR in Solution #2 at $P_{\text{H}_2\text{S}} = 69$ kPa.

### 2.4 Conclusions

The electrochemical corrosion behavior of high-strength low-alloy carbon drill steel API S-135 was investigated using in-situ electrochemical measurements, ex-situ surface analysis, and software modeling in alkaline brine solutions at pH of 7.9, 10.7, and 12.4 at four different $P_{\text{H}_2\text{S}}$ equal to 0 kPa, 0.83 kPa, 8.3 kPa, and 69 kPa at 85 °C. The main conclusions include:

1. For the dissociation of H$_2$S(aq), HS$^-$ (aq) was calculated to be the dominant sulfide species from pH 7.9 to 12.4. Considering OH$^-$ (aq), HCO$_3^-$ (aq), and HS$^-$ (aq) as reactants for anodic reactions, the dominant reactive ions changed from HCO$_3^-$ (aq) to OH$^-$ (aq) from Solution #1 to #3 with a comparable HS$^-$ (aq) concentration. In Solution #2, the reactive ions were most diverse and the HS$^-$ (aq) ratio was the largest.

2. Before 60 hours, $R_{\text{pol}}$ generally increased with time and was approaching the steady state in Solutions #1 and #3, whereas $R_{\text{pol}}$ decreased after the initial increase in Solution #2. After 60 hours, $R_{\text{pol}}$ increased as pH increased at $P_{\text{H}_2\text{S}} = 0$ kPa and 0.83 kPa, whereas $R_{\text{pol}}$ first decreased and then increased as pH increased at $P_{\text{H}_2\text{S}} = 8.3$ kPa and 69 kPa. At each pH, the lower $P_{\text{H}_2\text{S}}$ increased $R_{\text{pol}}$ or did not significantly change $R_{\text{pol}}$ and the higher $P_{\text{H}_2\text{S}}$ decreased $R_{\text{pol}}$. Two opposite effects from H$_2$S were proposed, an accelerating effect due to H$_2$S(aq) and HS$^-$ (aq) facilitating the Faradaic reactions and the localized corrosion and an inhibiting effect due to the protectiveness of the corrosion products. The solution pH had a larger effect on $R_{\text{pol}}$, and the effect of $P_{\text{H}_2\text{S}}$ did not become significant until 69 kPa in Solutions #2 and #3.
The experimental CRs followed the inverse trend of $R_{pol}$. The fastest CR was 0.26 mm y$^{-1}$ in Solution #2 with $P_{H_{2}S} = 69$ kPa, and the slowest CR was 0.0053 mm y$^{-1}$ in Solution #3 with $P_{H_{2}S} = 0.83$ kPa. The modeled CR with OLI Analyzer software was generally higher than the experimental CR in Solution #1, lower in Solution #2, and in better agreement in Solution #3.

The EIS results showed that the electrochemical impedance did not change significantly at different stir rates, indicating that mass transport in the bulk solution did not influence the rate determining step for the overall corrosion process. Two well-defined time constants were observed at each $P_{H_{2}S}$ in Solution #2 and at higher $P_{H_{2}S}$ in Solutions #1 and #3.

The chemical compositions on the corroded surfaces indicated a combination of iron carbonate, iron sulfide, and iron oxide in the three solutions at $P_{H_{2}S} = 8.3$ and 69 kPa. The amount of S was larger at $P_{H_{2}S} = 69$ kPa. In Solution #1 at both $P_{H_{2}S}$, there were massive corrosion products on the corroded steel surface. The ball-like structures were aggregated from cubic crystals with the chemical composition similar to FeCO$_3$(s). In Solution #2, non-homogeneity and some characteristics of localized corrosion were observed at both $P_{H_{2}S}$, which corresponded to the smallest $R_{pol}$. In Solution #3, the Fe$_3$O$_4$(s)-like product was detected on the surface. The corrosion products generally followed the trend of changing from iron carbonate and sulfides to iron oxide as pH increased, which agreed with the Pourbaix diagrams. The thickness of the corrosion product layers and the localized corrosion were consistent with the trend of $R_{pol}$ changing among the three solutions.

References


Chapter 3

Effects of pH and Hydrogen Sulfide on Corrosion of Carbon Steel UD-165 in Alkaline Brines

This chapter presents the results and conclusions on corrosion of UD-165 at pH 7.9, 10.7, and 12.4 at 85 °C with \( P_{H_2S} \) equal to 0 and 8.3 kPa, the same conditions as for S-135. The effect of \( H_2S \) was determined by comparison of the corrosion rate and corrosion products between with and without \( H_2S \). The reaction mechanisms were further studied through Tafel analysis and electrochemical impedance spectroscopy.

Abstract

In-situ electrochemical measurements were performed to investigate the effects of pH and \( H_2S \) on corrosion of ultra-high strength low alloy carbon steel, grade UD-165, in 5 %wt. NaCl solutions at pH 7.9, 10.7, and 12.4 at 85 °C. After 60 hours, the corrosion rate (CR) without \( H_2S \) decreased as the pH increased. The CR accelerated at \( H_2S \) partial pressure (\( P_{H_2S} \)) equal 8.3 kPa. \( HS^- (aq) \) was calculated to be the primary sulfide species from pH 7.9 to 12.4. The modeled CR was in good agreement with experimental CR. Anodic limiting current was observed without \( H_2S \) but disappeared in the presence of \( H_2S \). Electrochemical impedance spectroscopy (EIS) data was fitted to a two-time-constant equivalent circuit indicating different mechanisms. The increase of CR at \( P_{H_2S} \) 8.3 kPa could be due to an alternative reaction path of HS (aq) and non-homogeneity.

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2 The text in this chapter was originally prepared for the publication as “Ruishu Feng, Justin Beck, Margaret Ziomek-Moroz, and Serguei Lvov. Effects of pH and Hydrogen Sulfide on Corrosion of Carbon Steel UD-165 in Alkaline Brines. Journal of The Electrochemical Society, in review.”
of the corrosion product film. Both the Pourbaix diagrams and the surface analyses suggested that the corrosion products shifted from iron carbonate and sulfides to iron oxide as the pH increased.

3.1 Introduction

The effect of \( \text{H}_2\text{S} \) on the corrosion of martensitic carbon steels in brines has been of great interest due to the relevance to the gas and oil exploration. High-strength low-alloy carbon steels are commonly used for deep drilling, and they have been found to be susceptible to hydrogen induced cracking (HIC)/sulfide stress cracking (SSC), stress corrosion cracking (SCC), and corrosion fatigue (CF) in the presence of \( \text{H}_2\text{S} \). As the exploration gets deeper, the environment becomes more aggressive in the wells due to high pressure, high temperature, and high concentrations of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \). Therefore, ultra-deep drilling requires materials of higher mechanical properties and better corrosion resistance.

Grade UD-165 is an ultra-high-strength low-alloy carbon steel specially developed for ultra-deep drilling. Its mechanical performance has been studied under neutral-basic conditions in the presence of \( \text{H}_2\text{S} \). It was found that at ambient temperature fatigue crack growth rate was controlled by hydrogen diffusion at pH = 7, whereas the cracks seemed to be plugged by corrosion products at pH = 12 and showed the characteristic for SCC. It was suspected that the initiation and propagation of the cracks under cyclic stress might be influenced by dissolved \( \text{H}_2\text{S(aq)} \).

Most studies of \( \text{H}_2\text{S} \) corrosion have focused on the electrochemical reactions between \( \text{Fe(s)} \) and \( \text{H}_2\text{S(aq)} \) and the nature of the corrosion products. Shoesmith et al.\(^7\) proposed a solid-state reaction mechanism which involved the formation of ferrous monosulfide layers according to Reaction [3-1] and the hydrogen evolution reaction through the reduction of \( \text{H}_2\text{S(aq)} \) as shown in Reaction [3-2]. While mackinawite was found in many studies due to its fast kinetics of
formation, there were different phases of ferrous sulfides with varying morphology and mechanical features\(^5\). As a result, the corrosion product layers could be protective or non-protective in different conditions\(^9,10\).

\[
\text{Fe(s) + H}_2\text{S(aq) → FeS(s) + 2 H}^+(\text{aq}) + 2 \text{ e}^-
\]

\[3-1\]

\[2 \text{ H}_2\text{S(aq) + 2 e}^- \rightarrow 2 \text{ HS}^-(\text{aq}) + \text{ H}_2(\text{g})\]

\[3-2\]

As the practice of deep drilling, a drilling fluid is circulating in the wells with elevated pH typically between 10 and 12, and the drilling steel is exposed to an alkaline environment with the corrosive substances. However, most studies on H\(_2\)S corrosion were conducted in acidic conditions\(^7,11–17\). According to Bockris et al., OH\(^-\)(aq) could form an intermediate with Fe(s) during the anodic dissolution\(^18\). Thus, the corrosion mechanism might be altered under the influence of high pH. The present work was focused on the electrochemical corrosion behavior of UD-165 at neutral-basic conditions. The effects of pH and H\(_2\)S were investigated through the electrochemical measurements, software modeling, and the surface analysis.

### 3.2 Experimental

#### 3.2.1 Materials and preparation

The material investigated in this study was an ultra-high-strength low-alloy carbon steel (UHSLA), Grade UD-165. Its chemical composition and mechanical properties are listed in Table 3-1.\(^4,19\)
Table 3-1. Chemical composition (%wt.) of UD-165.4,19

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Al</th>
<th>Ni</th>
<th>Cu</th>
<th>Nb</th>
<th>Si</th>
</tr>
</thead>
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<tr>
<td>Bal</td>
<td>0.79</td>
<td>0.88</td>
<td>0.67</td>
<td>0.03</td>
<td>0.81</td>
<td>0.19</td>
<td>0.02</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.007</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.27</td>
<td>0.007</td>
<td>0.07</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td></td>
</tr>
</tbody>
</table>

The steel samples were cut into 10×20×5 mm planar samples and were coated with a bisphenol-amine epoxy so that only the 10×20 mm face opposite the counter electrode was exposed to the test solutions. To minimize the surface defects and keep the surface area as consistent as possible, the exposed surface was ground with 400, 600, and 800 grit SiC papers and then polished by 0.1 and 0.05 microns alumina polishing slurries until a mirror finish was observed. The working electrode was rinsed with isopropanol and distilled water and then wiped dry. The electrode wire attached to the steel sample was coated by shrinkable polytetrafluoroethylene (PTFE) tubing.

3.2.2 System setup

A three-electrode system was adopted to perform the electrochemical measurements. The working electrode consisted of the prepared UHSLA steel sample, and the counter electrode was a 10×20×1 mm platinum plate which was coated by epoxy in the same manner as the working electrode. The two electrodes were held in place between two PTFE plates with the polished surfaces parallel to each other. The distance between electrodes was 10 mm. The PTFE plates were tightened by two PTFE-coated screws threaded into the plates.

A double junction Ag/AgCl electrode was used as the reference electrode to avoid the contamination from the test solutions. The fill solution was 5 %wt. NaCl(aq) solution in order to minimize the concentration gradient, and thus the junction potential, between the reference
electrode and the test solutions. The magnitude of diffusion potential was calculated to be within 1.5 mV.\textsuperscript{20} The Ag/AgCl electrode was inserted into a PTFE tube filled with the 5 \%wt. NaCl(aq) solution saturated with AgCl(s). The top of the tube was sealed with epoxy, while the bottom was fitted with a porous glass frit. This inner assembly was inserted into a glass tube, which was filled with the 5 \%wt. NaCl(aq) solution. The top was again sealed with epoxy while the bottom was plugged with a second glass frit to form the junction with the test solution. The silver wire from the Ag/AgCl electrode was connected to a platinum wire and coated with shrinkable PTFE tubing.

A 600 mL autoclave was chosen as the reactor vessel. The vessel was constructed of 316 stainless steel, and a PTFE liner was used to separate the test solution from the reactor vessel. The autoclave lid was used to mount a thermocouple, a pressure transducer, and a plastic tube for the transfer of gas and solutions. A polymer-coated thermocouple was selected to prevent corrosion damage of the sensor and possible contamination of the test solution with undesired corrosion products. A heating mantle around the autoclave and the thermocouple were used to control the temperature. The stirrer impeller was coated with epoxy to prevent undesired corrosion. The electrode leads were sealed using a PTFE compression gland fitted inside the lid. A schematic diagram of the autoclave system is shown in Figure 3-1.
The autoclave controller was connected to a computer to allow recording of the system temperature and pressure over the corrosion test. A computer-controlled Gamry Reference 600 potentiostat was used to perform linear polarization resistance (LPR), electrochemical frequency modulation (EFM), electrochemical impedance spectroscopy (EIS), and linear sweep voltammetry (LSV) measurements.

3.2.3 Experimental procedure

The autoclave vessel was held at 85 °C. The test solutions were 5 %wt. (0.9 mol kg⁻¹) NaCl solutions buffered with NaHCO₃/Na₂CO₃/NaOH. The compositions of the test solutions are listed in Table 3-2.
Table 3-2. Solution compositions (mol kg\(^{-1}\)) and pH at different \(P_{H_2S}\).

<table>
<thead>
<tr>
<th>Soln.</th>
<th>NaCl</th>
<th>NaHCO(_3)</th>
<th>Na(_2)CO(_3)</th>
<th>NaOH</th>
<th>pH at (P_{H_2S} = 0) kPa</th>
<th>pH at (P_{H_2S} = 8.3) kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.9</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>7.9</td>
<td>7.9</td>
</tr>
<tr>
<td>#2</td>
<td>0.9</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>10.7</td>
<td>10.7</td>
</tr>
<tr>
<td>#3</td>
<td>0.9</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>12.4</td>
<td>12.4</td>
</tr>
</tbody>
</table>

After the solution was prepared with 250 g deionized water, it was deaerated by bubbling with \(N_2\) for at least one hour. The deaerated solution was transferred into the well-sealed autoclave vessel by pressure difference through the plastic tubing (No. 6 in Figure 3-1). Then, the autoclave was deaerated by flushing with \(N_2\) for at least 10 min. When the system was heated up to 85 °C, a \(H_2S/N_2\) mixture gas (10%vol. \(H_2S\)) was put into the system through the plastic tubing. Once \(P_{H_2S}\) reached 8.3 kPa, the valves were closed. The amount of \(H_2S\) in the autoclave was estimated by the ideal gas law with the available vapor volume of 236.3 mL, and the \(H_2S(aq)\) concentration was calculated to be \(2.63\times10^{-3}\) mol kg\(^{-1}\) at 85 °C. The pH in the three solutions at \(P_{H_2S} = 0\) and 8.3 kPa were calculated using OLI Analyzer software.\(^{21}\) The pH calculation took into account the system temperature, total system pressure, and the composition using the mixed solvent electrolyte (MSE) framework within the software. From Solution #1 to #3, pH increased from 7.9 to 12.4. The addition of \(P_{H_2S} = 8.3\) kPa did not change the pH as shown in Table 3-2, although the dissociation of \(H_2S\) could decrease the pH slightly.

The solution was under the stir rate of 525 RPM up to 60 hours. LPR, EFM, and EIS were carried out every two hours during the exposure test. LPR was measured with the sweep rate of 1 mV s\(^{-1}\) over the potential range of ±20 mV around the measured open circuit potential (OCP). EFM was measured with 25 mV as the amplitude around the OCP at the base frequency of 0.01 Hz with multipliers of 2 and 5. EIS was measured within ±10 mV around the OCP at least over the frequency from 300 kHz to 5 mHz. After 60 hours, different stir rates were applied to
investigate the effect of mass transport in the solution. Under the stir rate of 525 RPM, LSV was carried out at the sweep rate of 5 mV s$^{-1}$ (2 mV s$^{-1}$ for Solution #1 at $P_{H2S} = 8.3$ kPa) within the overpotential range of ± 0.2 V. After the electrochemical measurements were completed, the corroded surfaces were investigated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

### 3.2.4 Calculation of corrosion rate

In a three-electrode cell, when a small current flows through the working and counter electrodes and the reaction is under activation control, the corrosion current density, $j_{\text{corr}}$, can be calculated according to the Stern-Geary equation shown in Equations [3-3] and [3-4]$^{20,22,23}$.

\[
  j_{\text{corr}} = \frac{1}{R_{\text{pol}} B'}
\]  

[3-3]

\[
  B' = (\ln 10) \left( \frac{b_c + b_a}{b_c b_a} \right)
\]  

[3-4]

where $R_{\text{pol}}$ is the area specific polarization resistance and $B'$ is a combination of the cathodic, $b_c$, and anodic, $b_a$, Tafel slopes. $R_{\text{pol}}$ was calculated from LPR after correcting for the solution resistance ($R_{\text{sol}}$) obtained from EIS. Tafel slopes were obtained from EFM.

The corrosion rate (CR) is defined as the depth of corrosion penetration per time assuming uniform corrosion and can be calculated following Equation [3-5].

\[
  CR = j_{\text{corr}} M / (nF\rho)
\]  

[3-5]
where $M$ is the molecular mass of the corroding metal, $n$ is the electron number transferred in the dissolution reaction, $F$ is the Faraday constant (96485 C mol$^{-1}$), and $\rho$ is the metal density.

### 3.3 Results and Discussion

#### 3.3.1 Primary species in the solutions

The speciation (concentrations of aqueous species) in the NaCl(aq)-based solutions given in Table 3-2 at 85 °C were calculated with OLI Analyzer software.\(^{21}\) The carbonate speciation without $\text{H}_2\text{S}$ is shown in Figure 3-2. The predicted concentrations of carbonate species at $P_{\text{H}_2\text{S}} = 8.3$ kPa were almost the same as Figure 3-2. It can be seen that the concentrations of $\text{CO}_2^{(aq)}$ and $\text{HCO}_3^{-}(aq)$ decreased as pH increased from 7.9 to 12.4 whereas $\text{CO}_3^{2-}(aq)$ concentration increased. The concentrations of sulfide species at $P_{\text{H}_2\text{S}} = 8.3$ kPa are shown in Figure 3-3. $\text{HS}^{-}(aq)$ is the primary ion from the dissociation and the concentrations were similar among the three solutions. As pH increased, the concentration of non-dissociated $\text{H}_2\text{S}(aq)$ decreased whereas $\text{S}^{2-}(aq)$ increased.

It has been proposed that $\text{OH}^{-}(aq)$, $\text{HCO}_3^{-}(aq)$, and $\text{HS}^{-}(aq)$ are the possible reactive ions to form intermediates with Fe for anodic reactions.\(^7,18,24,25\) The computed concentrations of $\text{OH}^{-}(aq)$, $\text{HCO}_3^{-}(aq)$, and $\text{HS}^{-}(aq)$ in the different solutions are listed in Table 3-3. The dominant reaction would depend on the concentrations of reactive ions in the solutions and their surface coverage on the steel. The dominant reactive species generally changed from $\text{HCO}_3^{-}(aq)$ to $\text{OH}^{-}(aq)$ as pH increased from Solution #1 to #3.
Figure 3-2. The primary carbonate species in the three solutions without H₂S at 85 °C. Conditions: Solution #1: 0.9 mol kg⁻¹ NaCl, 0.5 mol kg⁻¹ NaHCO₃, pH = 7.9; Solution #2: 0.9 mol kg⁻¹ NaCl, 1 mol kg⁻¹ Na₂CO₃, pH = 10.7; Solution #3: 0.9 mol kg⁻¹ NaCl, 1 mol kg⁻¹ Na₂CO₃, 1 mol kg⁻¹ NaOH, pH = 12.4.

Figure 3-3. The primary sulfide species in the three solutions at P₄H₂S = 8.3 kPa and 85 °C. Conditions: Solution #1: 0.9 mol kg⁻¹ NaCl, 0.5 mol kg⁻¹ NaHCO₃, pH = 7.9; Solution #2: 0.9 mol kg⁻¹ NaCl, 1 mol kg⁻¹ Na₂CO₃, pH = 10.7; Solution #3: 0.9 mol kg⁻¹ NaCl, 1 mol kg⁻¹ Na₂CO₃, 1 mol kg⁻¹ NaOH, pH = 12.4.
Table 3-3. The concentrations (mol kg\(^{-1}\)) of reactive ions calculated with OLI Analyzer software.

<table>
<thead>
<tr>
<th>(P_{H_2S})</th>
<th>Solution</th>
<th>(\text{OH}^{\text{aq}})</th>
<th>(\text{HCO}_3^{\text{aq}})</th>
<th>(\text{HS}^{\text{aq}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 kPa</td>
<td>#1</td>
<td>(4.20 \times 10^{-5})</td>
<td>(4.57 \times 10^{-1})</td>
<td>0</td>
</tr>
<tr>
<td>#2</td>
<td>(2.35 \times 10^{-2})</td>
<td>(2.43 \times 10^{-2})</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td>(9.63 \times 10^{-1})</td>
<td>(5.16 \times 10^{-4})</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>8.3 kPa</td>
<td>#1</td>
<td>(4.01 \times 10^{-5})</td>
<td>(4.56 \times 10^{-1})</td>
<td>(2.48 \times 10^{-3})</td>
</tr>
<tr>
<td>#2</td>
<td>(2.22 \times 10^{-2})</td>
<td>(2.56 \times 10^{-2})</td>
<td>(2.62 \times 10^{-3})</td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td>(9.60 \times 10^{-1})</td>
<td>(5.17 \times 10^{-4})</td>
<td>(2.54 \times 10^{-3})</td>
<td></td>
</tr>
</tbody>
</table>

3.3.2 Corrosion potential and steady state behavior

In anaerobic alkaline conditions, the anodic reaction involved in the corrosion process is the dissolution of Fe(s), the simplified reduction reaction of which is shown in Equation [3-6]. The cathodic reaction is the hydrogen evolution reaction (HER), and the hydrogen source could possibly be \(H^+(aq), H_2O(l), H_2CO_3(aq), H_2S(aq)\), and other hydrogen-containing species. Some of these reactions are given in Equations [3-7] – [3-10] as examples of HER. The standard electrode potential, \(E^0\), is given for each reaction at 85 °C, which was calculated using the data from HCh chemical simulation software and OLI Analyzer software\(^{26,27}\). The Nernst equations for Reactions [3-6] – [3-8] are given in Equations [3-11] – [3-13]. According to Appendix (A), the equilibrium potentials of all HERs were equal when the dissociations were at equilibrium. Therefore, \(E(H^+|H_2)\) in Equation [3-12] could represent the potentials of all HERs as cathodic reactions.

\[
\begin{align*}
\text{Fe}^{2+}(aq) + 2 e^- &= \text{Fe(s)} , \ E^0 = -0.473 \text{ V vs SHE, 85 °C} & [3-6] \\
2 \text{H}^+(aq) + 2 e^- &= \text{H}_2(g), \ E^0 = 0 \text{ V vs SHE, 85 °C} & [3-7] \\
2 \text{H}_2\text{O(l)} + 2 e^- &= \text{H}_2(g) + 2 \text{OH}^-(aq), \ E^0 = -0.890 \text{ V vs SHE, 85 °C} & [3-8] \\
2 \text{H}_2\text{CO}_3(aq) + 2 e^- &= \text{H}_2(g) + 2 \text{HCO}_3^-(aq), \ E^0 = -0.449 \text{ V vs SHE, 85 °C} & [3-9]
\end{align*}
\]
\[ 2 \text{H}_2\text{S(aq)} + 2 \text{e}^- = \text{H}_2(\text{g}) + 2 \text{HS}^-\text{(aq)}, \quad E^0 = -0.463 \text{ V vs SHE, 85 }^\circ\text{C} \]  

\[ E_{\text{Fe}^{2+}\text{|Fe}} = E_{\text{Fe}^{2+}\text{|Fe}}^0 + \frac{RT}{2F} \ln \alpha_{\text{Fe}^{2+}\text{(aq)}} \]  

\[ E_{\text{H}^+\text{|H}_2} = E_{\text{H}^+\text{|H}_2}^0 + \frac{RT}{2F} \ln \frac{\alpha_{\text{H}^+(\text{aq})}}{P_{\text{H}_2(\text{g})}} \]  

\[ E_{\text{H}_2\text{O}|\text{H}_2} = E_{\text{H}_2\text{O}|\text{H}_2}^0 + \frac{RT}{2F} \ln \frac{\alpha_{\text{H}_2\text{O}(\text{l})}}{\alpha_{\text{H}^+(\text{aq})}P_{\text{H}_2(\text{g})}} \]  

The corrosion potential \( E_{\text{corr}} \) is the mixed potential for both anodic and cathodic reactions. \( E_{\text{corr}} \) was measured with respect to the Ag/AgCl reference electrode and was converted to the standard hydrogen electrode (SHE) scale at 85 °C. Figure 3-4 shows the \( E_{\text{corr}} \) of UD-165 changing with time for all of the conditions tested. The \( E_{\text{corr}} \) generally increased or fluctuated with time and then reached a plateau, which indicated that the corrosion reached a steady state by 60 hours of exposure.

