

Effect of Different H₂S and CO₂ Concentrations on Corrosion of Mild Steel at Elevated Temperatures (120-160 °C)

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ABSTRACT

Both H₂S and CO₂, ubiquitous in hydrocarbon production, can severely compromise asset integrity. While both are corrosive, H₂S-containing environments tend to be more aggressive, causing faster and more severe corrosion than CO₂—especially in high-temperature oil and gas systems.

Research on H₂S corrosion at elevated temperatures has been limited, leading to an incomplete understanding of the mechanisms behind observed phenomena. As a result, corrosion in the presence of H₂S remains a key concern for the oil and gas industry. This experimental work aimed to examine the effects of varying CO₂ and H₂S concentrations at high temperatures.

Data for autoclave experiments conducted at pH_{initial} 5.0, 0.00385-0.0385 M [H₂S]_{aq} (0.13-1.65 bar pH₂S), 0.009-0.093 M [CO₂]_{aq} (1-13 bar pCO₂) contrasting corrosion product layers at 120 and 160 °C are reported. The corrosion specimens were machined from X65 steel. Experimental results demonstrate that corrosion rates at 120 and 160 °C for different concentrations of CO₂ and H₂S were essentially the same, within error, with a combination of various iron sulfides (pyrrhotite, mackinawite, pyrite, troilite) and magnetite found as corrosion products. Also, localized corrosion appeared on the X65 steel specimens in select cases, with no clear pattern identified yet.

Keywords: H₂S, CO₂, iron sulfide, high temperature

INTRODUCTION

North American, Central Asian, and Middle Eastern oil and gas fields can be highly sour, with H₂S contents of several percent in the gas phase present with CO₂.¹ It is important to be able to understand corrosion phenomena that can occur in such environments. However, there is limited research on the internal corrosion of pipelines and production tubulars in such H₂S/CO₂ environments, especially at high temperatures due to the complexity of experiments. In H₂S/CO₂ environments, high temperature, typically in the range of 100 to 200 °C, governs the type of corrosion product formed: pyrite (FeS₂) and pyrrhotite (Fe_{1-x}S) become favored over mackinawite (FeS), and magnetite (Fe₃O₄) over siderite (FeCO₃) as temperature increases.² The formation of protective layers in H₂S/CO₂ environments can lessen the extent of corrosion-mitigation treatments required, however, the heterogeneity of the layer could become a cause of localized corrosion.¹

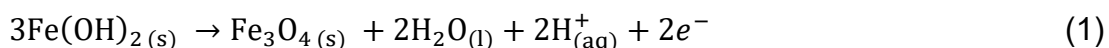
The mechanism for H₂S corrosion at high temperatures is poorly understood, mainly due to the complexity and safety considerations associated with high temperature experimentation with this toxic gas. Nevertheless, different theories have been proposed to explain corrosion product formation mechanisms in a sour system at elevated temperatures.

Gao³ conducted a series of experiments in H₂S environments (no CO₂) at elevated temperatures 80-200 °C, 0.10-0.18 bar pH₂S using nitrogen as the balance gas. XRD analysis of the corrosion product formed confirmed that different iron sulfide types were formed based on the temperature and time exposure of the steel specimen.³ His results indicated that iron sulfide would transform from troilite to pyrrhotite to pyrrhotite/pyrite to pyrite associated with an increase in temperature and time.⁴ Interestingly, the presence of pyrite was associated with occurrence of localized corrosion on the steel. By investigating cross-sections of the mild steel specimens, Gao³ also observed that there was an inner layer of iron oxide underneath the iron sulfide, which was not shown in the surface XRD analysis. This iron oxide was proven to be a magnetite layer by using transmission electron microscopy (TEM) analysis and selected area diffraction (SAD).³

Also, Gao, et al.,² compared cross-sections and EDS results from experiments in H₂S/CO₂ environments at two different pCO₂ of 10 and 55 bar, both with 0.1 bar H₂S, pH 5.0, and 120 °C. Similar to experiments in an H₂S environment with no CO₂, there was an iron oxide formed underneath the iron sulfide layer in H₂S/CO₂ systems. It was observed that with a decrease in content of CO₂, magnetite thickness increased, which indicated that the presence of CO₂ retarded the formation of magnetite underneath the iron sulfide layer.