![Figure 3-4](image-url)

Figure 3-4. The corrosion potential of UD-165 changing with time at 85 °C. Conditions: \( P_{\text{H}_2\text{S}} = 0 \) kPa and 8.3 kPa. Solution #1: 0.9 mol kg\(^{-1}\) NaCl, 0.5 mol kg\(^{-1}\) NaHCO\(_3\), pH = 7.9; Solution #2: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), pH = 10.7; Solution #3: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), 1 mol kg\(^{-1}\) NaOH, pH = 12.4.
$E_{\text{corr}}$ at steady state in different conditions are summarized in Table 3-4. $E_{\text{corr}}$ at steady state became more negative when the solution pH increased, which can be easily explained by Equation [3-12] when $H^+(\text{aq})$ concentration decreased. The addition of $P_{\text{H}_2S} = 8.3$ kPa made $E_{\text{corr}}$ more negative in each solution. Since the pH without and with H$_2$S were almost the same for each solution, it is speculated that the addition of H$_2$S increased $P_{\text{H}_2(g)}$ through a faster CR and, therefore, decreased the ratio of $a^2_{\text{H}^+(\text{aq})}P_{\text{H}_2(g)}$ in Equation [3-12]. This speculation was in accordance with the trend of $P_{\text{H}_2(g)}$ and the solution redox potential computed with OLI Analyzer.

Table 3-4. $E_{\text{corr}}$ of UD-165 at steady state (V, vs SHE).

<table>
<thead>
<tr>
<th>$P_{\text{H}_2S}$ / kPa</th>
<th>Soln. #1</th>
<th>Soln. #2</th>
<th>Soln. #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.282</td>
<td>-0.366</td>
<td>-0.418</td>
</tr>
<tr>
<td>8.3</td>
<td>-0.376</td>
<td>-0.452</td>
<td>-0.495</td>
</tr>
</tbody>
</table>

### 3.3.3 Polarization resistance and corrosion rate

In the LPR plots, it was observed that the net current was not equal to zero at $E_{\text{corr}}$ which was the measured OCP. Additionally, the sign of the net current at $E_{\text{corr}}$ changed between sweeping up and down. This behavior could be related to a capacitance effect in the system, like the electric double layer capacitance at the steel/solution interface. Assuming that the double layer structure did not change during the small polarization and that it behaved like an ideal capacitor, the capacitive current $I_c$ was expected to be constant at a constant potential sweep rate according to $I_c = C \frac{dE}{dt}$. The symbol $C$ represents the capacitance and $dE/dt$ represents the rate of potential changing with time, i.e. the sweep rate. The constant value of $I_c$ would shift the total current but would not change the slope of $I$-$E$ plot and, therefore, would not affect $R_{\text{pol}}$ around $E_{\text{corr}}$. The sweep direction changed the sign of $dE/dt$ and thus changed the sign of $I_c$. $R_{\text{pol}}$ was
obtained as the average value from sweep up and down plots taking account of the capacitance effect.

Figure 3-5 shows the area specific polarization resistance $R_{pol}$ changing with time in different conditions. As can be seen, $R_{pol}$ increased or decreased or fluctuated with time and reached a plateau by 60 hours, which confirmed the steady state. The early stage of corrosion was usually unstable, but the fluctuation of $R_{pol}$ could be related to some phenomena during the corrosion. An increase in $R_{pol}$ could be related to the formation of corrosion products and the decrease in available reactive sites, as in Solution #3 without H$_2$S. A drop in $R_{pol}$ could be related to the initiation of localized corrosion due to defects in the product layer or the corrosion products stripping off the surface, as in Solution #1 and #2 without H$_2$S.

![Figure 3-5](image_url)

Figure 3-5. $R_{pol}$ of UD-165 changing with time at 85 °C. Conditions: $P_{H2S} = 0$ kPa and 8.3 kPa. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.
The measured $R_{\text{pol}}$ of UD-165 at steady state in different conditions are compared in Figure 3-6. In the tests without H$_2$S, $R_{\text{pol}}$ increased as the solution pH increased, which could be attributed to the suppressed cathodic reactions and the protectiveness of the corrosion products. In the presence of $P_{\text{H}_2\text{S}} = 8.3$ kPa, $R_{\text{pol}}$ decreased to different extents in the three solutions, indicating that H$_2$S accelerated the corrosion. And $R_{\text{pol}}$ at pH 10.7 became the largest among the three solutions.

The CR of UD-165 at steady state in the three solutions at $P_{\text{H}_2\text{S}} = 0$ and 8.3 kPa are compared in Figure 3-7. Calculated according to the Stern-Geary equation, CR followed the inverse trend of $R_{\text{pol}}$. The CR without H$_2$S decreased from 0.19 mm y$^{-1}$ to 0.009 mm y$^{-1}$ as pH increased from 7.9 to 12.4. At $P_{\text{H}_2\text{S}} = 8.3$ kPa, the CR decreased from 0.30 mm y$^{-1}$ to 0.05 mm y$^{-1}$ when pH increased from 7.9 to 10.7, and then slightly increased to 0.06 mm y$^{-1}$ at pH = 12.4. By comparison, the corrosion rate was accelerated at $P_{\text{H}_2\text{S}} = 8.3$ kPa by factors of 0.2, 2, and 7 from pH 7.9 to 12.4, respectively.

CR was computed as a generic carbon steel RDE at a rotating rate of 500 RPM using the OLI Analyzer modeling. The results are also shown in Figure 3-7. It was predicted that the CR at pH = 7.9 was higher than those at pH of 10.7 and 12.4 regardless of $P_{\text{H}_2\text{S}}$ and that the addition of H$_2$S increased CR at pH = 7.9 and 10.7 but decreased CR at pH = 12.4. The modeled CR values were in a good agreement with experimental results, and the divergence was within one order of magnitude. The CR at pH = 10.7 without H$_2$S was predicted to have a very low value of 0.003 mm y$^{-1}$ whereas the experimental CR was 0.046 mm y$^{-1}$, which was the largest difference.
Figure 3-6. $R_{pol}$ at steady state in different conditions at 85 °C. Conditions: $P_{H2S} = 0$ kPa and 8.3 kPa. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.

Figure 3-7. Experimental CR at steady state and CR from OLI modeling at 85 °C. Conditions: $P_{H2S} = 0$ and 8.3 kPa. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.
3.3.4 The effect of stir rate

The effect of stir rate was investigated by comparing EIS results at different stir rates after the corrosion reached the steady state at 525 RPM. As an example, Figure 3-8 shows the Nyquist plots of UD-165 corroded in Solution #2 with $P_{H2S} = 8.3$ kPa. The EIS plot did not change significantly at different stir rates, indicating that the mass transport in the bulk solution was not the rate limiting step in the corrosion process. Similar results were found in the other conditions as well.

Figure 3-8. Nyquist plots of UD-165 at different stir rates in Solution #2 with $P_{H2S} = 8.3$ kPa at 85 °C. Conditions: Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7.

3.3.5 LSV results

The anodic and cathodic LSV plots are compared in Figures 3-9 and 3-10, respectively.
Figure 3-9. The LSV plots of UD-165 in anodic region with $P_{H_2S} = 0$ and 8.3 kPa at 85 °C with the scan rate of 5 mV s$^{-1}$ (2 mV s$^{-1}$ for Solution #1 at $P_{H_2S} = 8.3$ kPa). Conditions: Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.

Figure 3-10. The LSV plots of UD-165 in cathodic region with $P_{H_2S} = 0$ and 8.3 kPa at 85 °C with the scan rate of 5 mV s$^{-1}$ (2 mV s$^{-1}$ for Solution #1 at $P_{H_2S} = 8.3$ kPa). Conditions: Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.
Limiting current density was observed in the anodic LSV plot in each of the solutions without H$_2$S, and the current density decreased as pH increased from pH 7.9 to 12.4. No obvious limiting current density was observed in the anodic LSV plots at the $P_{\text{H}_{2}\text{S}} = 8.3$ kPa other than the LSV plot at pH 12.4 turning slightly flat at the highly polarized end.

Mass transport, passivation, or chemical steps are the common reasons for a limiting current. Firstly, mass transport of reactive species in the bulk solution was less likely based on the fact that changing the stir rate did not affect the impedance significantly. However, aqueous diffusion through the porous film on the steel surface could be the limiting step. Secondly, passivation could limit the current through the formation of a passive film over the steel surface when without H$_2$S, and the passive film could have broken down in the presence of H$_2$S due to the non-homogeneity of the corrosion product film. Thirdly, chemical steps like adsorption / desorption and formation of the intermediates could also be the rate limiting step. For example, if Step I is the RDS in the Bockris or Heusler mechanism as described in Reactions [3-14] to [3-18], the formation of FeOH(ad) could reach a maximum surface coverage and therefore limit the current. OH$^-$ (aq) could be substituted with HCO$_3$ (aq). In the presence of H$_2$S, HS$^-$ (aq) could specifically adsorb on the surface and provide an alternative reaction path for anodic reaction$^{7,25}$, eliminating the limiting current.

\[
\text{Step I (RDS): } \text{Fe(s)} + \text{OH}^-(\text{aq}) \rightarrow \text{FeOH(ad)} + e^- \quad [3-14]
\]
\[
\text{Step II: } \text{FeOH(ad)} \leftrightarrow \text{FeOH}^+ (\text{aq}) + e^- \quad \text{(Bockris) [3-15]}
\]
\[
\text{or } \text{Fe(s)} + \text{OH}^- (\text{aq}) + \text{FeOH(ad)} \leftrightarrow \text{FeOH}^+(\text{aq}) + \text{FeOH(ad)} + 2 e^- \quad \text{(Heusler) [3-16]}
\]
\[
\text{Step III: } \text{FeOH}^+ (\text{aq}) + \text{H}^+ (\text{aq}) \leftrightarrow \text{Fe}^{2+} (\text{aq}) + \text{H}_2\text{O} \quad [3-17]
\]
\[
(I) + (II) + (III): \text{Fe(s)} \rightarrow \text{Fe}^{2+} (\text{aq}) + 2 e^- \quad [3-18]
\]
The anodic Tafel slopes at $P_{H_2S} = 8.3$ kPa are listed in Table 3-5. Assuming the symmetry coefficient $\beta$ to be 0.5, the anodic Tafel slope calculated according to $2.303RT/[n(1-\beta)F]$ for one-electron mechanism ($n = 1$) and two-electron mechanism ($n = 2$) at 85 °C were 0.142 V dec$^{-1}$ and 0.071 V dec$^{-1}$, respectively. The measured $b_a$ values in Solutions #2 and #3 with H$_2$S were roughly in this range.

Table 3-5. Tafel slopes in the three solutions at $P_{H_2S} = 0$ kPa (I) and 8.3 kPa (II) at 85 °C.

<table>
<thead>
<tr>
<th>Tafel slope / (V dec$^{-1}$)</th>
<th>I-#1</th>
<th>I-#2</th>
<th>I-#3</th>
<th>II-#1</th>
<th>II-#2</th>
<th>II-#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_a$</td>
<td>limiting</td>
<td>limiting</td>
<td>limiting</td>
<td>0.288</td>
<td>0.134</td>
<td>0.096 (limiting)</td>
</tr>
<tr>
<td>$b_c$</td>
<td>0.290</td>
<td>0.498</td>
<td>0.372</td>
<td>0.273</td>
<td></td>
<td>0.238</td>
</tr>
</tbody>
</table>

There were no obvious limiting current densities observed in the cathodic LSV plots except for Solution #2 at $P_{H_2S} = 8.3$ kPa. For lack of H$^+$ (aq) in the alkaline solutions, HER could be mainly the reduction of H$_2$O, which explained the absence of limiting current.$^30$ The current density $j$ decreased as pH increased, and $j$ was higher in the presence of H$_2$S. This indicated the effect of the H$^+$ (aq) and H$_2$S (aq) although their concentrations were very low in all cases. The Volmer-Heyrovsky (V-H) and Volmer-Tafel (V-T) mechanisms are two commonly accepted mechanisms for HER (see Appendix B). $^31$ The cathodic Tafel slopes, $b_c$, for these two mechanisms were calculated to be 0.142 V dec$^{-1}$ and 0.0355 V dec$^{-1}$ at 85 °C, respectively, assuming the symmetry coefficient $\beta$ to be 0.5.$^31$ The measured cathodic Tafel slopes in Table 3-5 were larger than these values, which could suggest a different mechanism.
3.3.6 EIS at different pH and $P_{H2S}$

The EIS results of UD-165 after 60 hours in the three solutions at $P_{H2S} = 0$ and 8.3 kPa are shown in Figure 3-11. The phase angle plots showed one broad time constant or two time constants. EIS data in all the cases were fitted using the equivalent circuit in Figure 3-12. The fitting results are listed in Table 3-6.

In series with $R_{sol}$ consists of a constant phase element (CPE1) in parallel with a resistor $R1$ and another CPE2-$R2$ combo. The impedance of CPE, $Z_Q$, is defined as in Equation [3-19].

\[ Z_Q = (Y_0)^{-1} (i\omega)^p \]  

[3-19]

where $Y_0$ is the admittance modulus, $i$ the imaginary unit, $\omega$ the angular frequency and $p$ the exponent within 0-1. When $p = 1$, CPE is identical to an ideal capacitor; when $p = 0$, CPE behaves as a resistor; and when $p = 0.5$, CPE could turn into an infinite-length Warburg element, representing the diffusion of charge carrier. Use of CPE as a substitute for a capacitor in the Randles circuit is usually used to fit a depressed semi-circle due to the non-homogeneity of the double layer capacitance between the steel and the solution. CPE1 in the equivalent circuit serves for this function. According to Table 3-6, CPE1-$p$ values were mainly between 0.8 and 1, which indicated the non-ideality of the double layer. A smaller CPE1-$Y_0$ value always correlated to a larger $R1$ value, which indicated a correlation between the double layer capacitance and $R1$. $R1$ and $R2$ both decreased at $P_{H2S} = 8.3$ kPa compared with $P_{H2S} = 0$ kPa.
Figure 3-11. Nyquist plots and phase angles of UD-165 at steady state in the three solutions with $P_{H_2S} = 0$ and 8.3 kPa at 85 °C. (Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4).

Figure 3-12. The equivalent circuit to fit the EIS data.
Table 3-6. EIS fitting results in the three solutions at $P_{\text{H}_2\text{S}} = 0$ kPa (I) and 8.3 kPa (II) at 85 °C.

<table>
<thead>
<tr>
<th>unit</th>
<th>I-#1</th>
<th>I-#2</th>
<th>I-#3</th>
<th>II-#1</th>
<th>II-#2</th>
<th>II-#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{sol}}$</td>
<td>Ω cm$^2$</td>
<td>3.60</td>
<td>2.98</td>
<td>2.74</td>
<td>3.79</td>
<td>3.23</td>
</tr>
<tr>
<td>CPE1-$Y_0$</td>
<td>Ω$^{-1}$ cm$^2$ s$^\rho$</td>
<td>8.02×10$^{-3}$</td>
<td>2.39×10$^{-4}$</td>
<td>1.01×10$^{-3}$</td>
<td>3.08×10$^{-2}$</td>
<td>2.82×10$^{-3}$</td>
</tr>
<tr>
<td>CPE1-$p$</td>
<td>0-1</td>
<td>0.73</td>
<td>0.79</td>
<td>0.93</td>
<td>0.89</td>
<td>0.84</td>
</tr>
<tr>
<td>$R_1$</td>
<td>Ω cm$^2$</td>
<td>57</td>
<td>1640</td>
<td>114</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>CPE2-$Y_0$</td>
<td>Ω$^{-1}$ cm$^2$ s$^\rho$</td>
<td>4.71×10$^{-3}$</td>
<td>1.90×10$^{-3}$</td>
<td>5.00×10$^{-4}$</td>
<td>2.58×10$^{-2}$</td>
<td>1.96×10$^{-3}$</td>
</tr>
<tr>
<td>CPE2-$p$</td>
<td>0-1</td>
<td>0.73</td>
<td>0.82</td>
<td>0.83</td>
<td>0.86</td>
<td>0.83</td>
</tr>
<tr>
<td>$R_2$</td>
<td>Ω cm$^2$</td>
<td>12052</td>
<td>122884</td>
<td>45780</td>
<td>5100</td>
<td>8670</td>
</tr>
<tr>
<td>$R_{\text{pol}}$ from LPR</td>
<td>Ω cm$^2$</td>
<td>1450</td>
<td>16299</td>
<td>24163</td>
<td>1241</td>
<td>4910</td>
</tr>
</tbody>
</table>

With a good fit of the EIS data to the equivalent circuit, different interpretations for the two time constants have been found in literatures. Three plausible mechanisms are discussed here. The first mechanism could be that corrosion occurs at the bottom of a pore if the steel was covered with a porous film.$^{32}$ In this case, $R_1$ corresponds to the resistance of the pore solution, and $R_2$ corresponds to the charge transfer resistance. Pore solution resistance would become larger when the film porosity decreases and tortuosity increases. $R_2$ was the largest in Solution #2 without or with H$_2$S, which could relate to the small concentrations of reactive HCO$_3$ (aq) and OH (aq) in Solution #2. And $R_2$ decreased in the presence of $P_{\text{H}_2\text{S}} = 8.3$ kPa, which could be attributed to the alternative reaction path of HS (aq).

The second mechanism is focused on the passive film on the steel surface.$^{33,34}$ $R_1$ represents the charge transfer resistance, and CPE2-$R_2$ represents the reactive ions passing through the passive film. The addition of H$_2$S changed the composition of the film, and the specific adsorption of HS (aq) could have facilitated the transport through the passive film.

The third mechanism involves the adsorption/desorption step which corresponds to the low frequency capacitive behavior.$^{25}$ In this case, $R_1$ represents the charge transfer resistance, and CPE2-$R_2$ represents the adsorption/desorption step.$^{35}$ Charge transfer resistance $R_1$ was affected
by the reaction rate constant, reactant concentrations, and reactive sites on the surface. \( \text{H}_2\text{S} \) could specifically adsorb on the surface and promote corrosion, resulting in the decrease of both charge transfer resistance and the adsorption impedance.

Due to the complexity of the corrosion process and non-homogeneity of the surface, the two-time-constant circuit is an intrinsically simplified form.\(^{35} \) Each mechanism has put emphasis on a different crucial step of corrosion. These three mechanisms could have all impacted the corrosion, and constituted the EIS results. The mechanism of the rate determining step might vary at different pH. The separation of the different mechanisms need further research in a specifically designed system, for example, a rotating disk/cylinder electrode system with and without corrosion products on the steel surface.

As shown in Table 3-6, \( R_{\text{pol}} \) measured from LPR usually lay between the values of \( R_1 \) and \( R_2 \). Considering that LPR was measured at a certain sweep rate although fairly slow, \( R_{\text{pol}} \) corresponds to the impedance at the equivalent frequency in EIS, which usually was not at the frequency of zero. \( R_{\text{pol}} \) from LPR was probably partially impacted by both \( R_1 \) and CPE2-R2.

### 3.3.7 Corrosion products

The corrosion products were studied through thermodynamic prediction from Pourbaix diagrams and using surface analysis techniques. The Pourbaix diagrams in different conditions were prepared using the OLI Analyzer software to predict the thermodynamically favorable products.\(^{36,37} \) Figure 3-13 shows the Pourbaix diagram of the Fe-H\(_2\)O-H\(_2\)CO\(_3\) system in Solution #2 without \( \text{H}_2\text{S} \). The Pourbaix diagrams in Solutions #1 and #3 are similar to Figure 3-13. When the pH increased from 7.9 to 12.4, the thermodynamically predominant Fe species changed from \( \text{FeH(CO}_3)\text{)}_2\text{(aq)} \) to \( \text{FeCO}_3\text{(s)}/\text{Fe}_3\text{O}_4\text{(s)} \) then to \( \text{HFeO}_2\text{(aq)}/\text{Fe}_3\text{O}_4\text{(s)} \). Figure 3-14 shows the Pourbaix diagram of Fe-H\(_2\)O-H\(_2\)CO\(_3\)-H\(_2\)S system in Solution #2 with \( P_{\text{H}_2\text{S}} = 8.3 \text{ kPa} \). The
Pourbaix diagrams in Solutions #1 and #3 are similar to Figure 3-14. When pH increased from 7.9 to 12.4, the thermodynamically predominant Fe species changed from FeS(s)/FeS$_2$(s)/FeH(CO$_3$)$_2$(aq) to FeS(s)/FeS$_2$(s)/Fe$_3$O$_4$(s) then to HFeO$_2$~(aq)/Fe$_3$O$_4$(s). The products generally changed from iron carbonate species and iron sulfides to iron oxide as pH increased, which was consistent with the trend of dominant reactive ions changing with pH. It is worth noting that the less thermodynamically favorable species may be metastable products if kinetics is taken into account. A. Anderko and P. J. Shuler investigated the stability diagrams with the OLI modeling software and found that the replacement sequence (from precursor to most stable species) is FeHS$^+$~(aq) or FeCO$_3$~(siderite) $\rightarrow$ FeS~(amorphous) $\rightarrow$ FeS~(mackinawite) $\rightarrow$ FeS~(pyrrhotite) or FeS$_2$~(pyrite). It has been reported that the mackinawite is less protective than pyrrhotite and pyrite.

Figure 3-13. Pourbaix diagram of Fe-H$_2$O-H$_2$CO$_3$ system in Solution #2 without H$_2$S at 85 °C. (Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH 10.7; Titrants: NaOH/HCl.)
Figure 3-14. Pourbaix diagram of Fe-H₂O-H₂CO₃-H₂S system in Solution #2 at $P_{H₂S} = 8.3$ kPa and 85 °C. (Solution #2: 0.9 mol kg⁻¹ NaCl, 1 mol kg⁻¹ Na₂CO₃, pH 10.7; Titrants: NaOH/HCl.)

The corroded UD-165 surfaces were examined with SEM and EDS. The SEM images are shown in Figures 3-15 and 3-16 with the locations marked for EDS analysis. The corresponding EDS results are listed in Table 3-7. The EDS analysis was carried out with an accelerating voltage of 7 kV to avoid penetrating too deep into the substrate and stimulating too much background signal from the underlying steel.
Figure 3-15. SEM images of corroded UD-165 steel surfaces at $P_{\text{H}_{2}\text{S}} = 0$ kPa and 85 °C. a - Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; b - Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; c - Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.
Figure 3-16. SEM images of corroded UD-165 steel surfaces at $P_{H_2S} = 8.3$ kPa and 85 °C. a - Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; b - Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; c - Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.

For the steel samples corroded in the solutions without H$_2$S, the corrosion products were generally a mixture of iron carbonate and oxide according to Table 3-7. The morphology of the steel surfaces varied in different solutions. As shown in Figure 3-15 (a), the steel sample corroded in Solution #1 seemed to have two layers of corrosion products, an inner layer adjacent to the steel and an outer layer. The chemical composition of the cubical crystals which constituted the outer layer was very close to FeCO$_3$(s), as in Location 1. The corrosion products in Solution #2 formed a thin layer on the steel surface, as shown in Figure 3-15 (b). Besides some sparse
precipitation of Na$_2$CO$_3$(s), as in Location 4, the detected chemical compositions suggested the existence of FeCO$_3$(s) and Fe(s) on the surface, as the C/O atomic ratio was very close to 1:3 and the iron content was high in some spots like Location 5. The high iron content could be due to the stimulated signal from the steel substrate through the thin film. The corroded surface in Solution #3 in Figure 3-15 (c) contained a relatively high amount of O, which might be from the iron oxide on the surface.

Table 3-7. Results of EDS chemical analyses (%at.) on the corroded UD-165 surfaces.

<table>
<thead>
<tr>
<th>Figure</th>
<th>$P_{H_2S}$/kPa</th>
<th>pH</th>
<th>Location</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Na</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-15</td>
<td>0</td>
<td>10.7</td>
<td>5</td>
<td>58</td>
<td>7.6</td>
<td>23</td>
<td>-</td>
<td>1.2</td>
<td>0.1</td>
</tr>
<tr>
<td>3-16</td>
<td>8.3</td>
<td>10.7</td>
<td>5</td>
<td>36</td>
<td>3.6</td>
<td>58</td>
<td>0.2</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>17</td>
<td>14</td>
<td>67</td>
<td>0.5</td>
<td>1.7</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>36</td>
<td>11</td>
<td>21</td>
<td>28</td>
<td>2.4</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>11</td>
<td>8.6</td>
<td>55</td>
<td>4.0</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>35</td>
<td>12</td>
<td>50</td>
<td>0.1</td>
<td>-</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.4</td>
<td>8</td>
<td>78</td>
<td>5.6</td>
<td>14</td>
<td>0.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>40</td>
<td>19</td>
<td>40</td>
<td>0.1</td>
<td>-</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>
For the steel samples corroded in the solutions at $P_{H_2S} = 8.3$ kPa, a significant amount (25-70 %at.) of sulfur was detected at some spots on the steel corroded in Solution #1, Figure 3-16 (a), whereas there was less than 5 %at. of sulfur on the steels corroded in Solution #2, Figure 3-16 (b), and Solution #3, Figure 3-16 (c). This suggested that the corrosion products have changed from iron sulfides to oxide as the pH increased, which was consistent with the prediction from the Pourbaix diagrams.

The steel sample was corroded severely in Solution #1, and the corrosion products could be a mixture of FeS(s), FeS$_2$(s), and iron carbonate according to the EDS analyses and the Pourbaix diagram in Figure 3-14. In Solution #2 with pH of 10.7, the steel surface was covered by a thin dense black film. Because the O content was relatively high, iron oxide was suspected to be on the surface beside iron carbonate and iron sulfide. Corresponding to the highest $R_{pol}$ measured from LPR in Solution #2, this thin dense film was probably more protective than in Solutions #1 and #3. In Solution #3 with pH of 12.4, the steel surface was mildly corroded and was covered with a very thin film. In some areas such as Location 8, a very high amount of Fe was detected which probably was attributed to the signal from the steel substrate. The detected C and O elements might be related to a mixture of iron carbonate and iron oxide on the surface while their proportions in the mixture might be varying at different spots.

X-ray diffraction (XRD) analysis was only able to detect the presence of siderite in Solution #1 and iron in Solutions #2 and #3. The corrosion products were probably not in significant amount to be fully analyzed.
3.4 Conclusions

The electrochemical corrosion behavior of UD-165 was investigated in the three solutions with pH of 7.9, 10.7, and 12.4 at $P_{HS} = 0$ kPa and 8.3 kPa at 85 °C. The speciation modeling predicted that the dominant reactive species generally changed from $HCO_3^-$ (aq) to $OH^-$ (aq) as pH increased from Solution #1 to #3. $HS^-$ (aq) was calculated to be the primary sulfide ion from pH 7.9 to 12.4 at $P_{HS} = 8.3$ kPa.

After 60 hours, $R_{pol}$ at $P_{HS} = 0$ kPa increased as the solution pH increased, which could be attributed to the suppressed cathodic reaction and the protectiveness of the corrosion products. The presence of $P_{HS} = 8.3$ kPa resulted in the decrease of $R_{pol}$ and the increase of CR by factors of 0.2, 2, and 7 from pH 7.9 to 12.4, respectively. The modeled CR was in good agreement with experimental CR with the difference within one order of magnitude.

Limiting current density was found in the anodic LSV plots without $H_2S$ but not observed at $P_{HS} = 8.3$ kPa. The cathodic LSV plots did not show limiting current densities regardless of $P_{HS}$. $H_2O$ was probably the main reactant for HER at high pH and the addition of $H_2S$ increased the cathodic current. EIS data was fitted using an equivalent circuiting containing two time constants. Different mechanisms has been discussed for LSV and EIS results, and the role of $H_2S$ in increasing CR was believed to include the specific adsorption, the alternative reaction path of $HS^-$ (aq), and the non-homogeneity of the corrosion product film in the presence of $H_2S$.

The surface analysis showed that the corrosion products were generally a mixture of iron carbonate and oxide in the solutions without $H_2S$ although the morphology was different in each solution. At $P_{HS} = 8.3$ kPa, the corrosion products showed a trend of changing from iron carbonate and sulfides to oxide as pH increased, which agreed with the primary reactive ions and the Pourbaix diagrams.
References


Chapter 4

Corrosion of Ultra-high Strength Carbon Steel UD-165 in Alkaline Brines Containing Hydrogen Sulfide

This chapter presents the results and conclusions on corrosion of UD-165 at pH 7.9, 10.7, and 12.4 at 85 °C with \( P_{\text{H}_2\text{S}} \) extended to 0.83 and 69 kPa from the study in Chapter 3. The experimental results of corrosion rate and corrosion products were analyzed and compared with the modeling results from OLI Analyzer software. The reaction mechanisms were further discussed based on Tafel analysis and EIS, taking account of solution speciation and corrosion products.

Abstract

Corrosion behavior of carbon steel UD-165 was investigated using in-situ electrochemical methods in H\(_2\)S-containing alkaline brines (5%wt. NaCl; pH 7.9, 10.7, and 12.4) with H\(_2\)S partial pressure (\( P_{\text{H}_2\text{S}} \)) of 0.83 kPa and 69 kPa at 85 °C. The corrosion rate (CR) was the fastest at pH 10.7 and the slowest at pH 12.4. Higher \( P_{\text{H}_2\text{S}} \) accelerated CR at pH 10.7 and 12.4 but slightly decreased CR at pH 7.9. At higher \( P_{\text{H}_2\text{S}} \), anodic limiting current disappeared and cathodic current increased. The corrosion products changed from iron carbonate and sulfides to iron oxides as the pH increased.

\(^3\) The text in this chapter was originally prepared for the publication as “Ruishu Feng, Justin Beck, Margaret Ziomek-Moroz, and Serguei Lvov. Corrosion of Ultra-high Strength Carbon Steel in Alkaline Brines Containing Hydrogen Sulfide. Corrosion Science, in review.”
4.1 Introduction

Sour corrosion has been extensively studied due to its relevance to oil and natural gas industry. High strength low alloy carbon steels are commonly used for oil and natural gas exploration and production due to their mechanical properties and economical cost. However, H₂S has been found to make the carbon steels more susceptible to hydrogen induced cracking (HIC)/sulfide stress cracking (SSC), which could lead to catastrophic failure and drastic cost increase \(^1,2\). With the exploration of offshore wells going deeper to beyond 4572 m (15,000 feet), the carbon steels are exposed to higher pressure, higher temperature, and more corrosive environment with acid gas CO₂ and H₂S increasing exponentially \(^1\). Thus, it is important to understand sour corrosion of carbon steels in deep and ultra-deep wells to reduce and mitigate failure risks.

Electrochemical reactions and the formation of iron sulfides are two major factors of significance for sour corrosion. For anodic reaction of Fe dissolution, Shoesmith \(^3\) proposed a chemisorption-oxidation mechanism for H₂S corrosion, and Ma \(^4\) proposed a similar mechanism with two consecutive electron transfer steps. These two mechanisms are both analogous to the Fe dissolution reaction mechanism with OH (aq) proposed by Bockris \(^5\). With corrosion reactions taking place, iron sulfides are produced and form different layers on the steel surface. The layers could be weakly or strongly protective, depending on the products and the morphology \(^6-9\). Mackinawite was usually observed at the initial stage and formed the base layer on the steel surface. At the spots where the base layer cracks, localized corrosion or pitting corrosion tends to occur \(^3,10,11\). For the hydrogen evolution reaction (HER) at the cathode, a direct reduction reaction of H₂S was proposed in acidic conditions \(^12\) which provides an alternative path for HER. Moreover, it has been proposed that non-dissociated H₂S could have a catalytic effect for the cathodic reaction following Reactions [4-1] and [4-2]. \(^7\)
The regeneration of \( \text{H}_2\text{S(ad)} \) is favorable in an acid environment, as seen from Equation [4-2]. However, a drilling fluid of pH 10 to 12 is usually used in the drilling practice to limit corrosion. Most of the studies were conducted from pH 3 to 8 \(^6,13-20\), and the data has been limited for \( \text{H}_2\text{S} \)-containing conditions at relatively high pH. High pH could alter the reaction paths for both the anodic and cathodic reactions and influence the structures of corrosion products.

UD-165, an ultra-high strength low-alloy carbon steel, was designed especially for ultra-deep drilling. Some mechanical performance tests have been carried out in neutral-alkaline conditions in the presence of \( \text{H}_2\text{S} \). At 20 °C and \( \text{H}_2\text{S} \) partial pressure (\( P_{\text{H}_2\text{S}} \)) of 0.83 kPa (0.12 psi), it was found that fatigue crack growth was controlled by hydrogen diffusion at pH = 7, whereas it showed characteristics of stress corrosion cracking at pH = 12 \(^{21-23}\). In order to better understand the initiation and propagation of the cracking from the perspective of corrosion reactions, in situ electrochemical measurements and ex situ surface analysis were conducted in this work. The results from the authors’ previous study showed that the addition of \( P_{\text{H}_2\text{S}} \) 8.3 kPa affected the corrosion rate of UD-165 in carbonate buffered alkaline solutions, where the accelerating or retarding effect of \( \text{H}_2\text{S} \) varied with pH \(^{24}\). The present work further studied the electrochemical corrosion of UD-165 from pH 7 to 12 with two different partial pressures of \( \text{H}_2\text{S} \) gas (0.83 kPa and 69 kPa). Some researchers found that a significant amount of \( \text{HCO}_3^- \) (aq) accelerated the anodic reaction. \(^{25,26}\) Therefore, the effects of \( \text{H}_2\text{S(aq)}, \text{HCO}_3^- \) (aq), and \( \text{OH}^- \) (aq) were all taken into account for sour corrosion in alkaline brines. The experimental results were also compared with the modeling results from OLI Analyzer software, including corrosion rates and Pourbaix diagrams.
4.2 Materials and Methods

4.2.1 Material and sample preparation

The investigated material was an ultra-high strength low-alloy carbon steel, grade UD-165, and its chemical composition is listed in Table 4-1.  

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Al</th>
<th>Ni</th>
<th>Cu</th>
<th>Nb</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal</td>
<td>0.79</td>
<td>0.88</td>
<td>0.67</td>
<td>0.03</td>
<td>0.81</td>
<td>0.19</td>
<td>0.02</td>
<td>0.26</td>
<td></td>
</tr>
</tbody>
</table>

Steel samples were cut into 10×20×5 mm plates and then coated with epoxy so that only one 10×20 mm face was exposed to the solutions. The exposed surface was ground with 600 and 800 grit SiC papers and then polished by 0.1 and 0.05 micron alumina polishing slurries to minimize the surface defects and keep the surface area as consistent as possible. After rinsing with propanol and distilled water, the steel samples were wiped dry and ready for the assembly.

The wire attached to the steel sample was coated with shrinkable polytetrafluoroethylene (PTFE) tubing to avoid undesirable corrosion and short circuit with the autoclave.

4.2.2 System setup

The electrochemical measurements were carried out in a three-electrode system. The working electrode was the carbon steel sample prepared as described earlier. The counter
electrode was a platinum plate with dimensions of 10×20×1 mm. The two electrodes were held in place with the polished surfaces parallel to each other between two PTFE plates, which were tightened by two PTFE-coated screws. There was a spacing of 10 mm between the electrode surfaces. All the leads from the electrodes were coated with shrinkable PTFE tubing.

The reference electrode was a double-junction silver-silver chloride (Ag/AgCl) electrode specially designed to avoid contamination from the test solutions for a longer time. The solution inside the reference electrode was 5 %wt. NaCl(aq) solution to minimize the concentration gradient, and thus the junction potential, between the reference electrode and the test solutions. More details about the reference electrode can be found in Reference 24.

The 600 mL reactor vessel of the autoclave was constructed of 316L stainless steel. A PTFE liner inside the autoclave was used to contain the corrosive test solutions. The autoclave lid was mounted with a thermocouple, a pressure transducer, and a polyether ether ketone (PEEK) tube for transferring the gas and solutions. The thermocouple was coated with polymer for the protection against corrosion. The temperature was controlled at 85 °C by a heating mantle around the autoclave body and a digital controller connected with the thermocouple. The rod and the impeller of the magnetic stirrer were coated with epoxy to protect from undesired corrosion. A schematic of the autoclave system is shown in Figure 4-1 24. The system temperature and pressure were recorded during the test. A computer-controlled potentiostat was used to perform in-situ electrochemical measurements.
4.2.3 Test conditions and experimental procedure

The test solution compositions are listed in Table 4-2. The initial concentration of NaCl was 5%wt. (0.9 mol kg⁻¹) before adding the other chemicals. The solution was prepared with 250 g of deionized water at room temperature and then deaerated by bubbling with N₂ for at least one hour. The deaerated solution was transferred to the autoclave by pressure difference after the autoclave vessel was flushed with N₂. When the system was heated up to 85 °C, H₂S was introduced to the system as a H₂S/N₂ gas mixture (10%vol. H₂S) through tubing No. 6 in Figure 4-1. Once \( P_{\text{H₂S}} \) in the autoclave reached 0.83 kPa (0.12 psi) or 69 kPa (10 psi), all the valves were closed. Thus, the total amount of H₂S in the system was well defined. According to the ideal gas law, the H₂S concentrations were estimated to be \( 2.63 \times 10^{-4} \) mol kg⁻¹ and \( 2.19 \times 10^{-2} \) mol kg⁻¹, respectively, with the gaseous phase volume in the reactor vessel measured as 236.3 mL.
The solution pH was computed at 85 °C using OLI Analyzer modeling software, taking into account the system temperature, pressure, and components. According to Table 4-2, the pH increased from 7.9 to 12.4 from Solution #1 to #3 without H₂S. The pH slightly decreased with the addition of H₂S due to the dissociation of H₂S. Note that when referring to the trend with pH for both \( P_{H2S} \) in the following text, the pH at the lower \( P_{H2S} \) is used for both \( P_{H2S} \) in each solution (pH = 7.9, 10.7, and 12.4).

Linear polarization resistance (LPR), electrochemical frequency modulation (EFM), and electrochemical impedance spectroscopy (EIS) were performed every two hours over the exposure period. LPR was measured within ± 20 mV around the measured open circuit potential (OCP), and the sweep rate was 1 mV/s. EFM was measured within ± 25 mV around the OCP at the base frequency of 0.01 Hz with multipliers of 2 and 5. EIS was measured within ± 10 mV around the OCP at least over the frequency from 300 kHz to 5 mHz. The system was stirred at 525 RPM up to 60 hours. After 60 hours, the stir rate was reduced to check the effect of mass transport in the bulk solution. Linear sweep voltammetry (LSV) was carried out at the stir rate of 525 RPM at \( P_{H2S} = 0.83 \) kPa and 69 kPa with the sweep rate of 5 mV s\(^{-1}\) and 2 mV s\(^{-1}\), respectively. After the corrosion exposure, the corrosion products on the steel surface were examined using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and cross-sectional analysis.

Table 4-2. Solution compositions (mol kg\(^{-1}\)) and pH at different \( P_{H2S} \).

<table>
<thead>
<tr>
<th>Soln.</th>
<th>NaCl</th>
<th>NaHCO(_3)</th>
<th>Na(_2)CO(_3)</th>
<th>NaOH</th>
<th>pH, ( P_{H2S} = 0 ) kPa</th>
<th>pH, ( P_{H2S} = 0.83 ) kPa</th>
<th>pH, ( P_{H2S} = 69 ) kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.9</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>7.9</td>
<td>7.9</td>
<td>7.7</td>
</tr>
<tr>
<td>#2</td>
<td>0.9</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>10.7</td>
<td>10.7</td>
<td>10.5</td>
</tr>
<tr>
<td>#3</td>
<td>0.9</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
</tr>
</tbody>
</table>
4.2.4 Calculation of the corrosion rate

In a three-electrode cell, when corrosion is under activation control and the polarization is sufficiently small, the corrosion current density, \( j_{\text{corr}} \), can be calculated according to the Stern-Geary equation as shown in Equations \([4-3]\) and \([4-4]\) \(^{29-31}\).

\[
\begin{align*}
  j_{\text{corr}} &= 1 / (R_{\text{pol}} B') \quad [4-3] \\
  B' &= (\ln10) \left( b_c + b_a \right) / (b_c b_a) \quad [4-4]
\end{align*}
\]

where \( R_{\text{pol}} \) is the area-specific polarization resistance and \( B' \) is a combination of the cathodic, \( b_c \), and anodic, \( b_a \), Tafel slopes. \( R_{\text{pol}} \) was obtained from LPR corrected for the solution resistance \( R_{\text{sol}} \) measured in EIS. Tafel slopes were obtained from EFM.

The corrosion rate (CR), \( r \), defined as the depth of corrosion penetration per time, can be calculated with \( j_{\text{corr}} \) following Equation \([4-5]\).

\[
r = j_{\text{corr}} M / (n F \rho) \quad [4-5]
\]

where \( M \) is the molecular mass of the corroding metal, \( n \) is the electron number, \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), and \( \rho \) is the metal density.

4.3 Results and discussion

4.3.1 Carbonate and sulfide species in the solutions

The speciation of carbonate and sulfide species at 85 °C were calculated with OLI Analyzer at \( P_{\text{H2S}} = 0.83 \) kPa and 69 kPa and are depicted in Figures 4-2 and 4-3, respectively.\(^{28}\)
The concentrations of CO$_2$(aq), HCO$_3$-(aq), and H$_2$S(aq) decreased as the pH increased, whereas the concentrations of CO$_3^{2-}$(aq) and S$^2$-(aq) increased. HS (aq) was calculated to be the primary sulfide species, and its concentration was similar among the three solutions at both $P_{H_2S}$ = 0.83 kPa and 69 kPa. When $P_{H_2S}$ increased from 0.83 kPa to 69 kPa, the concentrations of sulfide species increased by two orders of magnitude, whereas the carbonate species did not change significantly due to the relatively low total H$_2$S concentration.

It has been proposed that OH (aq), HCO$_3$ (aq), and HS (aq) could react with Fe for anodic reactions. $^3-^5, ^26$ Their concentrations are given and compared in Table 4-3. It can been seen that the primary reactive ions changed from HCO$_3$ (aq) to OH (aq) with a similar concentration of HS (aq) as pH increased from Solution #1 to #3.

![Figure 4-2. The primary carbonate and sulfide species at 85 °C and $P_{H_2S}$ = 0.83 kPa. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.](image-url)
Figure 4-3. The primary carbonate and sulfide species at 85 °C and $P_{H_2S} = 69$ kPa. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.7; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.5; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.

<table>
<thead>
<tr>
<th>$P_{H_2S}$</th>
<th>Solution</th>
<th>OH$^-$ (aq)</th>
<th>HCO$_3^-$ (aq)</th>
<th>HS$^-$ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83 kPa</td>
<td>#1</td>
<td>4.18×10$^{-5}$</td>
<td>4.57×10$^{-1}$</td>
<td>2.48×10$^{-4}$</td>
</tr>
<tr>
<td>69 kPa</td>
<td>#2</td>
<td>2.33×10$^{-2}$</td>
<td>2.44×10$^{-2}$</td>
<td>2.62×10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>#3</td>
<td>9.63×10$^{-1}$</td>
<td>5.17×10$^{-4}$</td>
<td>2.54×10$^{-4}$</td>
</tr>
</tbody>
</table>

|   | #1       | 2.74×10$^{-5}$ | 4.52×10$^{-1}$ | 2.01×10$^{-2}$ |
| 69 kPa | #2       | 1.49×10$^{-2}$ | 3.73×10$^{-2}$ | 2.19×10$^{-2}$ |
|       | #3       | 9.41×10$^{-1}$ | 5.22×10$^{-4}$ | 2.12×10$^{-2}$ |

### 4.3.2 Corrosion potential ($E_{corr}$)

The anodic reaction for the corrosion of carbon steel is oxidation of Fe(s) to Fe$^{2+}$(aq), the reduction reaction of which is shown in Equation [4-6]. The cathodic reaction in acidic solutions is the reduction of H$^+$ (aq) to hydrogen. In the anaerobic alkaline conditions, the H$^+$ (aq)
concentration was quite low. \( \text{H}_2\text{S(aq)}, \text{H}_2\text{O(l)}, \text{H}_2\text{CO}_3\text{(aq)}, \) and other hydrogen-containing species can provide hydrogen for the cathodic reaction. Equations [4-7] – [4-9] show the example of \( \text{H}^+\text{(aq)}, \text{H}_2\text{O(l)} \) and \( \text{H}_2\text{S(aq)} \) as the hydrogen source. The standard electrode potential \( E^0 \) at 85 °C was calculated using the Gibbs free energy values from HCh chemical simulation software and OLI Analyzer software 31–33. The Nernst equations for Reactions [4-6] – [4-9] are listed in Equations [4-10] – [4-13]. Both the anodic and cathodic reactions are written as reduction reactions. The activity, \( a \), is used to account for concentration effects for the ionic species. \( P_{\text{H}_2(g)} \) represents the partial pressure of \( \text{H}_2(g) \) and the fugacity coefficient is assumed to be unity.

\[
\text{Fe}^{2+}(\text{aq}) + 2 \, \text{e}^- = \text{Fe(s)} , \quad E^0 = -0.473 \, \text{V vs SHE}, \quad 85 \, ^\circ\text{C} \tag{4-6}
\]

\[
2 \, \text{H}^+(\text{aq}) + 2 \, \text{e}^- = \text{H}_2(g), \quad E^0 = 0 \, \text{V vs SHE}, \quad 85 \, ^\circ\text{C} \tag{4-7}
\]

\[
2 \, \text{H}_2\text{O(l)} + 2 \, \text{e}^- = \text{H}_2(g) + 2 \, \text{OH}^{-} (\text{aq}), \quad E^0 = -0.890 \, \text{V vs SHE}, \quad 85 \, ^\circ\text{C} \tag{4-8}
\]

\[
2 \, \text{H}_2\text{S(aq)} + 2 \, \text{e}^- = \text{H}_2(g) + 2 \, \text{HS}^{-} (\text{aq}), \quad E^0 = -0.463 \, \text{V vs SHE}, \quad 85 \, ^\circ\text{C} \tag{4-9}
\]

\[
E_{\text{Fe}^{2+}|\text{Fe}} = E_{\text{Fe}^{2+}|\text{Fe}}^0 + \frac{RT}{2F} \ln a_{\text{Fe}^{2+}(\text{aq})} \tag{4-10}
\]

\[
E_{\text{H}^{+}|\text{H}_2} = E_{\text{H}^{+}|\text{H}_2}^0 + \frac{RT}{2F} \ln \frac{a_{\text{H}^+(\text{aq})}}{P_{\text{H}_2(g)}} \tag{4-11}
\]

\[
E_{\text{H}_2\text{O}|\text{H}_2} = E_{\text{H}_2\text{O}|\text{H}_2}^0 + \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}(\text{l})}}{a_{\text{OH}^{-}(\text{aq})} P_{\text{H}_2(g)}} \tag{4-12}
\]

\[
E_{\text{H}_2\text{S}|\text{H}_2} = E_{\text{H}_2\text{S}|\text{H}_2}^0 + \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{S}(\text{aq})}}{a_{\text{HS}^{-}(\text{aq})} P_{\text{H}_2(g)}} \tag{4-13}
\]

The potential of the working electrode was measured with respect to the Ag/AgCl reference electrode at temperature and is converted to the standard hydrogen electrode (SHE) scale at 85 °C. \( E_{\text{corr}} \) changing with time in all the cases are shown in Figure 4-4. \( E_{\text{corr}} \) generally increased before approaching a steady state by 60 hours. The dissolution of the steel with time
increased the concentration of Fe\textsuperscript{2+}(aq) and made the potential of Fe dissolution more positive according to Equation [4-10]. $E_{\text{corr}}$ at steady state varied with pH and H\textsubscript{2}S concentration. $E_{\text{corr}}$ became more negative as the pH increased, except for Solution #3 at $P_{H_2S} = 0.83$ kPa. The effect of pH can be easily explained according to Equations [4-11] and [4-12]. $E_{\text{corr}}$ was more positive at higher H\textsubscript{2}S concentration, probably because the potential of Reaction [4-9] was more positive than the other cathodic reactions.

![Graph](image)

**Figure 4-4.** The corrosion potential of UD-165 changing with time at 85 °C. Conditions: $P_{H_2S} = 0.83$ kPa and 69 kPa. Solution #1: 0.9 mol kg\textsuperscript{-1} NaCl, 0.5 mol kg\textsuperscript{-1} NaHCO\textsubscript{3}, pH = 7.9; Solution #2: 0.9 mol kg\textsuperscript{-1} NaCl, 1 mol kg\textsuperscript{-1} Na\textsubscript{2}CO\textsubscript{3}, pH = 10.7; Solution #3: 0.9 mol kg\textsuperscript{-1} NaCl, 1 mol kg\textsuperscript{-1} Na\textsubscript{2}CO\textsubscript{3}, 1 mol kg\textsuperscript{-1} NaOH, pH = 12.4.