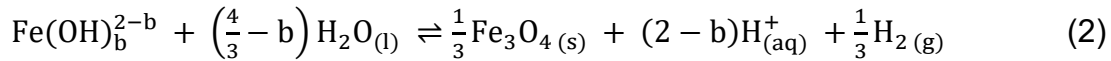
Kvarekvål and Tjelta¹ tested several temperatures (25-120 °C) and brines with high concentrations of H₂S and CO₂ (>10 bars). Corrosion product layers for all experimental conditions consisted of several layers of various iron sulfides and iron oxides. Iron sulfides that were detected primarily consisted of pyrrhotite, mackinawite and troilite, but no pyrite was identified. Localized corrosion appeared in all cases. Several studies reported a reason for localized corrosion in H₂S/CO₂ environment to be the heterogeneity of the corrosion product layer.⁵⁻⁷

Magnetite formation has been studied for a long time due to the growing interest in corrosion mechanisms in water coolant systems of power plants. The well-known Schikorr⁸ solid-state reaction was proposed in 1929, remaining commonly accepted as a correct path for magnetite formation:



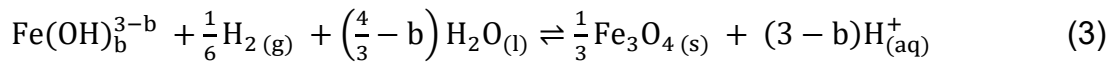
However, using calculations based on Pourbaix diagrams, Beverskog and Puigdomenech⁹ concluded that the Schikorr reaction, Equation (1), is valid only for temperatures below ~85 °C since iron(II) hydroxide is not thermodynamically stable above that value. As part of their conclusion, they used experiments of Linnenbom¹⁰ in which iron(II) hydroxide was found at 25 °C but not at 60 °C or 300 °C.

In another well-known study by Sweeton & Baes¹¹ in 1970, they pointed to the Schikorr reaction as being a result of a more complex scheme based on existing Fe^{2+} , FeOH^+ , Fe(OH)_2 , and Fe(OH)_3^- species in alkaline and acid solutions that they analyzed. Based on that, the following reaction was proposed:



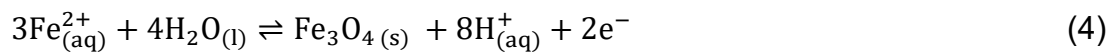
where b is the number of hydroxyl groups in a particular ferrous complex.¹¹

Tremaine & LeBlanc proposed an additional reaction to that of Sweeton & Baes for more alkaline pH.¹² Their results and thermodynamic analysis indicated that the equilibrium hydrogenated solutions in contact with magnetite under the coolant conditions of power systems at temperatures below 300 °C (i.e., at pH ~7-8) were dominated by ferrous (Fe^{2+}) species, with ferric (Fe^{3+}) species becoming more important at higher alkalinities via reaction:

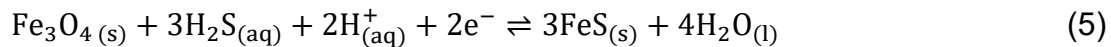


They also reported fractional contributions of each species to equilibrium solubility at different pH values; at more acidic values (pH < 6) the predominant species is Fe^{2+} with little Fe(OH)_2 , which becomes dominant at higher pH.

Since the initial pH of the current experiments is pH 5.0, Equation (2) with predominant species Fe^{2+} can be applied. Firstly, the metal surface (Fe) starts dissolving under the influence of H_2S corrosion and the released Fe^{2+} ions react to form an oxide:



H_2S also reacts with Fe_3O_4 at the Fe_3O_4 /solution interface which, as a result, contributes to the formation and growth of the FeS layer³:



Eventually, the rate of formation of Fe_3O_4 matches the rate of its transformation to FeS, and the Fe_3O_4 layer thickness reaches a constant value. The iron sulfide layer can also grow at the FeS/solution interface by precipitation, when the saturation value of FeS in the bulk exceeds the solubility limit of iron sulfide.³

In this investigation, high-temperature $\text{H}_2\text{S}/\text{CO}_2$ corrosion of mild steel is studied with the focus on the types of corrosion products formed and their correlation to the corrosion rates. Conducting this study is essential since the literature on the topic is limited.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental setup for high temperature corrosion measurements is shown in Figure 1. The 7.5 liter autoclave contains a three electrode system using a platinum coated niobium counter electrode (CE), an X65 carbon steel working electrode (WE), and a Ag/AgCl refillable reference electrode (RE) for high temperature and high pressure systems purchased from Corr Instruments[†].

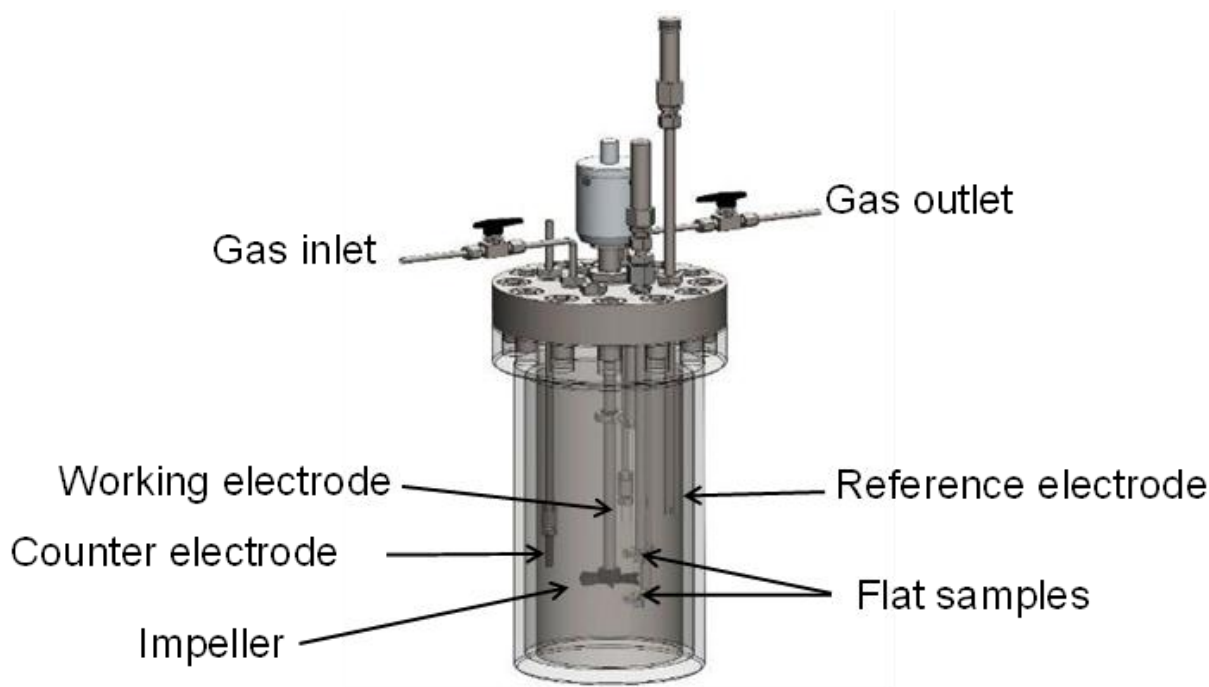


Figure 1. Experimental 7.5-liter autoclave setup with parts labeled

The full experimental procedure and methodology used are available elsewhere.¹³ In this series of experiments, only one API 5L X65 material was used, with composition shown in Table 1. The choice of material was done mainly to match previous work performed by Gao³. It is understood that API 5L X65 is a pipeline material and is not typically used for downhole environments, where high temperature conditions could be encountered. However, it is fully expected that corrosion rates experienced by API 5CT steel grades would be very close, in similar environments.