### 4.3.3 Polarization resistance and corrosion rate

$R_{\text{pol}}$ and CR of UD-165 are plotted with time in Figures 4-5 and 4-6, respectively. $R_{\text{pol}}$ generally increased with time and approached the steady state by 60 hours. The increase of $R_{\text{pol}}$ could be related to the formation of the corrosion product layer, which would decrease the
reactive area. The fluctuation in $R_{\text{pol}}$ could be related to the breakdown of the corrosion product film and onset of localized corrosion. It can be seen that $R_{\text{pol}}$ at pH = 10.6 were the smallest over time for both $P_{\text{H}_2\text{S}} = 0.83$ kPa and 69 kPa. Compared to lower $P_{\text{H}_2\text{S}}$, $R_{\text{pol}}$ at $P_{\text{H}_2\text{S}} = 69$ kPa slightly increased in Solution #1 and decreased in Solutions #2 and #3. CR in Figure 4-6 showed a reverse trend of $R_{\text{pol}}$.

![Graph showing $R_{\text{pol}}$ vs. time for different conditions.](image)

Figure 4-5. $R_{\text{pol}}$ of UD-165 changing with time at 85 °C. Conditions: $P_{\text{H}_2\text{S}} = 0.83$ kPa and 69 kPa. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.
Figure 4-6. The corrosion rate of UD-165 changing with time at 85 °C. Conditions: \( P_{\text{H}_2\text{S}} = 0.83 \) kPa and 69 kPa. Solution #1: 0.9 mol kg\(^{-1}\) NaCl, 0.5 mol kg\(^{-1}\) NaHCO\(_3\), pH = 7.9; Solution #2: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), pH = 10.7; Solution #3: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), 1 mol kg\(^{-1}\) NaOH, pH = 12.4.

CR of UD-165 after 60 hours in different conditions are plotted in Figure 4-7. For \( P_{\text{H}_2\text{S}} = 0.83 \) kPa and 69 kPa, the experimental CR was the fastest at pH = 10.7 (0.22 and 0.39 mm y\(^{-1}\)) and the slowest at pH = 12.4 (0.011 and 0.020 mm y\(^{-1}\)). The experimental CR at pH = 7.9 slightly decreased when \( P_{\text{H}_2\text{S}} \) increased from 0.83 kPa to 69 kPa, whereas CR at pH = 10.7 and 12.4 increased at higher \( P_{\text{H}_2\text{S}} \). H\(_2\)S could provide an alternative cathodic reaction path following Reaction [4-9] and facilitate pitting corrosion and, therefore, increase the CR at pH = 10.7 and 12.4. \(^{14}\) The variation of pH changed the CR in a larger degree than \( P_{\text{H}_2\text{S}} \) did, indicating that the effect of pH on CR was larger than \( P_{\text{H}_2\text{S}} \).
Figure 4-7. Experimental CR after 60 hours and modeled CR at 85 °C. Conditions: $P_{H_2S} = 0.83 \text{ kPa and } 69 \text{ kPa}$. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.

CR in different conditions calculated using OLI analyzer are also shown in Figure 4-7. The CR was calculated as a rotating disk electrode made of generic carbon steel. The modeled CR at pH 7.9 was higher than those at pH 10.7 and 12.4 by almost two orders of magnitude. CR at 10.7 was predicted to be the slowest at $P_{H_2S} = 0.83 \text{ kPa}$, which was much lower than the experimental CR. The experimental and modeled CR at pH = 12.4 were in good agreement. The higher $P_{H_2S}$ was predicted to increase the CR in the three solutions, which agreed with the experimental results.

4.3.4 The effect of stir rate

Figure 4-8 shows the EIS Nyquist plots at different stir rates in Solution #2 at $P_{H_2S} = 69 \text{ kPa}$, and the patterns were almost the same when changing the stir rate. Similar behavior was
found in the other conditions, except that some change was observed over time for tests where the system had not quite reached the steady state. This indicated that the electrochemical impedance was not changed by changing the hydrodynamics in the bulk solution, and the mass transport (diffusion or convection) from the bulk solution did not affect the rate determining step for the overall corrosion process.

Figure 4-8. The Nyquist plots for UD-165 at different stir rates in Solution #2 at $P_{H_2S} = 69$ kPa at 85 °C. Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.5.

4.3.5 LSV results

LSV plots at $P_{H_2S} = 0.83$ kPa and 69 kPa were corrected for $R_{sol}$. The anodic and cathodic LSV plots are shown in Figures 4-9 and 4-10, respectively. The Tafel slopes obtained from the linear regions are listed in Table 4-4. At $P_{H_2S} = 0.83$ kPa, limiting current densities were observed at high anodic polarization regions in Solutions #1 and #2. The current density in Solution #3 was more than two orders of magnitude lower. Peaks were observed around +0.2 V vs $E_{corr}$ in Solution #1 and #2, which could be related to the additional reactions or the breakdown of corrosion product layers. Note that the $b_n$ values at $P_{H_2S} = 0.83$ kPa in Table 4-4 were obtained from the
linear regions before the peak and the limiting current because the behavior close to $E_{corr}$ more likely represents the natural corrosion. At $P_{H2S} = 69$ kPa, the anodic current densities increased and there were no obvious limiting current densities. The accelerating effect of higher $P_{H2S}$ could be related to the higher concentration of HS\(^{-}\)(aq) which provided an alternative reaction path. The Tafel slope reflected a comprehensive effect from all of the reactants including OH\(^-\)(aq), HCO\(_3\)\(^-\)(aq), and HS\(^-\)(aq). The $b_a$ values at $P_{H2S} = 69$ kPa were much smaller than at lower $P_{H2S}$, which could be due to the larger contribution of HS\(^-\)(aq) reaction path at higher $P_{H2S}$.

Figure 4-9. The anodic LSV plots of UD-165 at $P_{H2S} = 0.83$ and 69 kPa at 85 °C. Conditions: Solution #1: 0.9 mol kg\(^{-1}\) NaCl, 0.5 mol kg\(^{-1}\) NaHCO\(_3\), pH = 7.9; Solution #2: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), pH = 10.7; Solution #3: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), 1 mol kg\(^{-1}\) NaOH, pH = 12.4.
Figure 4-10. The cathodic LSV plots of UD-165 at \( P_{\text{H2S}} = 0.83 \) and 69 kPa at 85 °C. Conditions: Solution #1: 0.9 mol kg\(^{-1}\) NaCl, 0.5 mol kg\(^{-1}\) NaHCO\(_3\), pH = 7.9; Solution #2: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), pH = 10.7; Solution #3: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), 1 mol kg\(^{-1}\) NaOH, pH = 12.4.

Table 4-4. Tafel slopes in the three solutions at \( P_{\text{H2S}} = 0.83 \) kPa (I) and 69 kPa (II) at 85 °C.

<table>
<thead>
<tr>
<th>Tafel slope / (V dec(^{-1}))</th>
<th>I-#1</th>
<th>I-#2</th>
<th>I-#3</th>
<th>II-#1</th>
<th>II-#2</th>
<th>II-#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_a )</td>
<td>0.296</td>
<td>0.160</td>
<td>0.414</td>
<td>0.115</td>
<td>0.069-0.132</td>
<td>0.062</td>
</tr>
<tr>
<td>( b_c )</td>
<td>0.311</td>
<td>0.174</td>
<td>0.327</td>
<td>limiting</td>
<td>0.500</td>
<td>0.360</td>
</tr>
</tbody>
</table>

Assuming the symmetry coefficient \( \beta \) to be 0.5, the anodic Tafel slopes calculated according to \( 2.303RT/(n(1-\beta)F) \) were 0.142 V dec\(^{-1}\) and 0.071 V dec\(^{-1}\) for a one-electron mechanism \( (n=1) \) and a two-electron mechanism \( (n=2) \), respectively. \( R \) represents the gas constant and \( T \) the absolute temperature. At \( P_{\text{H2S}} = 69 \) kPa, \( b_a \) in Solution #1 was close to the one-electron mechanism, \( b_a \) in Solution #3 was close to the two-electron mechanism, and \( b_a \) in Solution #2 was close to the two-electron mechanism at small polarization and the one-electron
mechanism at larger polarization. According to Table 4-3, the ratio of HS(aq) concentration to the total concentration of OH(aq)+HCO$_3$ (aq)+HS(aq) was the largest in Solution #2, where the HS(aq) reaction path probably became more pronounced.

Based on the effect of HS(aq) discussed above, it is speculated that the HS(aq) reaction path might involve two electrons transferring simultaneously and OH(aq) and HCO$_3$ (aq) only one electron transferring at the rate determining step (RDS). Reactions [4-14] to [4-26] could be the plausible steps of these two mechanisms, modified from the mechanisms proposed previously by other researchers.$^3$-$^5$,$^{34}$

One-electron mechanism for OH(aq) or HCO$_3$ (aq)

Step I (RDS): Fe(s) + OH(aq) → FeOH(ad) + e$^-$ $^4$-$^14$

Step II: FeOH(ad) ↔ FeOH$^+$ (aq) + e$^-$ $^4$-$^15$

Step III: FeOH$^+$ (aq) + H$^+$ (aq) ↔ Fe$^{2+}$ (aq) + H$_2$O(l) $^4$-$^16$

or FeOH$^+$ (aq) + H$_2$O(l) ↔ Fe(OH)$_2$(s) + H$^+$ (aq) $^4$-$^17$

(I) + (II) + (III): Fe(s) → Fe$^{2+}$ (aq) + 2 e$^-$ $^4$-$^18$

or Fe(s) + 2 OH(aq) → Fe(OH)$_2$(s) + 2 e$^-$ $^4$-$^19$

\[ b_a = 2.303 \left( \frac{RT}{(1-\beta)F} \right) \] $^4$-$^20$

Two-electron mechanism for HS(aq)

Step I (RDS): Fe(s) + HS(aq) → FeHS$^+$ (ad) + 2 e$^-$ $^4$-$^21$

Step II: FeHS$^+$ (ad) ↔ Fe$^{2+}$ (aq) + HS(aq) $^4$-$^22$

or FeHS$^+$ (ad) ↔ FeS(s) + H$^+$ (aq) $^4$-$^23$

(I) + (II): Fe(s) → Fe$^{2+}$ (aq) + 2 e$^-$ $^4$-$^24$

or Fe(s) + HS(aq) → FeS(s) + H$^+$ (aq) + 2 e$^-$ $^4$-$^25$

\[ b_a = 2.303 \left( \frac{RT}{[2(1-\beta)F]} \right) \] $^4$-$^26$
For the cathodic regions in Figure 4-10, the current density decreased as pH increased and increased at higher $P_{H_2S}$. Limiting current density was only observed in Solution #1 at $P_{H_2S} = 69$ kPa; however, the current density was the highest. In this condition, the concentration of H$_2$S(aq) was the highest according to the speciation in Figure 4-3; therefore, H$_2$S(aq) could have served as the main reactant for the HER and the limiting current was likely due to the mass transport or a chemical step related to H$_2$S(aq). With further negative polarization, H$_2$O(l) started to be reduced and the limiting current disappeared. In the other conditions, H$_2$O(l) could be the main reactant for lack of H$^+(aq)$ and, therefore, the current density was comparatively low but was not limited at higher polarization. The similar phenomenon was reported on the effect of pH on the cathodic polarization by Stern 35. The Volmer-Heyrovsky (V-H) and Volmer-Tafel (V-T) mechanisms are commonly accepted for the HER mechanism, and these two mechanisms are given in Appendix (B) 34. The cathodic Tafel slopes at 85 °C were calculated to be 0.142 V dec$^{-1}$ and 0.036 V dec$^{-1}$ for the V-H and V-T mechanisms, respectively, assuming the symmetry coefficient $\beta$ to be 0.5. The measured $b_c$ values in Table 4-4 were much larger, indicating either a different mechanism or a limiting current effect being incorporated.

### 4.3.6 EIS results

The EIS results of UD-165 after 60 hours are shown in Figure 4-11. For both $P_{H_2S} = 0.83$ and 69 kPa, the phase angles showed one broad time constant in Solutions #1 and #3 and two separated time constants in Solution #2, which could be related to different mechanisms. The EIS data in Solutions #1 and #3 were fitted using the equivalent circuit (a) in Figure 4-12, which consisted of a solution resistance ($R_{sol}$) in series with a parallel combination of a constant phase
element (CPE) and a resistor. As a substitute for the capacitor in the Randles circuit, a CPE was used to represent the non-ideality of the double layer capacitance.

Figure 4-11. EIS results of UD-165 steel in the three solutions at 85 °C. Conditions: $P_{	ext{H}_2\text{S}} = 0.83$ kPa and 69 kPa. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.
The impedance of CPE, $Z_Q$, is defined as in Equation [4-27].

$$Z_Q = (Y_0)^{-1} (i\omega)^{-p} \quad [4-27]$$

where $Y_0$ is the admittance modulus, $i$ the imaginary unit, $\omega$ the angular frequency and $p$ the exponent within 0 to 1. When $p = 1$, CPE is identical to an ideal capacitor; when $p = 0$, CPE behaves as a resistor; and when $p = 0.5$, CPE can serve as an infinite-length Warburg element, representing diffusion of the charge carrier.

In Circuit (a), $R_1$ can be seen as the polarization resistance for the corrosion process, and CPE1 represents the non-ideal double layer capacitor. The phase angles were larger than 45° and changing the stir rate showed little effect on the corrosion behavior; therefore, the Warburg element was not included in Circuit (a). The fitting results are listed in Table 4-5. CPE1-$p$ was between 0.8 to 1, which was the usual range due to the non-ideality of double layer capacitor between the steel surface and the solution. Compared with $R_{pol}$ values from LPR, which are also given in Table 4-5, $R_1$ values basically agreed with $R_{pol}$ from LPR, although slightly larger in some cases. $R_1$ in Solution #3 was one order of magnitude larger than in Solution #1.
Circuit (b) in Figure 4-12 was used to fit the EIS data from Solution #2. There was a second parallel combination of CPE2 and R2 in series with R1. This circuit has been reported to represent multiple phenomena, like corrosion with a porous film, passivation, and adsorption/desorption.\textsuperscript{37–39} For lack of data at low frequency, \( R_2 \) in Solution #2 was calculated to be relatively large, especially at \( P_{\text{H}_2\text{S}} = 69 \) kPa. Unlike the good agreement in Solutions #1 and #3, \( R_{\text{pol}} \) from LPR was one order of magnitude larger than \( R_1 \) and much smaller than \( R_2 \) in Solution #2. LPR was measured at a sweep rate (1 mV s\(^{-1}\)) which could be in the frequency range between \( R_1 \) and \( R_2 \). Regardless, \( R_1 \) in Solution #2 decreased at higher \( P_{\text{H}_2\text{S}} \).

Table 4-5. EIS fitting results in the three solutions at \( P_{\text{H}_2\text{S}} = 0.83 \) kPa (I) and 69 kPa (II) at 85 °C.

<table>
<thead>
<tr>
<th>element</th>
<th>( \text{unit} )</th>
<th>I-#1</th>
<th>I-#2</th>
<th>I-#3</th>
<th>II-#1</th>
<th>II-#2</th>
<th>II-#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{\text{sol}} )</td>
<td>( \Omega \text{ cm}^2 )</td>
<td>3.41</td>
<td>3.26</td>
<td>2.79</td>
<td>3.72</td>
<td>3.18</td>
<td>2.83</td>
</tr>
<tr>
<td>CPE1-( Y_0 )</td>
<td>( \Omega \text{ cm}^2 \text{s}^p )</td>
<td>6.76( \times )10(^{-4})</td>
<td>7.63( \times )10(^{-3})</td>
<td>5.43( \times )10(^{-4})</td>
<td>7.70( \times )10(^{-3})</td>
<td>3.62( \times )10(^{-3})</td>
<td>3.93( \times )10(^{-3})</td>
</tr>
<tr>
<td>CPE1-( p )</td>
<td>0-1</td>
<td>0.89</td>
<td>0.85</td>
<td>0.94</td>
<td>0.92</td>
<td>0.78</td>
<td>0.94</td>
</tr>
<tr>
<td>( R_1 )</td>
<td>( \Omega \text{ cm}^2 )</td>
<td>2526</td>
<td>272</td>
<td>32004</td>
<td>8104</td>
<td>154</td>
<td>12064</td>
</tr>
<tr>
<td>CPE2-( Y_0 )</td>
<td>( \Omega \text{ cm}^2 \text{s}^p )</td>
<td>-</td>
<td>5.43( \times )10(^{-3})</td>
<td>-</td>
<td>-</td>
<td>9.71( \times )10(^{-3})</td>
<td>-</td>
</tr>
<tr>
<td>CPE2-( p )</td>
<td>0-1</td>
<td>-</td>
<td>0.69</td>
<td>-</td>
<td>-</td>
<td>0.68</td>
<td>-</td>
</tr>
<tr>
<td>( R_2 )</td>
<td>( \Omega \text{ cm}^2 )</td>
<td>-</td>
<td>13556</td>
<td>-</td>
<td>-</td>
<td>8.88( \times )10(^{11})</td>
<td>-</td>
</tr>
<tr>
<td>( R_{\text{pol}} )-LPR</td>
<td>( \Omega \text{ cm}^2 )</td>
<td>2681</td>
<td>1850</td>
<td>27635</td>
<td>5075</td>
<td>1138</td>
<td>9407</td>
</tr>
</tbody>
</table>

4.3.7 Analysis of corrosion products

Pourbaix diagrams at 85 °C were generated with OLI Analyzer.\textsuperscript{40} Figures 4-13 and 4-14 show the diagrams for Solution #2 at \( P_{\text{H}_2\text{S}} = 0.83 \) and 69 kPa, respectively, and the diagrams for Solutions #1 and #3 were similar. As pH increased from 7.9 to 10.7 to 12.4, the thermodynamically predominant species changed from FeS(s)/FeS\(_2\)(s)/FeCO\(_3\)(aq) to
FeS(s)/FeS₂(s)/Fe₃O₄(s) and then to HFeO₂(aq)/Fe₃O₄(s). There was a trend of changing from iron carbonate and sulfides to iron oxide as pH increased. As $P_{H₂S}$ increased from 0.83 kPa to 69 kPa, the stable regions of FeS(s) and FeS₂(s) expanded.

Figure 4-13. Pourbaix diagram for Fe-H₂O-H₂CO₃-H₂S system in Solution #2 at $P_{H₂S} = 0.83$ kPa and 85 °C. Solution #2: 0.9 mol kg⁻¹ NaCl, 1 mol kg⁻¹ Na₂CO₃, pH = 10.7; Titrants: NaOH/HCl.

Figure 4-14. Pourbaix diagram for Fe-H₂O-H₂CO₃-H₂S system in Solution #2 at $P_{H₂S} = 69$ kPa and 85 °C. Solution #2: 0.9 mol kg⁻¹ NaCl, 1 mol kg⁻¹ Na₂CO₃, pH = 10.5; Titrants: NaOH/HCl.
The SEM images at $P_{\text{H}_2\text{S}} = 0.83$ kPa and 69 kPa are shown in Figures 4-15 and 4-16, respectively. The EDS results of some selected locations are given in Table 4-6. The accelerating voltage of EDS was 7 kV, as a larger voltage was found to penetrate too deep into the substrate.

Figure 4-15. SEM images of UD-165 steel surfaces after the corrosion tests at $P_{\text{H}_2\text{S}} = 0.83$ kPa and 85 °C. A - Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; B - Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; C - Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.
Figure 4-16. SEM images of UD-165 steel surfaces after the corrosion tests at $P_{\text{H}_2\text{S}} = 69$ kPa and 85 °C. A - Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.7; B - Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.5; C and D - Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.

At $P_{\text{H}_2\text{S}} = 0.83$ kPa, S was detectable on the surface, but the amount was quite low. There were some cubic crystals with chemical composition close to FeCO$_3$(s) found on the surface in Solution #1. In Solution #2, the surface was probably covered by a mixture of iron carbonate, iron oxides, and sulfides. The SEM image showed non-homogeneity on the surface. The corroded surface in Solution #3 was covered by a thin black film with the composition close to iron oxide. The amount of Fe was around 65 %at. at some spots, indicating that either it was active surface
exposed to the solution, or that the corrosion product film was so thin that even 7 kV accelerating voltage could penetrate into the underlying steel substrate. The corrosion products generally changed from iron carbonate and sulfides to iron oxides as pH increased, which agreed with the Pourbaix diagram.

Table 4-6. Results of EDS chemical analyses (%at.) on the corroded UD-165 surfaces.

<table>
<thead>
<tr>
<th>Figure</th>
<th>$P_{H_2S}$ / kPa</th>
<th>pH</th>
<th>Location</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>7.9</td>
<td>2</td>
<td>20</td>
<td>16</td>
<td>59</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>17</td>
<td>7.0</td>
<td>29</td>
<td>1.5</td>
</tr>
<tr>
<td>4-15</td>
<td>0.83</td>
<td>10.7</td>
<td>4</td>
<td>22</td>
<td>12</td>
<td>47</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>7</td>
<td></td>
<td>65</td>
<td>-</td>
<td>30</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.4</td>
<td>8</td>
<td>8.6</td>
<td>-</td>
<td>65</td>
<td>4.8</td>
</tr>
<tr>
<td>4-16</td>
<td>69</td>
<td>10.5</td>
<td>5</td>
<td>28</td>
<td>30</td>
<td>38</td>
<td>1.7</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>11</td>
<td></td>
<td>60</td>
<td>10</td>
<td>23</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.7</td>
<td>2</td>
<td>31</td>
<td>9.4</td>
<td>26</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>12.4</td>
<td>8</td>
<td>30</td>
<td>14</td>
<td>41</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td></td>
<td>30</td>
<td>16</td>
<td>44</td>
<td>7.6</td>
</tr>
</tbody>
</table>
At $P_{\text{H}_2\text{S}} = 69$ kPa, the amount of S was much higher than that at $P_{\text{H}_2\text{S}} = 0.83$ kPa. According to Table 4-6, the corrosion products in the three solutions contained Fe, C, O and S, which were probably a mixture of iron carbonate, iron sulfides, and iron oxides due to the multiple reactants. However, the morphology of the corrosion products were different. The microstructure of the corrosion products was comparatively loose in Solution #1. In Solution #2, massive corrosion products were detected along Locations 5 and 6 whereas the other areas were quite flat, suggesting the characteristics of localized corrosion. This could be the reason that the CR in Solution #2 was the fastest. Location 4 appeared to contain 60 % at. of Fe, indicating that it could be active steel surface or that the corrosion product film was very thin. In Solution #3, the microstructure of the corrosion products were like a honeycomb as shown in Figure 4-16(D), which could act as a barrier for the transport of the reactive and produced ions. This might be one of the reasons why $R_{\text{pol}}$ was the largest in Solution #3.

Figure 4-17 shows the XRD results for the uncorroded UD-165 and corroded steel samples. Limited information was obtained from XRD because the corrosion product layer was relatively thin and the amounts of iron sulfides were quite low. Iron and siderite (FeCO$_3$) were detected in almost all the corroded samples due to the large amount of carbonate buffers. A small peak of Fe(II) hydroxide was detected on the sample corroded in Solution #2 and $P_{\text{H}_2\text{S}} = 69$ kPa.

Figure 4-18 shows the EDS mapping result on the cross-section of UD-165 corroded in Solution #1 at $P_{\text{H}_2\text{S}} = 0.83$ kPa and 85 °C. It can be seen that a thin film of corrosion products formed on the steel surface and the thickness was around 2 - 4 μm. The uneven thickness of the film suggested that localized corrosion occurred on the steel surface. The chemical composition indicated that the film mainly consisted of Fe, S, C, and O. Sulfur was mostly detected in the inner part of the film, which could be due to the specific adsorption of HS (aq) or the fast kinetics of mackinawite formation. This may be the reason that only a little amount of sulfur was detected on the outer part of the film.
Figure 4-17. XRD results of uncorroded and corroded UD-165 steel surfaces. Conditions: 85 °C. $P_{\text{H}_2\text{S}} = 0.83$ kPa and 69 kPa. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 10.7; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 12.4.

Figure 4-18. EDS elemental maps of cross-section of UD-165 corroded in Solution #1 at $P_{\text{H}_2\text{S}} = 0.83$ kPa and 85 °C. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 7.9. The light-colored dots represent the corresponding element distribution in the frames on the right-hand side.
4.4 Conclusions

Sour corrosion of UD-165 was investigated using in situ electrochemical measurements and ex situ surface characterization at pH of 7.9 to 12.4 with $P_{\text{H}_{2}\text{S}} = 0.83$ and 69 kPa at 85 °C. The conclusions are:

1) The calculated primary reactive species changed from HCO$_3$ (aq) to OH (aq) with a similar concentration of HS (aq) as pH increased from 7.9 to 12.4. HS (aq) was calculated to be the primary sulfide species.

2) At $P_{\text{H}_{2}\text{S}} = 0.83$ kPa and 69 kPa, the experimental CR was the fastest at pH = 10.7 and the slowest at pH = 12.4. The experimental CR at pH = 10.7 and 12.4 increased when $P_{\text{H}_{2}\text{S}}$ increased from 0.83 kPa to 69 kPa whereas CR at pH = 7.9 slightly decreased at higher $P_{\text{H}_{2}\text{S}}$. The effect of pH on CR was larger than $P_{\text{H}_{2}\text{S}}$.

3) Different stir rates did not change the impedance significantly, indicating that mass transport of diffusion or convection in the bulk solution did not affect the rate determining step for the overall corrosion process.

4) Anodic limiting current was observed at $P_{\text{H}_{2}\text{S}} = 0.83$ kPa but not at $P_{\text{H}_{2}\text{S}} = 69$ kPa, and $b_a$ values were smaller at higher $P_{\text{H}_{2}\text{S}}$. Cathodic current densities increased at $P_{\text{H}_{2}\text{S}} = 69$ kPa. The main reactant for HER could be H$_2$S(aq) in Solution #1 at $P_{\text{H}_{2}\text{S}} = 69$ kPa and H$_2$O(l) for the other conditions.

5) For both $P_{\text{H}_{2}\text{S}} = 0.83$ and 69 kPa, the phase angles showed one broad time constant in Solutions #1 and #3 and two time constants in Solution #2, which could be related to different mechanisms.

6) The corrosion products in the three solutions contained Fe, C, O, and S, and showed the trend of changing from iron carbonate and sulfides to iron oxides as pH increased. More S
was detected on the steel surfaces corroded at $P_{H2S} = 69$ kPa. Sulfur was mostly detected in the inner part of the film in Solution #1 at $P_{H2S} = 0.83$ kPa.

References


Chapter 5

Corrosion Behavior of Ultra-high Strength Drill Steel UD-165 in Alkaline Brines Containing Hydrogen Sulfide at High Temperature

This chapter presents the results and conclusions on corrosion of UD-165 at 200 °C in alkaline brines (pH 8 to 11) in the presence of $P_{H_2S} = 69$ kPa. The effects of high pH and high temperature were determined through the investigation on the corrosion rate and corrosion products. The solution speciation, Pourbaix diagram, and the corrosion rate were calculated with commercial software at 200 °C. The generalized Bulter-Volmer equation and EIS were employed to study the reaction mechanisms.

Abstract

In-situ electrochemical measurements were used to study the sour corrosion of ultra-high strength low alloy carbon steel (UD-165) in alkaline brines at 200 °C. The solutions were buffered with NaHCO$_3$ / Na$_2$CO$_3$ / NaOH to pH values calculated to be 8.1, 9.8, and 10.8 in the presence of H$_2$S gas at 200 °C. The partial pressure of H$_2$S was equivalent to 10 psi (69 kPa) at 85 °C. The dominant reactive ion changed from HCO$_3$ (aq) to OH (aq) with a comparable concentration of HS (aq) as pH increased. Polarization resistance values at 200 °C were one to two orders of magnitude lower than those at 85 °C, which corresponded to a drastic increase in

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$^4$ The text in this chapter was originally prepared for the publication as “Ruishu Feng, Justin R. Beck, Derek M. Hall, Ian Wolfe, Aysel Buyuksagis, Serguei N. Lvov, and Margaret Ziomek-Moroz. Corrosion Behavior of Ultra-high Strength Drilling Steel in Alkaline Brines Containing Hydrogen Sulfide at High Temperature. NACE CORROSION, 2016. Accepted.”
corrosion rate. After 60 hours, the corrosion rates (CR) were 0.84 mm y\(^{-1}\), 2.88 mm y\(^{-1}\), and 1.83 mm y\(^{-1}\) from pH 8.1 to 10.8. The CR calculated with commercial software was in reasonable agreement with the experimental CR. Limiting current was observed in the anodic region using linear sweep voltammetry (LSV) but not in the cathodic region. Even with the effect of limiting current, anodic Tafel slopes \(b_a\) were able to be gathered from LSV using a new method derived from the generalized Butler-Volmer equation. The \(b_a\) values indicated that the anodic reactions followed the Bockris mechanism at pH 8.1 and a two-electron mechanism at pH 9.8 and 10.8. Cathodic Tafel slopes corresponded to a two-electron mechanism in the three conditions. Two layers were observed on the surface at pH 8.1 and 9.8, and the outer layer spalled off in some regions. As the pH increased, the major corrosion products transitioned from pyrrhotite/siderite to magnetite, and the S distribution moved outward from the inner layer.

### 5.1 Introduction

Carbon steel has been widely used for deep drilling in oil and gas industry due to its high strength:weight ratio and economical cost. However, in the presence of H\(_2\)S, carbon steel has been found to be more susceptible to hydrogen induced cracking (HIC) / sulfide stress cracking (SSC), stress corrosion cracking (SCC), and corrosion fatigue (CF), which would lead to catastrophic failure and drastic cost increase during the exploration.\(^1,2\)

Sour corrosion has been extensively studied from many perspectives, which can generally be categorized to the reaction mechanism in the presence of H\(_2\)S and the effect of corrosion products.\(^3-8\) A solid state reaction was proposed between Fe and H\(_2\)S to form mackinawite in unstirred saturated aqueous H\(_2\)S solutions at 21 °C and atmospheric pressure.\(^9\) The corrosion rate and protectiveness of corrosion products were influenced by pH, H\(_2\)S concentration, and immersion time.\(^10\) The rate determining step changed from diffusion control to interfacial reaction
control when H\textsubscript{2}S concentration increased\textsuperscript{11,12}. Most of the studies were conducted from pH 3 to 8 at a mild temperature from 20 to 95 °C.

However, typically a drilling fluid of pH 10 to 12 flowing through the drilling pipe is used to increase the pH in practice, and the temperature in deep wells can reach above 200 °C. Therefore, the drilling steel is exposed to a neutral to basic environment containing corrosive substances such as H\textsubscript{2}S, CO\textsubscript{2}, and brine at high pressure and high temperature. Corrosion of carbon steel in H\textsubscript{2}S-containing deaerated alkaline brines has been studied previously by the authors at 85 °C\textsuperscript{13–15}. The corrosion rate was found to decrease as pH increased from 7.9 to 12.4 at low H\textsubscript{2}S partial pressure ($P_{H2S} < 0.12$ psi), whereas the CR was the fastest at the intermediate pH of 10.7 when $P_{H2S}$ increased to 1.2 and 10 psi. It was proposed that the diversity of reactive ions in the solutions and the non-homogeneity of the corrosion product film could have triggered an increase in localized corrosion at the intermediate pH. Further study was conducted to determine if the trend would continue at 200 °C in this work.

Corrosion studies at high temperature often encounter challenges due to the limitation of the equipment material and difficult handling and control. Ramanarayanan and Smith reported that diffusion of Fe\textsuperscript{2+} through a growing pyrrhotite film was the rate-limiting step in H\textsubscript{2}S-saturated, brine condition at 204 °C\textsuperscript{16}. In alkaline brines at 200 °C, the effects of high pH and high temperature on the corrosion rate and corrosion products were studied in the present work to understand the sour corrosion mechanism in drilling fluid conditions. The generalized Bulter-Volmer equation was employed to analyze LSV data to study the reaction mechanisms.
5.2 Experimental

5.2.1 Materials Investigated

UD-165 steel, a proprietary modification from UNS G41300, was investigated. Its chemical composition is listed in Table 5-1.\textsuperscript{17}

Table 5-1. Chemical composition (%wt.) of UD-165.\textsuperscript{17}

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Al</th>
<th>Ni</th>
<th>Cu</th>
<th>Nb</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal</td>
<td>0.79</td>
<td>0.88</td>
<td>0.67</td>
<td>0.03</td>
<td>0.81</td>
<td>0.19</td>
<td>0.02</td>
<td>0.26</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>P</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>V</th>
<th>Sn</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.007</td>
<td>&lt;0.005</td>
<td>0.27</td>
<td>0.007</td>
<td>0.07</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td></td>
</tr>
</tbody>
</table>

Steel samples were machined into 10×20×5 mm plate electrodes which were coated with epoxy so that only one 10×20 mm face was exposed the corrosive solutions. The exposed surface was ground with 600 and 800 grit SiC papers and then polished by 0.1 and 0.05 micron alumina polishing slurries to minimize the surface defects and keep the surface area as consistent as possible. The polished steel sample was rinsed with propanol and distilled water and wiped dry. Heat shrinkable polytetrafluoroethylene (PTFE) tubing was used to coat the electrode leads attached to the steel samples.

5.2.2 System Setup

A three-electrode system was adopted in a deaerated autoclave to carry out the electrochemical measurements. The working electrode was the prepared steel sample. The counter electrode was a 10×20×1 mm platinum plate which was also coated with epoxy. The
leads were coated with PTFE tubing the same way as the steel samples. The two electrodes were held in place with the polished surfaces parallel to each other with a distance of 10 mm between them.

A double-junction silver-silver chloride (Ag/AgCl) electrode was prepared inside a ceramic tube to be the reference electrode to prevent the contamination from the test solutions. The reference electrode was filled with 5 \%wt. NaCl(aq) solution to minimize the concentration gradient, and thus the junction potential, between the reference and test solutions. The Ag/AgCl reference electrode potential was calculated with Gibbs energy minimization to be 61 mV±12 mV vs SHE at 200 °C using thermodynamic values from literature and then with values from a commercial database.\textsuperscript{18}

The reactor vessel was a 600 mL autoclave constructed of stainless steel UNS S31600. A schematic diagram of the autoclave system is shown in Figure 5-1.\textsuperscript{15} The system temperature was controlled and recorded through a controller connected to a heating mantle. A computer-controlled potentiostat was used to perform in-situ electrochemical measurements.
Figure 5-1. Schematic diagram of the autoclave system. 1- Connection to pressure transducer; 2- Heating mantle; 3- Autoclave stainless steel vessel; 4- PTFE liner; 5- Polymer-coated thermocouple; 6- Plastic tubing; 7- Epoxy-coated stirrer; 8- PTFE-coated lead wire; 9- Ag/AgCl reference electrode; 10- PTFE assembly; 11- working electrode; 12- Pt counter electrode; 13- H₂S/N₂ cylinder.

5.2.3 Experimental Procedure

The test solutions contained 5 %wt. (0.9 mol kg⁻¹) NaCl and were buffered with different concentrations of NaHCO₃, Na₂CO₃, and NaOH. The solution compositions are listed in Table 5-2. All of the solutions were prepared in 250 g deionized water and then deaerated by Ar for at least one hour. The sealed autoclave was purged of oxygen with Ar as well. The deaerated solution was transferred to the autoclave through a plastic dip tube (No. 6 in Figure 5-1) by the pressure difference while Ar was flushing. After the system was heated up to 85 °C, a H₂S/N₂ mixture gas (10% vol. H₂S) was introduced into the autoclave through the plastic tube until $P_{H2S}$ reached 69 kPa (10 psi). This way the total amount of H₂S in the system was constant over the test
and comparable to the previous tests at 85 °C. Using the ideal gas law and the vapor volume in the reactor vessel (236.3 mL), the total H$_2$S concentration was estimated to be $2.19 \times 10^{-2}$ mol kg$^{-1}$. Ar gas was added to increase the total pressure to 250 psig. Then all of the valves were closed. The autoclave was further heated up to 200 °C. The total pressure went up to around 490 psig due to the increased temperature and water vaporization, and then kept steady around 460 psig over the course of corrosion. The solution pH at 200 °C with this amount of H$_2$S was computed using commercial software and is given in Table 5-2. The pH calculation was set to take into account the system pressure, temperature, and the components inside the autoclave. The addition of H$_2$S slightly decreased the pH due to the dissociation of H$_2$S. The pH in the same solution compositions at 85 °C were 7.7, 10.5, and 12.4 from Solution #1 to #3, respectively. The solution pH was changed at 200 °C due to a larger ionization constant of H$_2$O(l) and different dissociation constants of the components.

Table 5-2. Solution compositions (mol kg$^{-1}$) and pH at 200 °C.

<table>
<thead>
<tr>
<th>Soln.</th>
<th>NaCl</th>
<th>NaHCO$_3$</th>
<th>Na$_2$CO$_3$</th>
<th>NaOH</th>
<th>pH, no H$_2$S</th>
<th>pH with H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>8.2</td>
<td>8.1</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>9.9</td>
<td>9.8</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>10.8</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Linear polarization resistance (LPR), electrochemical frequency modulation (EFM), and electrochemical impedance spectroscopy (EIS) measurements were performed every two hours over the exposure period with the stir rate of 525 RPM. LPR was carried out over the potential range of ±10 mV with respect to the corrosion potential ($E_{corr}$), and the sweep rate was 1 mV s$^{-1}$. EFM was operated at the base frequency of 0.01 Hz with the multipliers of 2 and 5, and the amplitude was 20 mV with respect to $E_{corr}$. EIS was measured over the frequency range of 300
kHz to 5 mHz with the amplitude of 10 mV. After 60 hours, LSV was carried out with the sweep rate of 5 mV s\(^{-1}\) from -200 mV to +200 mV vs \(E_{\text{corr}}\). After the electrochemical corrosion tests, the corroded surfaces were examined using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD).

5.2.4 Calculation of the Corrosion Rate

In a three-electrode cell, when the corrosion is under the charge transfer control / activation control and the working electrode is polarized within a sufficiently small region around \(E_{\text{corr}}\), the corrosion current density, \(j_{\text{corr}}\), can be calculated according to the Stern-Geary equation as shown in Equations [5-1] and [5-2].\(^{21,22}\)

\[
j_{\text{corr}} = \frac{1}{(R_{\text{ct}} B')} = \frac{1}{(R_{\text{pol}} B')}
\]

\[
B' = (\ln10) \frac{(b_c + b_a)}{(b_c b_a)}
\]

where \(R_{\text{ct}}\) is the area-specific charge transfer resistance, which is equal to \(R_{\text{pol}}\), the area-specific polarization resistance, when corrosion is under the charge transfer control. \(B'\) is a combination of the cathodic, \(b_c\), and anodic, \(b_a\), Tafel slopes. \(R_{\text{pol}}\) can be obtained from the slope around \(E_{\text{corr}}\) in the LPR plot after correction for the solution resistance. The Tafel slopes can be obtained from real-time EFM. The corrosion rate (CR), defined as the depth of corrosion penetration per time assuming uniform corrosion, can be calculated following Equation [5-3].

\[
\text{CR} = j_{\text{corr}} M / (nF\rho)
\]

where \(M\) is the molecular mass of the corroding metal, \(n\) is the electron number, \(F\) is the Faraday constant (96485 C mol\(^{-1}\)), and \(\rho\) is the metal density.
The Stern-Geary equation is the application of the Butler-Volmer equation in corrosion when both anodic and cathodic reactions are under charge transfer control. However, when one of the reactions, anodic or cathodic, is limited by a non-electrochemical step like mass transport at $E_{\text{corr}}$, the Stern-Geary equation is no longer applicable. The generalized Butler-Volmer equation with terms of limiting current density has to be introduced to derive the relations between overpotential and current density. For a corrosion system, the generalized Butler-Volmer equation can be written in Equations \[5-4\] to \[5-5\], assuming that current densities from the reduction direction of anodic process and the oxidation direction of cathodic process are negligible. 23,24

$$
j = j_{\text{corr}} \left[ (1 - \frac{j}{j_{\text{lim},a}}) \exp \left( \frac{\eta}{B_a} \right) - (1 - \frac{j}{j_{\text{lim},c}}) \exp \left( -\frac{\eta}{B_c} \right) \right] \tag{5-4}
$$

$$
B_a = b_a / \ln 10, \quad B_c = b_c / \ln 10, \tag{5-5}
$$

where $j$ is the current density, $\eta$ the overpotential vs $E_{\text{corr}}$, $j_{\text{lim},a}$ the anodic limiting current density, $j_{\text{lim},c}$ the cathodic limiting current density, $B_a$ is the anodic Tafel parameter, and $B_c$ is the cathodic Tafel parameter.

Assuming only the anodic reaction is affected by a limiting current, $j_{\text{lim},c}$ is an infinite value and Equation \[5-4\] becomes Equation \[5-6\].

$$
j = j_{\text{corr}} \left[ (1 - \frac{j}{j_{\text{lim},a}}) \exp \left( \frac{\eta}{B_a} \right) - \exp \left( -\frac{\eta}{B_c} \right) \right] \tag{5-6}
$$

Two scenarios are discussed here. Scenario one is when $\eta$ is very large in the anodic region and the cathodic contribution is insignificant. Then Equation \[5-6\] becomes Equation \[5-7\] or \[5-8\]. Equation \[5-8\] allows us to obtain the Tafel slope $b_a$ as the slope of $\eta$-$\log_{10}[j/j_{\text{lim},a}]$ when the LSV plot is complicated by a limiting current.23

$$
j = j_{\text{corr}} \left[ (1 - \frac{j}{j_{\text{lim},a}}) \exp \left( \frac{\eta}{B_a} \right) \right] \tag{5-7}$$
or
\[ \eta = B_a \ln \left( \frac{j_{\text{lim,a}}}{j_{\text{corr}}} \right) + B_a \ln \left( \frac{j}{j_{\text{lim,a}}} \right) = b_a \log_{10} \left( \frac{j_{\text{lim,a}}}{j_{\text{corr}}} \right) + b_a \log_{10} \left( \frac{j}{j_{\text{lim,a}}} \right) \]  

Scenario two is when \( \eta \) is very large in the cathodic region and the anodic contribution is insignificant. It will be a normal Tafel plot expressed as in Equation [5-9].

\[ \eta = B_c \ln(j_{\text{corr}}) - B_c \ln(-j) = b_c \log_{10}(j_{\text{corr}}) - b_c \log_{10} \ln(-j) \]

5.3 Results and discussion

5.3.1 Primary Species in the Solutions

The speciation in each solution with \( \text{H}_2\text{S} \) was calculated using commercial software.\(^{19}\)

Figure 5-2 shows the primary carbonate and sulfide species at 200 °C with the \( \text{H}_2\text{S} \) concentration of 2.19x10^{-2} mol kg^{-1}. As pH increased from 8.1 to 10.8, the concentrations of \( \text{CO}_3^{2-}(\text{aq}) \), \( \text{HCO}_3^- (\text{aq}) \), and \( \text{H}_2\text{S}(\text{aq}) \) decreased, whereas the concentrations of \( \text{CO}_3^{2-}(\text{aq}) \) and \( \text{S}^2^- (\text{aq}) \) increased. \( \text{HS}^- (\text{aq}) \) concentration had a small fluctuation as pH increased. Comparing to the similar conditions at 85 °C from the authors’ previous work,\(^{14}\) the speciation trend with pH of carbonate and sulfide species were similar, however, the concentration of each species changed at 200 °C due to the differences in water ionization constant and dissociation constants, resulting in different pH values.

It has been proposed by different researchers that \( \text{OH}^-(\text{aq}) \), \( \text{HCO}_3^-(\text{aq}) \), and \( \text{HS}^- (\text{aq}) \) could be the reactive ions for the anodic reactions of Fe dissolution, and that \( \text{H}_2\text{O}(\text{l}) \), \( \text{H}^+(\text{aq}) \) and \( \text{H}_2\text{S}(\text{aq}) \) for hydrogen evolution reaction (HER) at the cathodic side.\(^{9,10,25,26}\) The concentrations of these reactive species are listed in Table 5-3. The concentrations of \( \text{H}^+(\text{aq}) \) and \( \text{H}_2\text{S}(\text{aq}) \) decreased from Solution #1 to #3. The dominant reactive ion for the anodic reactions generally changed
from HCO$_3$ (aq) to OH (aq) with a similar concentration of HS (aq) from Solution #1 to #3.

Solution #2 had the most diverse reactive ions with comparable concentrations of these three ions.

Figure 5-2. The primary carbonate and sulfide species in the three solutions at 200 °C with $b_{\text{H}_2\text{S}} = 2.19 \times 10^{-2}$ mol kg$^{-1}$. (Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 8.1; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 9.8; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 10.8).

Table 5-3. The concentrations of primary reactive species in the three solutions (mol kg$^{-1}$).

<table>
<thead>
<tr>
<th></th>
<th># 1</th>
<th># 2</th>
<th># 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$  (aq)</td>
<td>$1.02 \times 10^{-8}$</td>
<td>$1.51 \times 10^{-10}$</td>
<td>$1.28 \times 10^{-11}$</td>
</tr>
<tr>
<td>H$_2$S(aq)</td>
<td>$5.11 \times 10^{-4}$</td>
<td>$1.44 \times 10^{-5}$</td>
<td>$1.86 \times 10^{-6}$</td>
</tr>
<tr>
<td>OH(aq)</td>
<td>$1.56 \times 10^{-3}$</td>
<td>$9.66 \times 10^{-2}$</td>
<td>$9.08 \times 10^{-1}$</td>
</tr>
<tr>
<td>HCO$_3$ (aq)</td>
<td>$4.12 \times 10^{-1}$</td>
<td>$1.30 \times 10^{-1}$</td>
<td>$1.04 \times 10^{-2}$</td>
</tr>
<tr>
<td>HS(aq)</td>
<td>$2.08 \times 10^{-2}$</td>
<td>$2.11 \times 10^{-2}$</td>
<td>$1.78 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
5.3.2 Polarization Resistance and Corrosion Rate

Figures 5-3 and 5-4 show $R_{\text{pol}}$ and CR of the UD-165 steel changing with time in the three solutions at 200 °C with $b_{\text{H2S}} = 2.19 \times 10^{-2}$ mol kg$^{-1}$. $R_{\text{pol}}$ gradually increased in Solutions #1 and #3 before 60 hours, whereas $R_{\text{pol}}$ first increased and then decreased during the first 36 hours in Solution #2. The increase of $R_{\text{pol}}$ could be related to the formation of corrosion products and the decrease of reactive area on the surface. The decrease of $R_{\text{pol}}$ could be related to the corrosion products spalling from the surface or the increased occurrence of localized corrosion. $R_{\text{pol}}$ was approaching the steady state after 60 hours in all the three solutions. $R_{\text{pol}}$ at steady state was the smallest in Solution #2.

Figure 5-3. $R_{\text{pol}}$ of UD-165 changing with time in the three solutions at 200 °C with $b_{\text{H2S}} = 2.19 \times 10^{-2}$ mol kg$^{-1}$. (Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 8.1; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 9.8; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 10.8).
CR followed the inverse trend of the $R_{pol}$. In Solutions #1 and #3, CR gradually decreased with time. In Solution #2, CR decreased and then increased during the first 36 hours, and then slightly decreased until 60 hours. Due to the drastic increase of CR following the initial decrease, CR in Solution #2 was the highest at steady state, 2.88 mm y$^{-1}$. CR in Solutions #1 and #3 were relatively slower with the values of 0.84 and 1.83 mm y$^{-1}$, respectively. Interestingly, CR in the three solutions were within in a factor of 4 while there was at least one order of magnitude difference for the same conditions at 85 °C.\textsuperscript{13,15} Moreover, $R_{pol}$ were decreased by factors of 20, 12, and 70 from Solution #1 to #3 at 200 °C compared with 85 °C. Inversely, the corrosion rates were significantly accelerated at 200 °C.

The experimental CR at steady state was compared with CR calculated using commercial modeling software in Figure 5-5. The hydrodynamic model was based on the rotating disk.
The corrosion rates were predicted to be 4.77, 0.157, and 0.833 mm y\(^{-1}\), respectively. The modeled CR was higher at pH 8.1, and lower at pH 9.8 and 10.8. Despite the divergence, the modeling results were in reasonable agreement with the experimental CR.

![Figure 5-5](http://example.com/fig55.png)

**Figure 5-5.** Experimental and modeled CR of UD-165 in the three solutions at 200 °C with \(b_{\text{HES}} = 2.19 \times 10^{-2}\) mol kg\(^{-1}\). (Solution #1: 0.9 mol kg\(^{-1}\) NaCl, 0.5 mol kg\(^{-1}\) NaHCO\(_3\), pH = 8.1; Solution #2: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), pH = 9.8; Solution #3: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), 1 mol kg\(^{-1}\) NaOH, pH = 10.8).

### 5.3.3 Linear Sweep Voltammetry Results

LSV plots were corrected for solution resistance and are depicted in Figure 5-6. A limiting current density (\(j_{\text{lim}}\)) was observed on the anodic polarization region, and \(j_{\text{lim}}\) became smaller as pH increased from Solution #1 to #3. Mass transport, passivation, or a non-Faradaic chemical step were all possible to cause limiting current density. Firstly, the mass transport includes the diffusion and convection of reactants or products in the bulk solution or the pore solution within the corrosion product layers.\(^{27}\) Secondly, passivation occurs when a protective film is covering the surface. Since the current density did not drop radically, there was either a non-fully covered film or ions/vacancies still being able to pass through the passive film. The
former one would still maintain the feature of active corrosion only with a smaller current density magnitude, therefore, it is unlikely to be this case. The latter one is the mass transport of ions/vacancies through the lattice of a solid film. The transport of Fe\(^{2+}\) ion through the iron sulfide film proposed by Ramanarayanan and Smith can be seen as this case.\(^ {16}\) The transport of Fe\(^{2+}\) vacancy from the film/solution interface toward the metal/film interface would also be plausible.\(^ {28}\) Here we expanded the concept of mass transport from the commonly accepted diffusion/convection in the aqueous phase to include the transport through the lattice of solid film. Thirdly, the chemical step could be the adsorption of OH\(^-(aq)\), HCO\(_3^-\)(aq), and HS\(^-(aq)\) forming intermediates with Fe.\(^ {9,10,25,26}\) However, the adsorption of charged ions usually has a potential dependence, which would not cause a plateau in current density. Thus, mass transport in the solution or through the solid film is more likely to be the limiting step.