Table 1
Percent composition of API 5L X65 low alloy steel

	Material	C	Cr	Mo	Cu	V	Si	Al	Ni	Mn	Fe
WE, flat specimens	X65	0.05	0.23	0.07	0.11	0.03	0.22	0.02	0.24	1.40	Bal

[†] Trade company

Experimental parameters were defined so that the calculated aqueous molar concentrations of the dissolved acid gases, $[\text{CO}_2]_{\text{aq}}$ and $[\text{H}_2\text{S}]_{\text{aq}}$, were the same at the different environmental conditions for better comparison of results. As shown in Table 2, two aqueous H_2S concentrations of 0.00385 M and 0.0385 M are used as calculated from different partial pressures of H_2S in the gas phase for each temperature, plus two aqueous CO_2 concentrations of 0.009 M and 0.093 M are used as calculated from different partial pressures of CO_2 in the gas phase for each temperature.

Table 2
Experimental matrix for studying $\text{H}_2\text{S}/\text{CO}_2$ corrosion at high temperatures

Parameter	Conditions											
System	7.5-Liter autoclave											
Solution	1 wt.% NaCl											
Temperature, °C	120						160					
$p_{\text{H}_2\text{O}}$, bar	1.98						6.17					
$[\text{H}_2\text{S}]_{\text{aq}}$, M	0		0.00385		0.0385		0		0.00385		0.0385	
$p_{\text{H}_2\text{S}}$, bar	0		0.13		1.31		0		0.17		1.65	
$[\text{CO}_2]_{\text{aq}}$, M	0.009	0.093	0.009	0.093	0.009	0.093	0.009	0.093	0.009	0.093	0.009	0.093
p_{CO_2} , bar	1	10	1	10	1	10	1.26	13.0	1.26	13.0	1.26	13.0
Material	WE ($A_s=5.36 \text{ cm}^2$), and 3 flat specimens ($A_s=6.4 \text{ cm}^2$ each)											
Solution volume to specimen surface ratio, ml/cm ²	360											
Initial pH	5.0											
Duration	4 days											
Stirring speed	1000 rpm											
Measurement methods	Weight loss, LPR, EIS											
Surface characterization	XRD, SEM/EDS, Profilometry											

For each experiment, the solution in the autoclave was sparged with N_2 for two hours to remove oxygen, then heated to 50 °C before specimens were inserted in the autoclave, which was then closed and sealed by tightening bolts in a specific pattern. The autoclave was then pressurized with N_2 to check for leaks and the impeller was started (1000 rpm). After checking for leaks, the system was pressurized with a 13% H_2S in N_2 gas mixture to the calculated pressure to get the correct partial pressure of H_2S , and a gas sample taken. Another gas sample taken after 1 hour to check if the stabilized H_2S concentration in the gas phase matches the calculated value. After confirmation of the H_2S concentration, the test temperature was set and would increase to 120 °C or 160 °C within 2 hours. After the test temperature was achieved, electrochemical measurements were performed every 2 hours during the 4-day experiment. At the end of the test, the autoclave was cooled down to 50 °C, another H_2S gas sample was taken, and the final pH of the bulk solution was measured using a custom-made external probe holder; this allows fluid from the autoclave to flow past the probe into a controlled waste container with no loss of containment. The autoclave was then depressurized completely, purged with N_2 for one hour, and opened. Specimens were removed, rinsed with isopropanol, dried, kept in a vacuum, and a 10 mL liquid sample was taken to measure the Fe^{2+} concentration using FerroVer[‡] and UV-Vis. Based on the Fe^{2+} concentration and the assumption that any corrosion occurring during the temperature transition times had a negligible effect on the Fe^{2+} concentration, the expected pH values at test temperatures were calculated using a

[‡] Trade company

concentration-based water chemistry model, incorporating the CO₂ and H₂S species described in Appendix A.

RESULTS AND DISCUSSION

LPR Corrosion Rates

Figure 2 shows the change in LPR corrosion rate over time, with repeatability shown by the error bars in each curve for the two partial pressures of H₂S tested. Error bars represent the maximum and minimum of corrosion rates at each period. Each experiment was repeated twice. Note that the trend is similar for all cases, with LPR corrosion rate stabilizing after around 16 hours. The corrosion rates in both cases decrease with time due to the formation of a corrosion product layer. Corrosion rates were calculated using B values of 13 mV/decade at 120 °C and 17 mV/decade at 160 °C at 0.00385 M [H₂S]_{aq}, and 17 mV/decade at 120 °C and 19 mV/decade at 160 °C at 0.0385 M [H₂S]_{aq}. These B values were calculated using Equation (6):