![Figure 5-6](image-url)

Figure 5-6. The LSV plots at 200 °C with \(b_{\text{H}_2\text{S}} = 2.19 \times 10^{-2}\) mol kg\(^{-1}\) with the scan rate of 5 mV s\(^{-1}\). Conditions: Stir rate of 525 RPM. Solution #1: 0.9 mol kg\(^{-1}\) NaCl, 0.5 mol kg\(^{-1}\) NaHCO\(_3\), pH = 8.1; Solution #2: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), pH = 9.8; Solution #3: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), 1 mol kg\(^{-1}\) NaOH, pH = 10.8.
A peak was observed in the three solutions when the steel sample was positively polarized by ~200 mV, which might be the further oxidation of Fe(II) to Fe(III), and then the current was limited again. Another peak was observed at a smaller positive polarization (~50 mV) in Solutions #1 and #2 but not in Solution #3. This peak frequently appeared in H₂S-containing systems in the authors’ previous study, which might correspond to the sulfide-related reaction.

Because of the anodic limiting current densities, anodic Tafel slopes were obtained using the slope in \( E - \log_{10}[j/(j_{\text{lim},a})] \) plots as shown in Figure 5-7. This method was derived from the behavior predicted in Equation [5-8]. The transformed plots for Solutions #2 and #3 showed good linear regions and \( b_a \) values are given in Table 5-4. However, the plot in Solution #1 at the stir rate of 525 RPM was not showing an obvious linear region due to a relatively short range of limiting current between two peaks. Instead, the LSV result at 0 RPM was used for Figure 5-7, which gave a \( b_a \) value of 0.066 V dec⁻¹. On closer inspection, there was actually a short linear region before the limiting current in the LSV plot for Solution #1 in Figure 5-6. This region gave a \( b_a \) value of 0.070 V dec⁻¹, which was very close, and the average of these two is listed in Table 5-4 as the anodic Tafel slope for Solution #1.

Bockris et al proposed a mechanism of Fe dissolution as expressed in Reactions [5-10] to [5-12]. The rate determining step (RDS) is Step (II), the reduction of an intermediate FeOH(ad). Assuming the symmetry coefficient \( \beta \) to be 0.5, anodic Tafel slope of the Bockris mechanism was calculated to be 0.063 V dec⁻¹ at 200 °C according to Equation [5-13]. \( b_a \) in Solution #1 was 0.068 V dec⁻¹, indicating that the Bockris mechanism could be the anodic mechanism in Solution #1. \( b_a \) values in Solutions #2 and #3 were very close to 0.094 V dec⁻¹ which corresponded to a step of two electrons transferred simultaneously. The two-electron mechanism is written in a simplified form as shown in Reactions [5-14] and [5-15], and \( b_a \) was calculated according to Equation [5-16]. The \( b_a \) values indicated a two-electron reaction mechanism in Solutions #2 and #3. OH(aq) could be substituted with HCO₃⁻(aq) and HS⁻(aq). The produced Fe²⁺ could further transport to the
solution or transit to corrosion products on the steel surface. Note that Tafel slopes only illuminate the reaction mechanism without mass transport effect.

Figure 5-7. The transformed LSV results at 200 °C with \( b_{\text{H}_2\text{S}} = 2.19 \times 10^{-2} \) mol kg\(^{-1}\) with the scan rate of 5 mV s\(^{-1}\). Conditions: Solution #1: 0.9 mol kg\(^{-1}\) NaCl, 0.5 mol kg\(^{-1}\) NaHCO\(_3\), pH = 8.1, Stir rate of 0 RPM; Solution #2: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), pH = 9.8, Stir rate of 525 RPM; Solution #3: 0.9 mol kg\(^{-1}\) NaCl, 1 mol kg\(^{-1}\) Na\(_2\)CO\(_3\), 1 mol kg\(^{-1}\) NaOH, pH = 10.8, Stir rate of 525 RPM.

Table 5-4. Tafel slopes in the three solutions with \( b_{\text{H}_2\text{S}}=2.19 \times 10^{-2} \) mol kg\(^{-1}\) at 200 °C after 60 hours.

<table>
<thead>
<tr>
<th>Tafel slope / (V dec(^{-1}))</th>
<th>Solution #1</th>
<th>Solution #2</th>
<th>Solution #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_a )</td>
<td>0.068</td>
<td>0.098</td>
<td>0.085</td>
</tr>
<tr>
<td>( b_c )</td>
<td>0.105</td>
<td>0.117</td>
<td>0.095</td>
</tr>
</tbody>
</table>

The Bockris mechanism:

Step I: \( \text{Fe}(s) + \text{OH}^-(aq) \leftrightarrow \text{FeOH}(ad) + e^- \) \[5-10\]

Step II (RDS): \( \text{FeOH}(ad) \rightarrow \text{FeOH}^+(aq) + e^- \) \[5-11\]

Step III: \( \text{FeOH}^+(aq) + \text{H}^+(aq) \leftrightarrow \text{Fe}^{2+}(aq) + \text{H}_2\text{O} \) \[5-12\]

\[ b_a = 2.303 \left( \frac{R \ T}{((1 + \beta) \ F)} \right) \] \[5-13\]

where \( R \) is the gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)) and \( T \) the absolute temperature.
Two-electron mechanism for anodic reaction:

Step I (RDS): \( \text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{ad}) + 2 \, \text{e}^- \) \[5-14\]

Step II: \( \text{Fe}^{2+}(\text{ad}) \leftrightarrow \text{Fe}^{2+}(\text{aq}) \) \[5-15\]

\[ b_a = \frac{2.303 \, (R \, T)}{(2 \, \beta \, F)} \] \[5-16\]

In contrast, the cathodic region of the LSV plots showed a fairly linear region for Tafel analysis, and the cathodic Tafel slopes, \( b_c \), are listed in Table 5-4. The linear region was observed to extend to more negative regions in cyclic voltammetry (CV) plots, which indicated that the Faradaic behavior was not limited on the cathodic side. Considering the cathodic reaction occurred at the film/solution interface,\(^{29}\) the hydrogen-containing species were sufficient because of effective stirring in the aqueous solution. For lack of \( \text{H}^+(\text{aq}) \) and \( \text{H}_2\text{S}(\text{aq}) \) in alkaline condition, \( \text{H}_2\text{O}(\text{l}) \) is considered to be the main reactant for HER.\(^{30}\) Assuming the symmetry coefficient to be 0.5, cathodic Tafel slope of a two-electron reaction for HER was calculated to be 0.094 V dec\(^{-1}\), which was close to \( b_c \) values in Table 5-4. Hydrogen-containing species were possibly ready to lose two-electrons simultaneously at 200 °C due to the promoted kinetics at high temperature. The two-electron mechanism is written in Equations [5-17] to [5-18]. \( \text{H}_2\text{O}(\text{l}) \) could be substituted with \( \text{H}^+(\text{aq}) \) and \( \text{H}_2\text{S}(\text{aq}) \).\(^{31}\)

Two-electron mechanism for cathodic reaction:

Step I (RDS): \( 2 \, \text{H}_2\text{O}(\text{l}) + 2 \, \text{e}^- \rightarrow \text{H}_2(\text{ad}) + 2 \, \text{OH}^-(\text{aq}) \) \[5-17\]

Step II: \( \text{H}_2(\text{ad}) \leftrightarrow \text{H}_2(\text{g}) \) \[5-18\]

\[ b_c = \frac{2.303 \, (R \, T)}{(2 \, \beta \, F)} \] \[5-19\]

**5.3.4 EIS results**

The EIS results after 60 hours are given in Figure 5-8 in the forms of Nyquist plots and phase angle plots. The patterns of Nyquist plots were partial depressed semi-circles, and the phase
angles showed one time constant with the maximum phase angle around -50°. The EIS results were fitted using the equivalent electrical circuit in Figure 9, which consisted of a constant phase element (CPE) in parallel with a resistor representing $R_{pol}$. CPE was usually used to represent the non-ideality of electrical double layer. The fitting results are listed in Table 5-5.

CPE-$p$ was around 0.6 in each solution, indicating that the steel surface was non-ideal. This was caused by the non-homogeneity of the double layer due to the corrosion products. The CPE has also been referred to as the film capacitance on the surface by some researchers. 32 The film capacitance was related to the transport of ions/vacancies through the lattice structure of the corrosion product film. In this sense, CPE could be seen as the combination of the double layer capacitance and the film capacitance.

$R_{pol}$ obtained from EIS decreased from Solution #1 to #2 and then increased in Solution #3, which agreed with the trend of $R_{pol}$ from LPR. However, the $R_{pol}$ values from EIS were larger than those from LPR by factors of 2 to 4. Considering the LPR was measured at a certain sweep rate (1 mV s⁻¹), the equivalent frequency in EIS was not close to zero, which implied that LPR was influenced by some capacitance effect and therefore resulted in a smaller $R_{pol}$. Nevertheless, the EIS semi-circle was not complete and could not provide accurate interpretation of $R_{pol}$ either.
Figure 5-8. Nyquist plots (top) and phase angles (bottom) in the three solutions at 200 °C with $b_{\text{H}_2\text{S}} = 2.19 \times 10^{-2}$ mol kg$^{-1}$. (Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 8.1; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 9.8; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 10.8).

Figure 5-9. The equivalent electrical circuit used to fit the EIS results in the three solutions at 200 °C with $b_{\text{H}_2\text{S}} = 2.19 \times 10^{-2}$ mol kg$^{-1}$. 
Table 5-5. EIS fitting results in the three solutions at 200 °C with $b_{H2S} = 2.19 \times 10^{-2}$ mol kg$^{-1}$.

<table>
<thead>
<tr>
<th>Element</th>
<th>unit</th>
<th>Soln. #1</th>
<th>Soln. #2</th>
<th>Soln. #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{sol}$</td>
<td>$\Omega$ cm$^2$</td>
<td>3.05</td>
<td>2.66</td>
<td>2.36</td>
</tr>
<tr>
<td>CPE-$Y_0$</td>
<td>$\Omega^{-1}$ cm$^{-2}$ s$^p$</td>
<td>0.028</td>
<td>0.029</td>
<td>0.025</td>
</tr>
<tr>
<td>CPE-$p$</td>
<td>0-1</td>
<td>0.61</td>
<td>0.63</td>
<td>0.64</td>
</tr>
<tr>
<td>$R_{pol}$</td>
<td>$\Omega$ cm$^2$</td>
<td>869</td>
<td>308</td>
<td>547</td>
</tr>
<tr>
<td>$R_{pol}$ from LPR</td>
<td>$\Omega$ cm$^2$</td>
<td>219</td>
<td>139</td>
<td>203</td>
</tr>
</tbody>
</table>

5.3.5 Pourbaix Diagram

Figure 5-10 shows the Pourbaix diagram of Fe-H$_2$O-H$_2$CO$_3$-H$_2$S system in Solution #2 with H$_2$S concentration of $2.19 \times 10^{-2}$ mol kg$^{-1}$ at 200 °C. The Pourbaix diagrams in Solutions #1 and #3 are similar to in Solution #2. The thermodynamically predominant species changed from FeS(s)/FeS$_2$(s)/FeCO$_3$(s) to FeS(s)/Fe$_3$O$_4$(s) then to HFeO$_2$(aq) as pH changed from 8.1 to 9.8 then to 10.8.

Figure 5-10. The Pourbaix diagram of Fe-H$_2$O-H$_2$CO$_3$-H$_2$S system in Soln. #2 with $b_{H2S} = 2.19 \times 10^{-2}$ mol kg$^{-1}$ at 200 °C. (Soln. #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$; Titrants: NaOH/HCl.)
5.3.6 Surface Analysis

The SEM images of corroded UD-165 steel surfaces are shown in Figure 5-11. Some representative EDS results are listed in Table 5-6 and the corresponding locations are marked on the SEM images. The EDS analysis was carried out at the accelerating voltage of 10 kV.

![SEM images of the corroded UD-165 steel surfaces](image)

Figure 5-11. SEM images of the corroded UD-165 steel surfaces. Conditions: 200 °C, $b_{\text{H}_2\text{S}} = 2.19 \times 10^{-2}$ mol kg$^{-1}$. Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 8.1; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 9.8; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 10.8.

At 200 °C, the corrosion products were mixtures of iron carbonate, sulfide, and oxides in all of the three solutions, however, the morphology and elemental distribution varied. Two layers
were observed on the steel surfaces at pH 8.1 and 9.8, and the outer layer partially stripped off from the steel.

Table 5-6. EDS chemical analyses in %at. on the corroded UD-165 steel surfaces in selected locations marked in Figure 5-11. (200 °C, $b_{H_2S} = 2.19 \times 10^{-2}$ mol kg$^{-1}$).

<table>
<thead>
<tr>
<th>Location/pH</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Na</th>
<th>Cl</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 / 8.1</td>
<td>33</td>
<td>8.8</td>
<td>20</td>
<td>33</td>
<td>3.2</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td>2 / 8.1</td>
<td>14</td>
<td>3.6</td>
<td>51</td>
<td>10</td>
<td>6.2</td>
<td>-</td>
<td>9.5</td>
</tr>
<tr>
<td>3 / 8.1</td>
<td>22</td>
<td>5.6</td>
<td>20</td>
<td>46</td>
<td>3.0</td>
<td>0.3</td>
<td>2.9</td>
</tr>
<tr>
<td>4 / 8.1</td>
<td>32</td>
<td>9.5</td>
<td>26</td>
<td>26</td>
<td>5.1</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td>5 / 9.8</td>
<td>25</td>
<td>5.7</td>
<td>55</td>
<td>0.6</td>
<td>8.2</td>
<td>0.1</td>
<td>4.2</td>
</tr>
<tr>
<td>6 / 9.8</td>
<td>17</td>
<td>7.9</td>
<td>47</td>
<td>2.2</td>
<td>18</td>
<td>0.2</td>
<td>2.9</td>
</tr>
<tr>
<td>7 / 9.8</td>
<td>26</td>
<td>6.5</td>
<td>54</td>
<td>0.7</td>
<td>3.7</td>
<td>0.1</td>
<td>4.1</td>
</tr>
<tr>
<td>8 / 9.8</td>
<td>16</td>
<td>9.9</td>
<td>41</td>
<td>9.0</td>
<td>7.3</td>
<td>0.2</td>
<td>2.3</td>
</tr>
<tr>
<td>9 / 10.8</td>
<td>17</td>
<td>11</td>
<td>68</td>
<td>2.3</td>
<td>1.6</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>10 / 10.8</td>
<td>33</td>
<td>7.0</td>
<td>58</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>11 / 10.8</td>
<td>30</td>
<td>7.2</td>
<td>61</td>
<td>1.1</td>
<td>0.3</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>12 / 10.8</td>
<td>32</td>
<td>9.8</td>
<td>57</td>
<td>0.4</td>
<td>0.3</td>
<td>0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

The EDS results at pH 8.1 showed that the Fe:S ratios were from 1:1 to 1:2 and the C:O ratios in Locations 1 and 4 were close to 1:3. Pyrrhotite (Fe$_{1-x}$S) and siderite (FeCO$_3$) were verified in the XRD pattern as shown in Figure 5-12. High O was detected on the surface at pH 9.8 and 10.8 and much lower S than at pH 8.1, which indicated that the majority of the corrosion products changed from iron sulfide to iron oxide as pH increased. Magnetite was determined by XRD to be the main corrosion product at pH 9.8 and 10.8. At pH 10.8, the morphology was a film composed of mainly magnetite with some higher S-content particles on top of it. As the pH increased at 200 °C, the determined corrosion products changed from pyrrhotite/siderite to
magnetite, which agreed with the prediction from Pourbaix diagram. During this transition, the corrosion products at the intermediate pH of 9.8 could have been less protective, corresponding to the lowest $R_{\text{pol}}$ measured from LPR.

Figure 5-12. XRD results of corroded UD-165 surfaces in the three solutions with $b_{\text{H}_2\text{S}} = 2.19 \times 10^{-2}$ mol kg$^{-1}$ at 200 °C. Conditions: Solution #1: 0.9 mol kg$^{-1}$ NaCl, 0.5 mol kg$^{-1}$ NaHCO$_3$, pH = 8.1; Solution #2: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, pH = 9.8; Solution #3: 0.9 mol kg$^{-1}$ NaCl, 1 mol kg$^{-1}$ Na$_2$CO$_3$, 1 mol kg$^{-1}$ NaOH, pH = 10.8.

Another worth-noting observation was the distribution of S in the corrosion product layers at different pH. S was higher in the inner layer than the outer layer at pH 8.1, whereas S was relatively higher in the outer layer at pH 9.8. At pH 10.8, S was higher in the particles on top of the film. The S distribution moved outward from the inner layer as pH increased.

Considering OH$^-$ (aq), HCO$_3^-$ (aq), and HS$^-$ (aq) as the reactants for anodic reactions, the competition of the surface coverage is influenced by the concentration and the nature of each ion like the structure and the specific adsorption. HCO$_3^-$ (aq) ion has a larger size, so OH$^-$ (aq) and HS$^-$ (aq) could more easily occupy the inner Helmholtz plane on the steel surface than HCO$_3^-$ (aq).
Therefore, OH(aq) and HS(aq) could be more likely to form the inner layer. The variation of OH(aq):HS(aq) ratio corresponded to the major products in the inner layer being oxide or sulfide, which explained the pH dependence of S distribution in the corrosion product layers according to the solution speciation in Table 5-3.

If anodic reactions take place at the metal/film interface and cathodic reactions at the film/solution interface, we could incorporate the corrosion product layers with the electrochemical reaction mechanisms. According to LSV results, Fe could have formed intermediates with HS(aq), HCO$_3$-(aq) or OH(aq) for anodic reactions at pH 8.1, while at pH 9.8 and 10.8 Fe could have lost two electrons simultaneously at the metal/film interface. The reasons for limiting current could be (a) the mass transport of the aqueous reactive ions or the produced Fe$^{2+}$(aq) through the porous layers, or (b) the diffusion of Fe$^{2+}$ ion transporting through the solid passive film. Further calculation of diffusion in aqueous phase and solid phase could be made to distinguish them.

### 5.4 Conclusions

Solution pH in the three solutions were calculated to be 8.1, 9.8, and 10.8 at 200 °C, respectively, which were 7.7, 10.5, and 12.4 at 85 °C for the same composition. The dominant reactive ion generally changed from HCO$_3$-(aq) to OH(aq) with a comparable concentration of HS(aq) from Solution #1 to #3.

Polarization resistance values at 200 °C were consistently one to two orders of magnitude lower than at 85 °C, which corresponded to a drastic increase in corrosion rate at elevated temperature. At 200 °C, $R_{pol}$ at pH 9.8 was the smallest after 60 hours among the three solutions. The $R_{pol}$ obtained from EIS agreed with the trend of $R_{pol}$ from LPR. CR after 60 hours were 0.84
mm y⁻¹, 2.88 mm y⁻¹, and 1.83 mm y⁻¹, respectively, from pH 8.1 to 10.8. The modeled results were in reasonable agreement with the experimental CR values within a factor of 4.

A limiting current was observed in the anodic region of LSV but not in the cathodic region, which indicated that the anodic reactions were probably limited by the mass transport at 200 °C. Traditional Tafel analysis in the cathodic region gave cathodic Tafel slopes corresponding to a two-electron mechanism for the three solutions. A new method derived from the generalized Butler-Volmer equation allowed to obtain anodic Tafel slopes from LSV even with the effect of limiting current. The $b_a$ values indicated that the anodic reactions followed the Bockris mechanism at pH 8.1 and a two-electron mechanism at pH 9.8 and 10.8.

Two layers of corrosion products were observed on the surface at pH 8.1 and 9.8, and the outer layer spalled off in some regions. S was higher in the inner layer than the outer layer at pH 8.1, whereas S was relatively higher in the outer layer at pH 9.8. At pH 10.8, the morphology was a film with some higher S-content particles on it. As pH increased at 200 °C, the major corrosion products changed from pyrrhotite/siderite to magnetite although the corrosion products were a mixture of iron carbonate, sulfide and oxide. This trend was in accordance with the change of primary reactive ions and the Pourbaix diagram.

References


Chapter 6

Effects of CO₂ and H₂S on Corrosion of Martensitic Steels in NaCl(aq) at Low Temperature

This chapter presents the study on the corrosion behaviors of S-135 and UD-165 in 5%wt. NaCl(aq) solution at lower temperature representative of Arctic drilling environments. Three gas conditions were studied: CO₂ only, H₂S only, and a mixed gas with a CO₂:H₂S ratio of 1000 at 4 °C and 10 MPa total pressure. The transition from sweet (CO₂) corrosion to sour (H₂S) corrosion was observed.

Abstract

Corrosion studies were conducted for martensitic carbon steels in brine solutions at 4 °C and 10 MPa (1450 psi), which simulated the subsurface environments encountered in Arctic drilling. Three environments with a 5 % wt. NaCl brine were used: (1) 0.312 mol of CO₂ per mol of H₂O in brine, (2) 3.12 x 10⁻⁴ mol of H₂S per mol of H₂O in brine, and (3) a mixture of 3.12 x 10⁻⁴ mol H₂S and 0.312 mol CO₂ per mol of H₂O in brine. Two martensitic carbon steels were selected for the investigations: a high strength low alloy (S-135) carbon steel commonly used for drill pipe (G41000) and a newly designed ultra-high strength low alloy (UD-165) steel (G41300). Electrochemical and mass loss measurements found corrosion rates on the order of 0.05 mm y⁻¹ in the systems containing H₂S and CO₂+H₂S, while the CO₂ systems saw corrosion rates between

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5 The text in this chapter was originally prepared for the publication as “Ruishu Feng, Justin R. Beck, Derek M. Hall, Ayse Buyuksagis, Serguei N. Lvov, and Margaret Ziomek-Moroz. Effects of CO₂ and H₂S on Corrosion of Martensitic Steels in NaCl(aq) at Low Temperature. NACE CORROSION, 2016. Accepted.”
0.5 and 2 mm y⁻¹. Experimental corrosion rates were compared to model predictions, and a good agreement was found for the CO₂ and H₂S cases. However, the model predicted that corrosion rates in the mixed case would match those of the CO₂-only system. The CO₂+H₂S condition and H₂S condition had the similar anodic and cathodic Tafel slopes, which were smaller than the CO₂ only system. Surface analyses of the tested samples were performed using scanning electron microscopy and energy dispersive X-ray spectroscopy to identify corrosion products. The corrosion products were unstable and oxidized quickly after taking out of the system. All samples had a high oxygen content across the surface, though the samples exposed to H₂S and CO₂+H₂S had relatively higher levels of sulfur present in an inner region of the film. The experimental results showed that CO₂:H₂S ratios as high as 1000 can result in predominantly sour corrosion at the low temperature, high pressure conditions tested.

6.1 Introduction

The presence of CO₂ and H₂S in condensed water phases has for years been of considerable interest to scientists and engineers dealing with corrosion in oil and gas operations, from extraction through processing. One of the major effects of sweet corrosion is that dissolved CO₂ lowers the solution pH and increases the rate of corrosion. Sour corrosion, where H₂S is present, has generally been shown to reduce corrosion rates when low concentrations are present.¹ The mechanism for this drop is the quick formation of a relatively protective iron sulfide film. However, while the reduced material loss may be welcome, the tradeoff of H₂S content is an increased susceptibility for sulfide stress cracking (SSC). With drastically different failure modes being possible, the behavior of mixed systems becomes important for proper design of corrosion prevention and mitigation.
Currently, no widespread law or model exists for determining the transition between sweet and sour corrosion. NACE SP0110 Appendix A describes a rough rule for determining sweet-sour transitions by the CO$_2$:H$_2$S ratio based on previous experimental results. A ratio above 500 would be expected to produce predominantly sweet corrosion, while a ratio below 20 would be expected to show predominantly sour corrosion. A ratio between 20 and 500 may allow for a mixed corrosion mechanism where both FeCO$_3$ and FeS could coexist. Work by Smith investigated the assumption of 500 on the upper end of the ratio. Thermodynamic calculations on the stability of FeCO$_3$ and FeS showed that while a ratio of 500 could be justified, it was found to have minor to moderate sensitivity to temperature and ionic strength of the solution and extreme sensitivity to the quality of the thermodynamic data. An example was that a 1 % change in the free energy value for FeCO$_3$ could change the ratio by over a factor of 10.

Another consideration beyond stability of the corrosion products is the understanding of the kinetics for the corrosion process. Work has continued on laboratory experiments investigating the kinetic effects of different CO$_2$:H$_2$S ratios over a wide range of conditions. Experiments have shown over a range of conditions CO$_2$:H$_2$S ratios from 500 to as high as 10,000 can still see a decrease in corrosion rate by almost an order of magnitude relative to pure CO$_2$. Results at higher H$_2$S concentrations have ranged between no significant effects to notable increases in corrosion rates, though rates in CO$_2$-H$_2$S mixtures were generally lower than in pure CO$_2$. While a decrease in material loss may be welcome to corrosion engineers, the presence of the more protective iron sulfide films can also make the underlying steels more susceptible to pitting. The transition to sour corrosion can also increase the risk of sulfide stress cracking, and the recommendations from NACE MR0175 / ISO 15156 should be taken into account.

The purpose of the present work was to provide additional data on corrosion in sweet and sour environments related to oil and gas operations at lower temperatures representative of seafloor or Arctic operations. The tests investigated corrosion in brines at equilibrium with CO$_2$,
H$_2$S, and a mixed phase at a CO$_2$:$H_2$S ratio of 1000 at 4 °C and 10 MPa total pressure using electrochemical techniques, mass loss measurements, software modeling, and surface analyses.

6.2 Experimental

6.2.1 Test Conditions

The goal of the study was to investigate an environment representative of low temperature Arctic drilling conditions. A temperature of 4 °C was selected with a total system pressure of 10 MPa. A 5 % wt. NaCl (0.9 mol kg$^{-1}$) brine was selected for the test solution. The sweet/sour/mixed conditions were prepared by holding the test solution in equilibrium with one of three secondary non-aqueous phases: pure CO$_2$, an $H_2$S/Ar mixture, and a CO$_2$/H$_2$S/Ar mixture. It should be noted that the target test conditions were above the CO$_2$ critical pressure (7.39 MPa) but below the CO$_2$ critical temperature (31 °C), and it was above both the critical pressure (4.863 MPa) and critical temperature (-122.5 °C) of Ar. Care should be taken at high pressures when referring to such substances as “gas” or “vapor” phases, and describing their concentrations in terms of partial pressures may not accurately reflect their composition in the system.

Taking this into account, the conditions and test procedure were designed to allow consistent dosing of substances while maintaining concentrations representative of deep-well environments. The goal was to simulate downhole environments predicted for deep oil and gas wells.$^{14}$ Deep wells are predicted to encounter total pressures up to and above 100 MPa, and the “gas” phase may contain over 10 % CO$_2$ and 0.01 % H$_2$S. A simplified assumption was employed for this study. The tests systems were initially calculated to represent exposure to a pocket of CO$_2$ and/or H$_2$S-containing secondary phase (either gas or condensed phase) with 10 MPa of CO$_2$
and/or 0.01 MPa of H\textsubscript{2}S. A 1:1 ratio of aqueous:non-aqueous volume was considered as coming to equilibrium; this allowed a calculation of the total contents (in moles) of each component (water, NaCl, CO\textsubscript{2}, and H\textsubscript{2}S) in the total system. Thus, the entire system could be defined as a mole X:mole water ratio, where X represents any non-water species in the system.

The initial calculation results had to be adapted to account for physical limitations in the system when maintaining the proper mole ratios, particularly maintaining a safe amount of non-aqueous phase at the top of the autoclave vessel to prevent severe pressure increases if cooling was lost to the system. The final ratios used for these tests were 0.312 mol CO\textsubscript{2}:mol H\textsubscript{2}O and 3.12 x 10\textsuperscript{-4} mol H\textsubscript{2}S:mol H\textsubscript{2}O (maintaining a CO\textsubscript{2}:H\textsubscript{2}S = 1000:1 ratio for the mixed case). The Ar:H\textsubscript{2}O ratio was not controlled, but rather argon was used to dilute the H\textsubscript{2}S and balance the pressure between tests. Phase equilibria calculations were performed using commercial thermodynamic modeling software (OLI Analyzer) to determine the final amounts of each species needed to achieve the internal autoclave volume (476 mL assembled) at 4 °C and a total pressure of 10 MPa. The autoclave contents, in moles, for each of the three test environments are given in Table 6-1.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>V (mL)</th>
<th>H\textsubscript{2}S</th>
<th>CO\textsubscript{2}</th>
<th>H\textsubscript{2}O</th>
<th>NaCl</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>4</td>
<td>10</td>
<td>476</td>
<td>0</td>
<td>4.52</td>
<td>14.49</td>
<td>0.235</td>
<td>0</td>
</tr>
<tr>
<td>CO\textsubscript{2}+H\textsubscript{2}S</td>
<td>4</td>
<td>10</td>
<td>476</td>
<td>4.49x10\textsuperscript{-3}</td>
<td>4.49</td>
<td>14.40</td>
<td>0.233</td>
<td>0.0404</td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>4</td>
<td>10</td>
<td>476</td>
<td>6.30x10\textsuperscript{-3}</td>
<td>0</td>
<td>20.20</td>
<td>0.327</td>
<td>0.5597</td>
</tr>
</tbody>
</table>
6.2.2 Materials Investigated

Two high-strength low alloy martensitic drilling steels were tested. The first was a high strength low alloy (S-135) steel (G41000), while the second was an ultra-high strength low alloy (UD-165) steel (G41300) with a higher strength. Chemical compositions for each tested alloy are given in Table 6-2. The primary differences in composition were lower chromium and higher manganese, nickel, copper, and vanadium in UD-165 versus S-135. The level of sulfur was also higher for UD-165. The result is UD-165 with an 8 % higher yield strength and a 9 % higher ultimate tensile strength, as seen in Table 6-3. 

Table 6-2. Chemical compositions (mass%) of UD-165 and S-135. 

<table>
<thead>
<tr>
<th>Grade</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>Al</th>
<th>Ni</th>
<th>Cu</th>
<th>Nb</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD-165</td>
<td>Bal</td>
<td>0.79</td>
<td>0.88</td>
<td>0.67</td>
<td>0.03</td>
<td>0.81</td>
<td>0.19</td>
<td>0.02</td>
<td>0.007</td>
</tr>
<tr>
<td>S-135</td>
<td>Bal</td>
<td>1.39</td>
<td>0.78</td>
<td>0.68</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.002</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grade</th>
<th>P</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>V</th>
<th>Si</th>
<th>Sn</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD-165</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.27</td>
<td>0.007</td>
<td>0.07</td>
<td>0.26</td>
<td>&lt;0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>S-135</td>
<td>0.006</td>
<td>&lt;0.005</td>
<td>0.26</td>
<td>0.005</td>
<td>&lt;0.01</td>
<td>0.3</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Table 6-3. Mechanical properties of UD-165 and S-135.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Yield strength / MPa</th>
<th>Ultimate tensile stress / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD-165</td>
<td>1183</td>
<td>1278</td>
</tr>
<tr>
<td>S-135</td>
<td>1096</td>
<td>1168</td>
</tr>
</tbody>
</table>

Electrodes for the electrochemical tests were prepared using 10×10×5 mm plates. One 10×10 mm face served as the electrode surface, and a 304 stainless steel (UNS S30400) electrode lead was attached to the opposite face. The electrode lead was coated with shrinkable polytetrafluoroethylene (PTFE) tubing. Two to three electrode plates were placed into a PTFE
holder and all sides other than the 10×10 mm electrode surface were sealed to the PTFE using a high temperature epoxy. Mass loss samples were also prepared using 25×20×2 mm plates. A 3 mm ID hole was drilled near the top of the plate so that the samples could be suspended from a PTFE-coated wire. The electrode surface and mass loss sample were each ground with 600 grit SiC paper and then cleaned for 30 to 60 minutes in acetone inside a sonic bath.

6.2.3 System Setup

The electrochemical measurements were performed using a three electrode system. The working electrodes consisted of two to three of the steel samples prepared as described above. The counter electrodes were 20×10 mm sheets of either platinum plate or mesh. The electrode leads were coated with PTFE. Two to three of these counter electrodes were inserted through the edges of the PTFE working electrode assembly to allow each to be placed parallel to a working electrode in the system. The schematic of the autoclave system and an example of the completed assembly are shown in Figure 6-1. Two mass loss samples were suspended by PTFE-coated wire from the autoclave lid, with care taken to ensure that they would remain in the aqueous phase without contacting any of the inner surfaces.

Custom double-junction silver-silver chloride electrodes were prepared for the high pressure systems. The reference solution was 5 % wt. NaCl to reduce the effects of liquid junctions on the electrode potential. The inner junction of the reference electrodes consisted of solution-saturated zirconia sand with the Ag/AgCl electrode inside an alumina tube. The top of the tube was sealed with high temperature epoxy, and the bottom was supported using a porous zirconia-magnesia cement. The second junction was prepared by sealing a shrinkable PTFE tube around the outside of the ceramic tube. The inside of the PTFE tube was filled again with solution-saturated zirconia sand, and either another cement frit or a perforated PTFE plug was
used for the second junction. Two reference electrodes were used for each test in case one failed before the end of the exposure, and fresh electrodes were prepared for each assembled autoclave. The potential of the Ag/AgCl electrode in 5 % wt. NaCl at 4 °C was calculated to be 0.25 V vs. the standard hydrogen electrode (SHE) using the data from OLI Analyzer. The results were confirmed through comparison to calculations performed using thermodynamic properties and activity coefficients from literature.16–18

Figure 6-1. Schematic diagram of the autoclave system (left) and the working electrodes assembly (right). 1- Connection to pressure transducer; 2- Heating mantle; 3- Autoclave stainless steel vessel; 4- PTFE liner; 5- Polymer-coated thermocouple; 6- Dip tubing; 7- Epoxy-coated stirrer; 8- PTFE-coated lead; 9- Two Ag/AgCl reference electrodes; 10- Two mass loss samples; 11- PTFE assembly; 12- Three working electrodes; 13- Three Pt counter electrodes; 14- Supercritical CO\textsubscript{2} pump; 15- H\textsubscript{2}S/N\textsubscript{2} cylinder; 16- CO\textsubscript{2} cylinder.

All measurements were performed in a 600 mL autoclave vessel. A PTFE liner was used to isolate the test solution from the autoclave vessel. Temperature was controlled using a circulating chiller and a copper-coil heat exchanger wrapped around the autoclave vessel. All
tests were stirred using an impeller rotating at around 150 RPM. A computer-controlled
potentiostat was used to perform the electrochemical measurements.

6.2.4 Experimental Procedure

The experimental procedure was generally as follows due to requirements related to
achieving 10 MPa final system pressure. First, the autoclave was assembled dry with all
electrodes and mass loss samples. Only one kind of alloy (either S-135 or UD-165) was present in
each assembled autoclave. The desired amount of 5%wt. NaCl(s) was placed at the bottom of the
vessel before it was sealed. The sealed vessel was then purged of oxygen by repeated and slow
pressurization and depressurization cycles up to 20 bar (300 psi). Care had to be taken to prevent
gas bubbles from forming at the reference electrode junctions. This was believed to have caused
failure of some of the reference electrodes during exposure. During this process the cooling was
started to bring the system down to 4 °C. This usually involved letting the system chill overnight
to ensure it was at a stable temperature for H₂S injection. The temperature stability was typically
within ±1 °C, though on hot days the variability could be as high as ±3 °C.

After the autoclave was deaerated, the system was brought down to just above
atmospheric pressure (to maintain positive pressurization) and H₂S was added (if needed) using a
10 %vol. H₂S in Ar blend. The desired pressure was calculated using the autoclave volume (476
mL after assembly) and the ideal gas law at 4 °C. In the H₂S tests, the H₂S addition was followed
by further addition of argon to help balance the final pressure. The water injection was performed
using deaerated deionized water (deaerated with Ar for > 1 hour) and a high performance liquid
chromatography (HPLC) pump. The HPLC pump was set to a constant flow rate of 10 mL min⁻¹
and run until the desired amount of water had been transferred to the system. For the H₂S tests,
water injection was the final step and was used to bring the test system to its final pressure. It
should be noted that while the target pressure was 10 MPa, the actual pressure was in the range of 6 to 8 MPa due to small errors in water addition and determining the internal autoclave volume. These errors were magnified due to the small non-aqueous volume relative to the incompressible aqueous phase. For the CO₂ and CO₂+H₂S tests CO₂ was added as the final step to bring the system up to 10 MPa. CO₂ was added using a supercritical CO₂ pump which was a modified design of the HPLC pump. Additional CO₂ had to be added over the first 12 hours to account for pressure drops due to the dissolution of CO₂ into the aqueous solution.

After all components were added the autoclave was sealed for the remainder of the exposure period. The electrochemical measurements included linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and linear sweep voltammetry (LSV). LPR and EIS measurements were performed regularly for at least 60 hours until the system approached steady-state behavior. LPR was measured at 0.01 mV s⁻¹ over a range of ±15 mV around the corrosion potential, E_corr. EIS was performed with an amplitude of 10 mV over a frequency range from 300 kHz down to 5 mHz. After 60 hours, cyclic voltammetry sweeps were run at sweep rates of 100, 50, and 5 mV s⁻¹, and LSV were conducted at a scan rate of 1 mV s⁻¹. One of the working electrodes was used for surface analysis, so it was not polarized with CV and LSV. Total exposure time ranged from 90 to 120 hours and was recorded for mass loss calculations.

After the electrochemical tests were completed the autoclave systems were depressurized and disassembled. All electrodes and mass loss samples were rinsed with distilled water, dried with argon, and sealed in sample bags under argon. One working electrode for each alloy from each condition was used for surface analysis using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Mass loss samples were cleaned and analyzed according to ASTM G1 using Solution C.3.5 (HCl and hexamethylene tetramine) from Appendix
A1. Freshly polished, unexposed samples for each alloy were cleaned to serve as calibrations and account for material loss due to the cleaning procedure.

6.3 Results and discussion

6.3.1 The primary carbonate and sulfide species in the aqueous phase

The speciation in the three conditions were calculated with OLI Analyzer software, and the solution pH and the carbonate and sulfide species in the aqueous phase are given in Table 6-4. The solution pH was predicted to be around 3.0 for both environments containing CO$_2$ and 4.5 for the H$_2$S environment. From the CO$_2$ only condition to CO$_2$+H$_2$S condition, pH and carbonate speciation were barely changed with the addition of relatively small amount of H$_2$S (total H$_2$S:CO$_2$ = 0.001 mol/mol). In both conditions, CO$_3^{2-}$(aq) was the dominant active species and the H$_2$S(aq) concentration, if any, was three orders of magnitude lower. In the H$_2$S condition, the sulfide species concentrations were relatively higher than in CO$_2$+H$_2$S condition without the dissolution of H$_2$S in the CO$_2$-rich phase. H$_2$S(aq) was the dominant sulfide species in the H$_2$S-containing conditions.

Table 6-4. The calculated pH and carbonate and sulfide species in the aqueous phase (mol/kg H$_2$O).

<table>
<thead>
<tr>
<th>Conditions</th>
<th>CO$_2$</th>
<th>CO$_2$+H$_2$S</th>
<th>H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.0</td>
<td>3.0</td>
<td>4.5</td>
</tr>
<tr>
<td>CO$_2$(aq)</td>
<td>1.43</td>
<td>1.44</td>
<td>0</td>
</tr>
<tr>
<td>HCO$_3^-$ (aq)</td>
<td>9.29×10$^{-4}$</td>
<td>9.28×10$^{-4}$</td>
<td>0</td>
</tr>
<tr>
<td>CO$_3^{2-}$(aq)</td>
<td>1.48×10$^{-10}$</td>
<td>1.47×10$^{-10}$</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$S(aq)</td>
<td>0</td>
<td>3.29×10$^{-3}$</td>
<td>1.41×10$^{-2}$</td>
</tr>
<tr>
<td>HS$^-$ (aq)</td>
<td>0</td>
<td>2.12×10$^{-7}$</td>
<td>3.39×10$^{-5}$</td>
</tr>
<tr>
<td>S$^2$ (aq)</td>
<td>0</td>
<td>1.68×10$^{-19}$</td>
<td>7.75×10$^{-16}$</td>
</tr>
</tbody>
</table>
6.3.2 Polarization Resistance and Corrosion Rate from LPR, EIS, and Mass Loss

The polarization resistance, $R_{pol}$, of S-135 and UD-165 from LPR and EIS at each condition are depicted in Figure 6-2. $R_{pol}$ increased by more than one order of magnitude in the presence of H$_2$S, indicating the inhibiting effect of small amount of H$_2$S on corrosion. $R_{pol}$ in the H$_2$S condition was lower than CO$_2$+H$_2$S condition, which suggested that higher concentration of H$_2$S(aq) could accelerate the corrosion considering the speciation in Table 6-4.

The corrosion rate (CR) of S-135 and UD-165 from LPR, EIS, and mass loss samples are given in Table 6-5. Both alloys showed an obvious correlation between the corrosion rate and the presence of H$_2$S. The increase of $R_{pol}$ corresponded to a one order of magnitude drop in corrosion rate in the presence of H$_2$S. This matched behavior that has been reported for low concentrations of H$_2$S. A small increase in corrosion rate was observed when H$_2$S(aq) concentration increased in the aqueous phase from CO$_2$+H$_2$S to H$_2$S case, however, it was negligible when compared from the CO$_2$ only condition.

It can be seen that a CO$_2$:H$_2$S ratio as high as 1000 was still enough to transition from sweet to sour corrosion in the low temperature, high pressure environment tested here. While a decrease in material loss is generally welcome in corroding systems, the tradeoff for the protection of iron sulfide can be an increased risk for cracking. For this reason, laboratory corrosion measurements for sour corrosion should be coupled with mechanical testing where possible to determine if the decrease in corrosion rate due to the transition from sweet to sour corrosion coincides with increased susceptibility to sulfide stress cracking.
Table 6-5. Corrosion rate (mm y⁻¹) results for S-135 and UD-165.

<table>
<thead>
<tr>
<th></th>
<th>LPR</th>
<th>EIS</th>
<th>Mass Loss</th>
<th>OLI</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-135</td>
<td>CO₂</td>
<td>0.418±0.074</td>
<td>0.429±0.061</td>
<td>0.590±0.019</td>
</tr>
<tr>
<td></td>
<td>CO₂+H₂S</td>
<td>0.0189±0.0070</td>
<td>0.0187±0.0080</td>
<td>0.0599±0.0147</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>0.0346±0.0042</td>
<td>0.0350±0.0050</td>
<td>0.0798±0.0143</td>
</tr>
<tr>
<td>UD-165</td>
<td>CO₂</td>
<td>1.82±0.16</td>
<td>1.49±0.27</td>
<td>1.77±0.32</td>
</tr>
<tr>
<td></td>
<td>CO₂+H₂S</td>
<td>0.0334±0.0042</td>
<td>0.0328±0.0054</td>
<td>0.0877±0.0043</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>0.0510±0.0036</td>
<td>0.0515±0.0041</td>
<td>0.0678±0.0240</td>
</tr>
</tbody>
</table>
Very good agreement was seen between the LPR and EIS results in all cases. Good agreement was seen between the corrosion rates from the electrochemical and mass loss measurements in the CO\textsubscript{2}-only environment. However, the disagreement was greater when H\textsubscript{2}S was present, where corrosion rates from mass loss samples were consistently larger than those from the electrochemical tests. The difference was attributed to relatively larger errors in the mass loss measurements when the corrosion rates were lower. It was found that the material lost from each exposure to cleaning solution was of a similar order to the mass lost from corrosion in H\textsubscript{2}S-containing conditions, which likely resulted in an exaggerated corrosion rate. In all three environments the UD-165 alloy gave a higher overall corrosion rate than S-135 for the electrochemical tests, even after accounting for the standard deviation between samples. The difference was roughly a factor of two in the presence of H\textsubscript{2}S, but was as much as four times larger in the CO\textsubscript{2}-only system. The trend was not present in the mass loss data for the H\textsubscript{2}S-containing systems but was seen in the CO\textsubscript{2}-only system. This may again have been due to measurement error in the mass loss samples.

6.3.3 EIS Results

The Nyquist plots and Bode phase angle plots are given in Figure 6-3. Only one time constant was observed in all three environments. Small inductive- or capacitive-type behaviors were seen at frequencies above $10^5$ Hz, though no correlations were determined between these behaviors and the corrosion. One exception was the UD-165 samples in the CO\textsubscript{2} only system, where the higher frequency capacitive behavior extended down to around $10^3$ Hz. The impedances at the higher frequencies were small compared to the total impedance, which could explain why they were not found to affect the overall corrosion behavior. In addition to the
dramatic increase in impedance in the presence of H₂S, it can be seen in the phase angle plots in Figure 6-3 that the transition to sour corrosion doubled the maximum phase angle, suggesting that the double layer capacitances in H₂S-containing conditions were more ideal than those in the CO₂ only systems. There was no significant or consistent shift in the frequency at which the maximum peak was observed, suggesting that the overall capacitance of the corrosion product film did not change greatly with the change in corrosion rate. An increase in capacitance would require longer charging, which would then shift the phase angle peak to a lower frequency.

![Nyquist plots and Bode phase angle plots for S-135 (left) and UD-165 (right). Conditions: 4 °C, 0.9 mol kg⁻¹ NaCl. 10 MPa; x = CO₂, o = CO₂+H₂S, + = H₂S.](image-url)
The EIS results confirmed activation-controlled corrosion behavior, which was the assumption used to calculate the corrosion rates.\textsuperscript{18,22} The data was fitted using the Randles circuit without diffusion shown in Figure 6-4. $R_{sol}$ represents the solution resistance, and $R_{pol}$ represents the polarization resistance. A constant phase element (CPE) was used to account for non-ideality of the double layer capacitance. The $R_{pol}$ values were shown in Figure 6-2 and were used to calculate the CR in Table 6-5.

![Figure 6-4. Equivalent circuit used to fit EIS data.](image)

### 6.3.4 Cyclic Voltammetry Results

The CV curves for the two tested alloys are shown in Figure 6-5. All curves were corrected to take into account the solution resistance determined from EIS. Three distinct trends were observed. First and foremost, no obvious limiting currents were observed at anodic regions and the sweep up and down plots were almost overlaid, indicating that anodic reaction was not limited by mass transport. Secondly, a consistent peak was seen in the anodic sweep for both alloys in the H$_2$S and CO$_2$+H$_2$S systems that was absent in the CO$_2$-only system. It is believed that this peak thus corresponded to a sulfide-related process. This peak was within about 100 mV from the measured $E_{cor}$ in each case, meaning that the process was likely present as part of the corrosion process. The third trend was that the anodic slope for the H$_2$S and CO$_2$+H$_2$S curves notably steeper than for the CO$_2$ curve, suggesting that for both alloys the presence of H$_2$S was affecting the corrosion mechanism and not just reducing the available reactive area. Trends for the cathodic side of the sweep were inconsistent and no similar conclusions were drawn. Sweeps
at 100 mV s\(^{-1}\) showed nearly identical behavior to those shown in Figure 6-5 at 50 mV s\(^{-1}\), only with larger current densities. In sweeps at 10 mV s\(^{-1}\) the magnitude of the H\(_2\)S-related peak was much smaller than at 50 mV s\(^{-1}\) and in some cases was difficult to distinguish.

Figure 6-5. Cyclic voltammetry curves for S-135 (top) and UD-165 (bottom) at 50 mV s\(^{-1}\). Conditions: 4 °C, 10 MPa, 0.9 mol kg\(^{-1}\) NaCl. black = CO\(_2\), grey = CO\(_2\)+H\(_2\)S, dashed = H\(_2\)S.
6.3.5 Linear Sweep Voltammetry Results

The LSV plots for each alloy at three different gas conditions are given in Figure 6-6. All curves were corrected to take into account the solution resistance determined from EIS. With the polarization of at least 200 mV at both anodic and cathodic regions, no limiting current densities were observed for all of them, indicating both alloys were under active corrosion in the acidic solutions from the dissolved acid gases. The average Tafel slopes and standard deviations of working electrodes for each alloy in each condition are given in Table 6-6. The CO₂+H₂S condition and H₂S condition had the similar anodic and cathodic Tafel slopes, which were smaller than in the CO₂ only system. This indicated that the reaction mechanism was determined by H₂S even when its concentration was two orders of magnitude lower than CO₂. Beyond the general trend, there were small deviations in CO₂+H₂S condition of UD-165. The cathodic Tafel slope for UD-165 in CO₂+H₂S condition was between the CO₂ condition and H₂S condition without preference, however, it still confirmed that the presence of H₂S decreased the cathodic slope. In Figure 6-6, the high polarization region of anodic plot for UD-165 in CO₂+H₂S condition showed the slope close to the anodic slope in CO₂ only condition, which might be due to the limited concentration of H₂S. This region was at the far end of the polarization plot and was not taken for the anodic slope calculation.
Figure 6-6. LSV plots for S-135 (top) and UD-165 (bottom) at a scan rate of 10 mV s\(^{-1}\). Conditions: 4 °C, 10 MPa, 0.9 mol kg\(^{-1}\) NaCl. black = CO\(_2\), grey = CO\(_2\)+H\(_2\)S, dashed = H\(_2\)S.