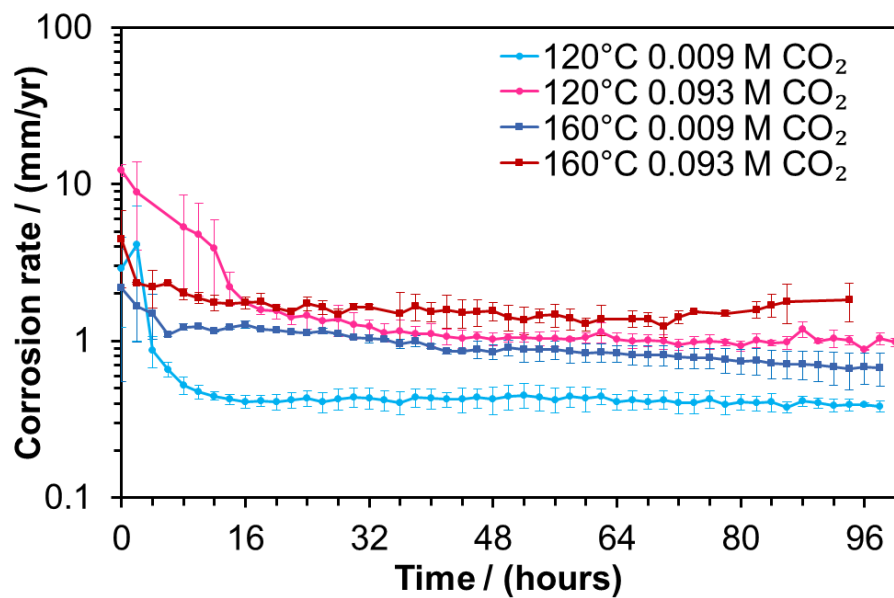
$$B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \quad (6)$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively. Their values can be found using Equations (7-8) described by Nesic, *et al.*, for Fe oxidative dissolution and H⁺ reduction reactions accordingly:

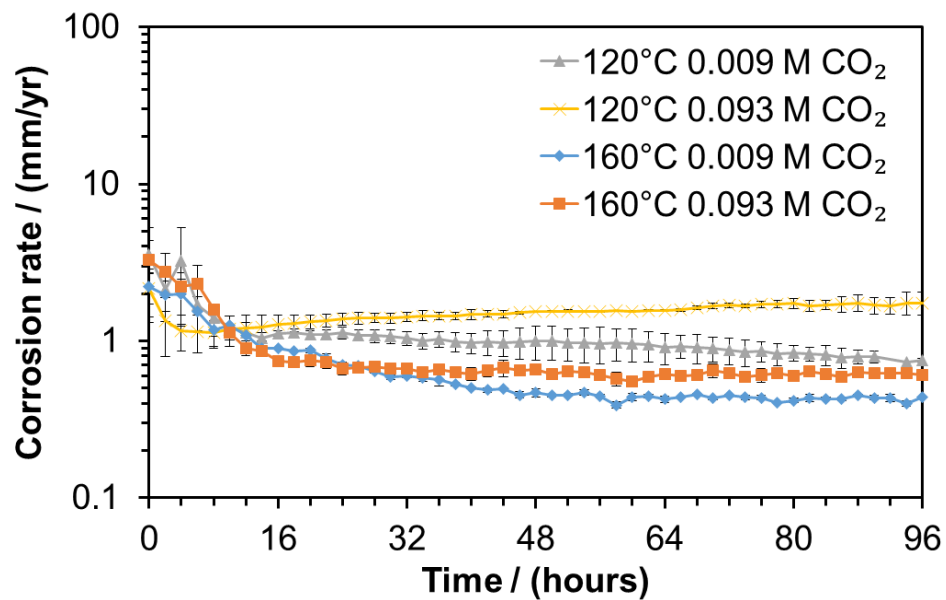
$$\beta_a = \frac{2.3RT}{1.5F} \quad (7)$$

$$\beta_c = \frac{2.3RT}{0.5F} \quad (8)$$

where R is gas constant in J/(mol-K), T is temperature in Kelvin, and F is the Faraday constant.¹⁵



(a)



(b)

Figure 2. LPR corrosion rate over time at (a) 0.00385 M and (b) 0.0385 M [H₂S]_{aq}

A summary of experimental conditions and results is shown in Table 3. The targeted initial and final conditions were calculated from the measured conditions at 50 °C for the beginning and the end of the experiments. Note the changes from targeted initial conditions to final calculated conditions show relatively small change from initial pH to final pH at target temperatures providing a good basis for comparison of results. Measured values of ferrous ions in solution also concur with the measured corrosion rate results.