Table 6-6. The Tafel slopes (V dec\(^{-1}\)) at the three different gas conditions.

<table>
<thead>
<tr>
<th>Gas</th>
<th>S-135</th>
<th>UD-165</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(b_a)</td>
<td>(b_c)</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.234±0.014</td>
<td>0.755±0.000</td>
</tr>
<tr>
<td>CO(_2)+H(_2)S</td>
<td>0.073±0.001</td>
<td>0.395±0.064</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>0.076±0.021</td>
<td>0.312±0.098</td>
</tr>
</tbody>
</table>
6.3.6 Corrosion Modeling Results

The experimental results were compared to those calculated for each condition using OLI Analyzer software, and the modeled CR results are given in Table 6-5. Calculations were performed assuming a rotating disk of generic carbon steel (G10100). The inputs for the test environments were those listed in Table 6-1 with the correction of 7 MPa for H\textsubscript{2}S system. Hydrodynamic effects were approximated as a 10 mm OD rotating disk electrode at 150 RPM, though hydrodynamic effects (rotating rate) were found to have only a minor impact on the calculations at the test conditions.

The modeled CR in the CO\textsubscript{2} condition agreed with the experimental CR for UD-165, and though it was four times higher than the experimental CR for S-135 it was still within a reasonable range. Good agreement was seen in the H\textsubscript{2}S condition for both UD-165 and S-135 within a factor of two. Overall, the model for these two conditions was considered quite to be good when considering that a generic carbon steel was assumed in place of the specific alloys tested. Substantial disagreement was seen in the CO\textsubscript{2}+H\textsubscript{2}S mixture. The experimental results found that the mixed case behaved very close to the H\textsubscript{2}S condition, indicating sour corrosion was dominant. However, the modeled results were quite similar to CO\textsubscript{2} corrosion, resulting in the prediction of overly high corrosion rates. Increasing the amount of H\textsubscript{2}S in the model, thereby decreasing the CO\textsubscript{2}:H\textsubscript{2}S ratio, only increased the predicted corrosion rate, showing that the issue was not a simple “tipping point” between sweet and sour corrosion. Decreasing the amount of CO\textsubscript{2} in the model (while keeping H\textsubscript{2}S constant) decreased the predicted corrosion rate but did not reach the low rates of the H\textsubscript{2}S case.

Table 6-7 shows comparisons of the measured $E$\textsubscript{corr} and those calculated using the OLI Analyzer software. It can be seen that, unlike the corrosion rate, $E$\textsubscript{corr} was strongly correlated in the presence of CO\textsubscript{2} rather than H\textsubscript{2}S. This suggested that the corrosion potential was more a
function of pH, which was predicted to be 3.0 for the systems containing CO\(_2\) and 4.5 for the system without. This would affect the equilibrium potential for the cathodic reaction, which could in turn shift the corrosion potential to a more positive value when the pH is lower. It could also affect the equilibrium potential for the anodic reaction by changing the solubility of corrosion products in the aqueous phase. The modeled \(E_{\text{corr}}\) values for all conditions were in good agreement with the experimental data. Importantly, the model correctly predicted the change in \(E_{\text{corr}}\) when CO\(_2\) was not present in the system.

Table 6-7. Experimental and modeled corrosion potentials (V, vs SHE).

<table>
<thead>
<tr>
<th>Gas</th>
<th>S-135</th>
<th>UD-165</th>
<th>Modeled</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>-0.353±0.001</td>
<td>-0.332±0.001</td>
<td>-0.374</td>
</tr>
<tr>
<td>CO(_2)+H(_2)S</td>
<td>-0.337±0.004</td>
<td>-0.337±0.004</td>
<td>-0.376</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>-0.444±0.002</td>
<td>-0.460±0.002</td>
<td>-0.463</td>
</tr>
</tbody>
</table>

6.3.7 Surface Analysis

Pourbaix diagrams were generated using OLI Analyzer to predict the thermodynamically predominant corrosion products in each gas conditions, which are depicted in Figures 6-7 to 6-9, respectively. At pH 3.0 for CO\(_2\) and CO\(_2\)+H\(_2\)S conditions, Fe\(^{2+}\)(aq) was predicted to be the thermodynamically favorable products, which confirmed the active corrosion. At pH 4.5 for H\(_2\)S condition, Fe\(^{2+}\)(aq) and FeHS\(^{+}\)(aq) were predicted to be stable. The addition of H\(_2\)S was predicted to favor the formation of FeS(s) at relatively higher pH in Figures 6-8 and 6-9. Considering the inhibiting effect of H\(_2\)S on corrosion rate, the protective FeS(s) might have formed at the steel surface where the pH and Fe\(^{2+}\)(aq) concentration might be higher than in the bulk solution.\(^8\)
Figure 6-7. Pourbaix diagram of Fe-H₂O-CO₂ system. Conditions: 4 °C, 10 MPa, 4.52 mol CO₂, 14.49 mol H₂O, 0.235 mol NaCl.

Figure 6-8. Pourbaix diagram of Fe-H₂O-CO₂-H₂S system. Conditions: 4 °C, 10 MPa, 4.49 mol CO₂, 4.49x10⁻³ mol H₂S, 14.40 mol H₂O, 0.233 mol NaCl.
Figure 6-9. Pourbaix diagram of Fe-H₂O-H₂S system. Conditions: 4 °C, 7 MPa, 6.30×10⁻³ mol H₂S, 20.20 mol H₂O, 0.327 mol NaCl.

In all the three conditions, the corrosion products on the sample surface changed from black to orange quickly during rinsing with distilled water and drying with argon after taking the samples out of the autoclave. A large amount of oxygen was detected using EDS on the surface for both UD-165 and S-135. The discoloration and a significant portion of the oxygen present on the sample surface may have been due to oxidation of the existing corrosion product to hematite after the system was disassembled. This showed that the stability of the corrosion products was quite conditional, and well upsets where the oxygen content of the downhole solution increases could result in a breakdown of the corrosion film.

Figure 6-10 shows SEM images of the corroded steel surfaces and the EDS analysis results on the selected locations are listed in Table 6-8. The accelerating voltage was 10 kV. In the CO₂ only condition for UD-165, the steel surface was covered with corrosion products of high oxygen content. The Fe:O ratio was close to 1:2. The corrosion product layer cracked and stripped off from the surface in some regions, and the steel surface was exposed. In the CO₂+H₂S
condition, two regions were observed on the corroded surface of UD-165: a thick product layer region with a composition close to 2Fe:3O, and a thin product film region containing lower O and relatively higher S as in Location 4. In the H₂S condition, the chemical composition over the surface was close to 1Fe:2O and 2Fe:3O. It could have been that FeO(OH) or Fe₂O₃ formed after drying the sample, as goethite, hydrohematite, or hematite could all give the reddish color.²⁵ S was relatively higher in the thin layer region (2.5%~6%at), while O was dominant across the surface. Generally, the morphology had two distinct regions in the presence of H₂S, and relatively higher S was found in the thin layer region. As this region correlated with a considerable drop in corrosion rate for the H₂S-containing systems, the S-containing products probably had a protective effect.

S-135 showed the similar trend of chemical compositions in the three different conditions like UD-165. However, subtle difference in surface morphology were observed. In many cases, surface features present on both alloys were found to be smaller on the S-135 samples. On both alloys, particularly for the H₂S-containing systems, pockets of high-O corrosion product tended to be round and appeared similar in shape to water droplets. This could be evidence that the highly-oxidized features occurred after the system was disassembled, and that the lower-O regions may be more representative of the surface at test conditions.
Figure 6-10. SEM images of the corroded UD-165 (a,b,c) and S-135 (d,e,f) steel surfaces. Conditions: 4 °C, 0.9 mol kg⁻¹ NaCl. 10 MPa, a,d: CO₂; b,e: CO₂+H₂S; c,f: H₂S.
Table 6-8. EDS chemical analyses in at.% on the corroded surfaces in selected locations marked in Figure 6-10.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Location</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Na</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>26</td>
<td>8</td>
<td>63</td>
<td>-</td>
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<tr>
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<td></td>
<td>78</td>
<td>13</td>
<td>6.6</td>
<td>-</td>
<td>0.3</td>
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</tr>
<tr>
<td>3</td>
<td></td>
<td>29</td>
<td>8.4</td>
<td>56</td>
<td>-</td>
<td>0.1</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>UD-165</td>
<td>47</td>
<td>16</td>
<td>24</td>
<td>3.7</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>33</td>
<td>5.0</td>
<td>60</td>
<td>0.1</td>
<td>0.2</td>
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<td></td>
<td>36</td>
<td>2.9</td>
<td>56</td>
<td>0.2</td>
<td>0.1</td>
<td>4.2</td>
</tr>
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<td>0.3</td>
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<tr>
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<td>5.9</td>
<td>55</td>
<td>0.5</td>
<td>0.3</td>
<td>3.8</td>
</tr>
<tr>
<td>10</td>
<td>S-135</td>
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<td>47</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>11</td>
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<tr>
<td>12</td>
<td></td>
<td>56</td>
<td>16</td>
<td>26</td>
<td>1.1</td>
<td>-</td>
<td>0.3</td>
</tr>
</tbody>
</table>

6.4 Conclusions

Experimental results for two drill steels, S-135 and UD-165, showed a distinct drop in corrosion rate when transitioning from sweet to sour corrosion in 5% wt. NaCl brine at 4 °C and 10 MPa total pressure. It was found that a CO₂:H₂S ratio as high as 1000 was still enough for sour corrosion to dominate the conditions tested. H₂S and CO₂+H₂S conditions gave corrosion rates on order of 0.05 mm y⁻¹, whereas corrosion rate in the CO₂ condition was on the order of 0.5 to 2 mm y⁻¹. The CO₂+H₂S condition and H₂S condition had the similar anodic and cathodic Tafel slopes, which were smaller than the CO₂ condition.

Comparisons were made between the experimental results and those from a commercial software model. Good agreement was seen in the CO₂ and H₂S conditions. However, the model
predicted that corrosion in the mixed CO$_2$+H$_2$S system would match that of CO$_2$ only condition, whereas experimental results found that it matched those from the H$_2$S system. In all cases the model was found to provide a good prediction for $E_{\text{corr}}$. Corrosion potentials in the CO$_2$ and CO$_2$+H$_2$S systems were almost identical, while a roughly 100 mV decrease was seen in the H$_2$S system. This suggested that while the corrosion behavior was strongly dependent on the H$_2$S content, the corrosion potential was instead tied to the CO$_2$ content and pH.

In the Pourbaix diagrams at each condition, soluble species like Fe$^{2+}$(aq) and FeHS$^+$ (aq) were predicted to be the thermodynamically favorable products, which confirmed the active corrosion. The presence of H$_2$S could have caused the formation of FeS(s) at the steel surface where the pH and Fe$^{2+}$(aq) concentration might be higher than in the bulk solution. The corrosion products for all tests were found to be quickly oxidized on exposure to air when the system was disassembled. All samples showed high oxygen content across the surface, while the samples exposed to H$_2$S and CO$_2$+H$_2$S appeared to have relatively higher level of sulfur at the inner film region. This suggests the formation of a protective sulfide layer on the metal surface, which would explain the drop in corrosion rate in the presence of H$_2$S.

References

Chapter 7

Conclusions

7.1 Conclusions

The electrochemical corrosion study of grades S-135 and UD-165 steels in a pH range of 7.9, 10.7, and 12.4 with $P_{\text{H}_2\text{S}}$ of 0, 0.83, 8.3, and 69 kPa at 85 °C resulted in the conclusions:

(1) For the dissociation of $\text{H}_2\text{S(aq)}$, HS$^{-}(\text{aq})$ was calculated to be the dominant sulfide species from pH 7.9 to 12.4 at 85 °C. Considering $\text{OH}^{-}(\text{aq})$, $\text{HCO}_3^{-}(\text{aq})$, and HS$^{-}(\text{aq})$ as reactants for anodic reactions, the dominant reactive ions changed from $\text{HCO}_3^{-}(\text{aq})$ to $\text{OH}^{-}(\text{aq})$ from pH 7.9 to 12.4 with a comparable HS$^{-}(\text{aq})$ concentration. At pH 10.7, the reactive ions were most diverse and the HS$^{-}(\text{aq})$ ratio was the largest.

(2) After 60 hours, $R_{\text{pol}}$ of S-135 increased as pH increased at lower $P_{\text{H}_2\text{S}}$ (0 kPa and 0.83 kPa), whereas $R_{\text{pol}}$ first decreased and then increased as pH increased at higher $P_{\text{H}_2\text{S}}$ (8.3 kPa and 69 kPa). At each pH, the lower $P_{\text{H}_2\text{S}}$ increased $R_{\text{pol}}$ or did not significantly change $R_{\text{pol}}$, whereas the higher $P_{\text{H}_2\text{S}}$ decreased $R_{\text{pol}}$. UD-165 showed a similar general trend with pH and $P_{\text{H}_2\text{S}}$. Two opposite effects from $\text{H}_2\text{S}$ were proposed, an accelerating effect due to $\text{H}_2\text{S(aq)}$ and HS$^{-}(\text{aq})$ facilitating the Faradaic reactions and the localized corrosion, and an inhibiting effect due to the protectiveness of the corrosion products. The inhibiting effect was often observed at relatively low $\text{H}_2\text{S}$ concentrations at pH 7.9 and 12.4.

(3) The EIS results showed that the electrochemical impedance of both S-135 and UD-165 did not change significantly at different stir rates, indicating that mass transport in the bulk solution did not influence the rate determining step for the overall corrosion process.
The corrosion products for S-135 and UD-165 generally followed the trend of changing from iron carbonate and sulfides to iron oxide as pH increased, which agreed with the Pourbaix diagrams.

For both S-135 and UD-165, anodic limiting current was generally observed at lower $P_{\text{H}_2\text{S}}$ but disappeared at higher $P_{\text{H}_2\text{S}}$. Anodic Tafel slope values were smaller at higher $P_{\text{H}_2\text{S}}$. The cathodic LSV plots suggested that the main reactant for HER could be $\text{H}_2\text{S}(\text{aq})$ at pH 7.7 with $P_{\text{H}_2\text{S}} = 69$ kPa and $\text{H}_2\text{O}(l)$ for the other conditions.

The study on electrochemical corrosion of UD-165 in the same solutions with $P_{\text{H}_2\text{S}} = 69$ kPa at 200 °C resulted in conclusions:

1. Solution pH in the three solutions were calculated to be 8.1, 9.8, and 10.8 at 200 °C, respectively. Polarization resistance values at 200 °C were consistently one to two orders of magnitude lower than at 85 °C, which corresponded to a drastic increase in corrosion rate at elevated temperature. At 200 °C, $R_{\text{pol}}$ at 9.8 was the smallest after 60 hours among the three solutions, which was similar to the results at 85 °C. The modeled results were in reasonable agreement with the experimental CR values within a factor of 4.

2. A limiting current was observed in the anodic region of LSV but not in the cathodic region, which indicated that the anodic reactions were probably limited by the mass transport at 200 °C. Comparatively, LSV at 85 °C did not show limiting currents on either anodic or cathodic region. Traditional Tafel analysis in the cathodic region gave cathodic Tafel slopes corresponding to a two-electron mechanism for the three solutions at 200 °C. A new modified Tafel analysis method allowed to obtain anodic Tafel slopes from LSV even with the effect of limiting current. The $b_a$ values indicated that the anodic reactions followed the Bockris mechanism at pH 8.1 and a two-electron mechanism at pH 9.8 and 10.8.

3. As pH increased at 200 °C, the major corrosion products changed from pyrrhotite/siderite to magnetite although the corrosion products were a mixture of iron carbonate,
sulfide and oxide. This trend was in accordance with the change of primary reactive ions with pH and the Pourbaix diagram, which was similar to the trend at 85 °C. The corrosion products at 200 °C were probably in a greater amount or more crystallized than those at 85 °C so that the phase could be detected by XRD.

The study on electrochemical corrosion of S-135 and UD-165 at 4 °C resulted in conclusions:

(1) Experimental results for two drill steels, S-135 and UD-165, showed a distinct drop in corrosion rate when transitioning from sweet to sour corrosion in 5% wt. NaCl brine at 4 °C and 10 MPa total pressure. It was found that a CO₂:H₂S ratio as high as 1000 was still enough for sour corrosion to dominate the conditions tested. The CO₂+H₂S condition and H₂S condition had the similar anodic and cathodic Tafel slopes, which were smaller than the CO₂ condition.

(2) Corrosion potentials in the CO₂ and CO₂+H₂S systems were almost identical, while a roughly 100 mV decrease was seen in the H₂S system. This suggested that while the corrosion behavior was strongly dependent on the H₂S content, the corrosion potential was instead tied to the CO₂ content and pH.

(3) In the Pourbaix diagrams at each condition, soluble species like Fe²⁺(aq) and FeHS⁺(aq) were predicted to be the thermodynamically favorable products, which confirmed the active corrosion. The presence of H₂S could have caused the formation of FeS(s) at the steel surface where the pH and Fe²⁺(aq) concentration might be higher than in the bulk solution. The surface analysis suggested that the formation of a protective sulfide layer on the metal surface could have decreased the corrosion rate in the presence of H₂S.

The conclusions in this study mainly include the effect of pH and P_H₂S on corrosion in alkaline brines, which could serve as references for pH selection in the drilling fluid/mud design. The measurements of corrosion rate and Tafel slopes and the discussion on corrosion mechanisms could contribute to the database building and modeling development for high pH corrosion with
H₂S. The mechanisms considering HS (aq), OH (aq), and HCO₃⁻ (aq) as reactive ions were proposed and discussed based on the experimental results.

7.2 Suggestions on further work

More interesting work can be done in the future based on the present study.

For the purpose of industrial application, the electrochemical measurements can be carried out to obtain corrosion rate in a solution simulating the drilling fluid / mud in reality more than the pH range. The comparison with the current study could demonstrate whether pH is still the predominant factor for H₂S corrosion or there are other factors with significant effects.

To better understand the relation between corrosion and cracking, further study can be done by monitoring corrosion and cracking in situ simultaneously at different conditions. This work will need a well-designed experimental setup to conduct both electrochemical and mechanical measurements.

To further verify and establish the corrosion mechanisms proposed in present study, more fundamental study can be performed on Faradaic reactions and corrosion products separately. The reactions produce the corrosion products on the steel surface which in turn can impact the further reactions, so the effects of these two are closely related and they might be untangled by studying separately. For example, Faradaic reactions can be investigated at the early stage of corrosion before the effect of corrosion products becomes significant. In contrast, the effect of corrosion products can be determined through the corrosion tests with the controlled pre-existing corrosion products. A simple and fundamental system with a rotating disk/cylindrical electrode is suggested.
Appendix A

Hydrogen evolution reaction potentials

\[ E_{\text{H}_2\text{O}|\text{H}_2} - E_{\text{H}^+|\text{H}_2} = \left[ E_{\text{H}_2\text{O}|\text{H}_2}^0 + \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}(l)}}{a_{\text{OH}^-(aq)}^2 P_{\text{H}_2(g)}} \right] - \left[ E_{\text{H}^+|\text{H}_2}^0 + \frac{RT}{2F} \ln \frac{a_{\text{H}^+(aq)}^2}{P_{\text{H}_2(g)}} \right] \quad \text{[A1]} \]

\[ E_{\text{H}^+|\text{H}_2}^0 = -\left[ \Delta_f G_{\text{H}_2(g)}^0 - 2\Delta_f G_{\text{H}^+(aq)}^0 \right] / (2F) \quad \text{[A2]} \]

\[ E_{\text{H}_2\text{O}|\text{H}_2}^0 = -\left[ \Delta_f G_{\text{H}_2(g)}^0 + 2\Delta_f G_{\text{OH}^-(aq)}^0 - 2\Delta_f G_{\text{H}_2\text{O}(l)}^0 \right] / (2F) \quad \text{[A3]} \]

\[ E_{\text{H}_2\text{O}|\text{H}_2}^0 - E_{\text{H}^+|\text{H}_2}^0 = -\left[ 2\Delta_f G_{\text{OH}^-(aq)}^0 + 2\Delta_f G_{\text{H}^+(aq)}^0 - 2\Delta_f G_{\text{H}_2\text{O}(l)}^0 \right] / (2F) \]

\[ = \left[ \Delta_f G_{\text{H}_2\text{O}(l)}^0 - \Delta_f G_{\text{OH}^-(aq)}^0 - \Delta_f G_{\text{H}^+(aq)}^0 \right] / F \quad \text{[A4]} \]

Hence, Equation [A1] is equal to zero, i.e.

\[ = \left[ \Delta_f G_{\text{H}_2\text{O}(l)}^0 - \Delta_f G_{\text{OH}^-(aq)}^0 - \Delta_f G_{\text{H}^+(aq)}^0 \right] / F + \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}(l)}}{a_{\text{OH}^-(aq)}^2 a_{\text{H}^+(aq)}} \]

For OH\(^{-}\)(aq) + H\(^{+}\)(aq) ↔ H\(_2\)O(l),

\[ \Delta_r G = \Delta_f G^0 + RT \ln \frac{a_{\text{H}_2\text{O}(l)}}{a_{\text{OH}^-(aq)} a_{\text{H}^+(aq)}} \]

\[ = \left[ \Delta_f G_{\text{H}_2\text{O}(l)}^0 - \Delta_f G_{\text{OH}^-(aq)}^0 - \Delta_f G_{\text{H}^+(aq)}^0 \right] + RT \ln \frac{a_{\text{H}_2\text{O}(l)}}{a_{\text{OH}^-(aq)} a_{\text{H}^+(aq)}} \quad \text{[A5]} \]

When the dissociation of H\(_2\)O(l) is at equilibrium, Equation [A5] is equal to zero. Therefore,

\[ \left[ \Delta_f G_{\text{H}_2\text{O}(l)}^0 - \Delta_f G_{\text{OH}^-(aq)}^0 - \Delta_f G_{\text{H}^+(aq)}^0 \right] = - RT \ln \frac{a_{\text{H}_2\text{O}(l)}}{a_{\text{OH}^-(aq)} a_{\text{H}^+(aq)}} \quad \text{[A6]} \]

Hence, Equation [A1] is equal to zero, i.e. \( E_{\text{H}_2\text{O}|\text{H}_2} = E_{\text{H}^+|\text{H}_2} \) when the dissociation of H\(_2\)O(l) is at equilibrium.

Similarly, \( E_{\text{H}_2\text{CO}_3|\text{H}_2} = E_{\text{H}^+|\text{H}_2} \), and \( E_{\text{H}_2\text{S}|\text{H}_2} = E_{\text{H}^+|\text{H}_2} \) could be proved as well. It is the same with the other HERs when other hydrogen-containing species as hydrogen source, like HS\(^{-}\)(aq) and HCO\(_3\)(aq).
Conclusion: The electrode potentials of all the HERs are equal as long as the dissociation reactions of the hydrogen sources are at equilibrium.
Appendix B

Hydrogen evolution reaction mechanisms

Volmer-Heyrovsky mechanism

Step I (RDS): \[ \text{H}^+(\text{aq}) + e^- \rightarrow \text{H(ad)} \] \[ \text{B1} \]

Step II: \[ \text{H}^+(\text{aq}) + \text{H(ad)} + e^- \leftrightarrow \text{H}_2(\text{g}) \] \[ \text{B2} \]

(I) + (II): \[ 2 \text{H}^+(\text{aq}) + 2 e^- \rightarrow \text{H}_2(\text{g}) \] \[ \text{B3} \]

\[ b_c = 2.303 \frac{(R \ T)}{(\beta F)} \] \[ \text{B4} \]

Volmer-Tafel mechanism

Step I: \[ \text{H}^+(\text{aq}) + e^- \leftrightarrow \text{H(ad)} \mid 2 \times \] \[ \text{B5} \]

Step II (RDS): \[ 2 \text{H(ad)} \rightarrow \text{H}_2(\text{g}) \] \[ \text{B6} \]

(I) + (II): \[ 2 \text{H}^+(\text{aq}) + 2 e^- \rightarrow \text{H}_2(\text{g}) \] \[ \text{B7} \]

\[ b_c = 2.303 \frac{(R \ T)}{(2 \ F)} \] \[ \text{B8} \]
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