Table 3
Summary of experimentally measured and calculated results

	Initial measured conditions at 50 °C		Targeted initial conditions, calculated at T (°C) and pH 5.0	Calculated conditions at the end of the test time at target temperature based on Fe ²⁺ measurements at 50 °C		Measured conditions at 50 °C, after cool-down procedures		
T (°C)	[CO ₂], M	pH ₂ S (bar)	pH ₂ S (bar)	pH ₂ S (bar)	pH	pH ₂ S (bar)	pH	Fe ²⁺ (ppm)
120	0.009	0.06±0.01	0.10±0.01	0.06±0.04	5.08±0.02	0.04	5.06±0.04	1.79±1.33
		0.88±0.08	1.70±0.11	0.86±0.13	5.11±0.06	0.47±0.06	5.24±0.28	2.64±1.89
	0.093	0.05±0.02	0.11±0.04	0.09±0.03	5.03±0.03	0.05±0.02	5.21±0.03	5.69±4.96
		0.66±0.08	1.05±0.04	1.25±0.55	5.07±0.06	0.68±0.30	5.19±0.07	0.30±0.09
160	0.009	0.05	0.13±0.02	0.14±0.08	5.02±0.06	0.08±0.05	5.10±0.10	0.43±0.02
		0.4	0.9	0.7	5.29±0.02	0.3	4.90±0.06	0.65±0.54
	0.093	0.07±0.01	0.18±0.01	0.13±0.02	5.03	0.07±0.01	5.18±0.07	3.32
		0.65	1.48	0.90±0.08	5.08±0.01	0.43±0.04	4.97±0.15	1.83±0.50

Surface and Cross-Section Analysis

SEM images of corrosion product layers formed at 120 and 160 °C after 4 days of exposure for different concentrations of H₂S and CO₂ in the aqueous phase are shown in Figure 3. At lower H₂S concentrations, morphologies look similar with two distinct compositions based on the contrast. However, the morphology in Figure 3c looks quite different, being more needle-like indicating possible troilite presence.³ Energy dispersive X-ray spectroscopy (EDS) analysis detects predominantly iron and sulfur, confirming the presence of iron sulfide.

At higher partial pressure of H₂S, SEM analysis shows different morphologies and crystal structures appearing on each surface indicating different types of iron sulfides that could be present. EDS analysis was conducted to determine the elements present on the surface of the steel. The main elements detected were again iron and sulfur, confirming that EDS can only indicate the presence of an iron sulfide; but not which polymorph(s). Consequently, specimens required further analysis by XRD to establish phase identity.

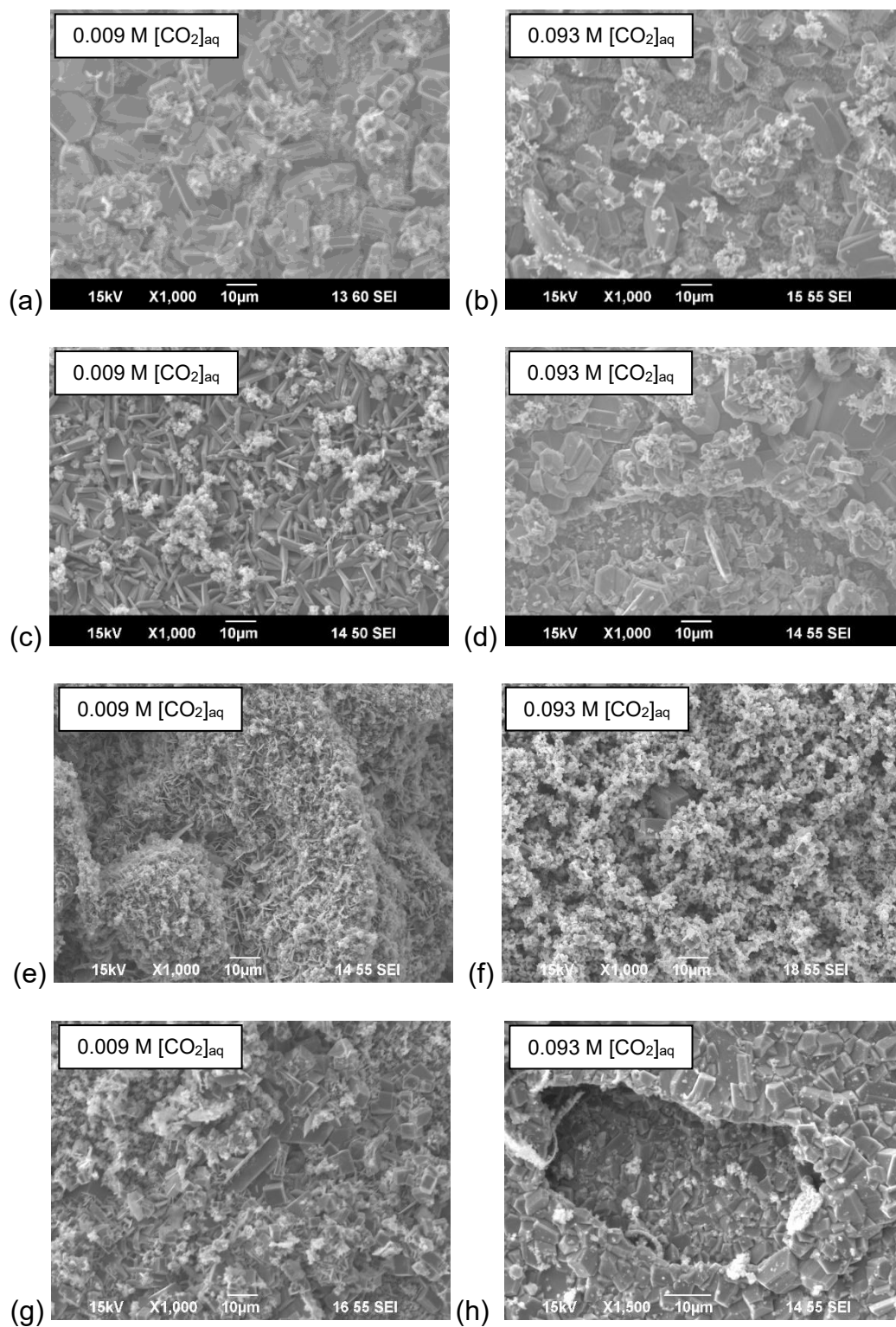


Figure 3. SEM pictures of specimen exposed to H₂S/CO₂ environment for 4 days at 0.00385 M [H₂S]_{aq}: (a-b) 120 °C, (c-d) 160 °C; 0.0385 M [H₂S]_{aq}: (e-f) 120 °C, (g-h) 160 °C and different [CO₂]_{aq}

XRD data for lower H_2S concentrations in Figure 4 shows that the most intense peaks are attributed to iron ($\alpha\text{-Fe}$), pyrrhotite, and siderite, indicating the presence of different iron sulfides together as well as iron carbonate. The iron peaks could appear due to having a thin iron sulfide layer on the surface that is easily penetrated by X-rays. Magnetite (Fe_3O_4) was not observed. (References for XRD peaks are listed in Appendix B)

Figure 5 combines XRD patterns for steel exposed to the same temperatures but at higher H_2S concentrations. The predominant corrosion product types are pyrrhotite, mackinawite, magnetite, and traces of pyrite. Magnetite (Fe_3O_4) was observed in previous research³ as an inner corrosion product layer between iron sulfides and the steel surface in an H_2S “only” environment. Magnetite could appear on XRD patterns due to the iron sulfide layer being thin enough that X-rays could achieve full penetration. The lowest intensity peaks were attributed to pyrite and troilite.

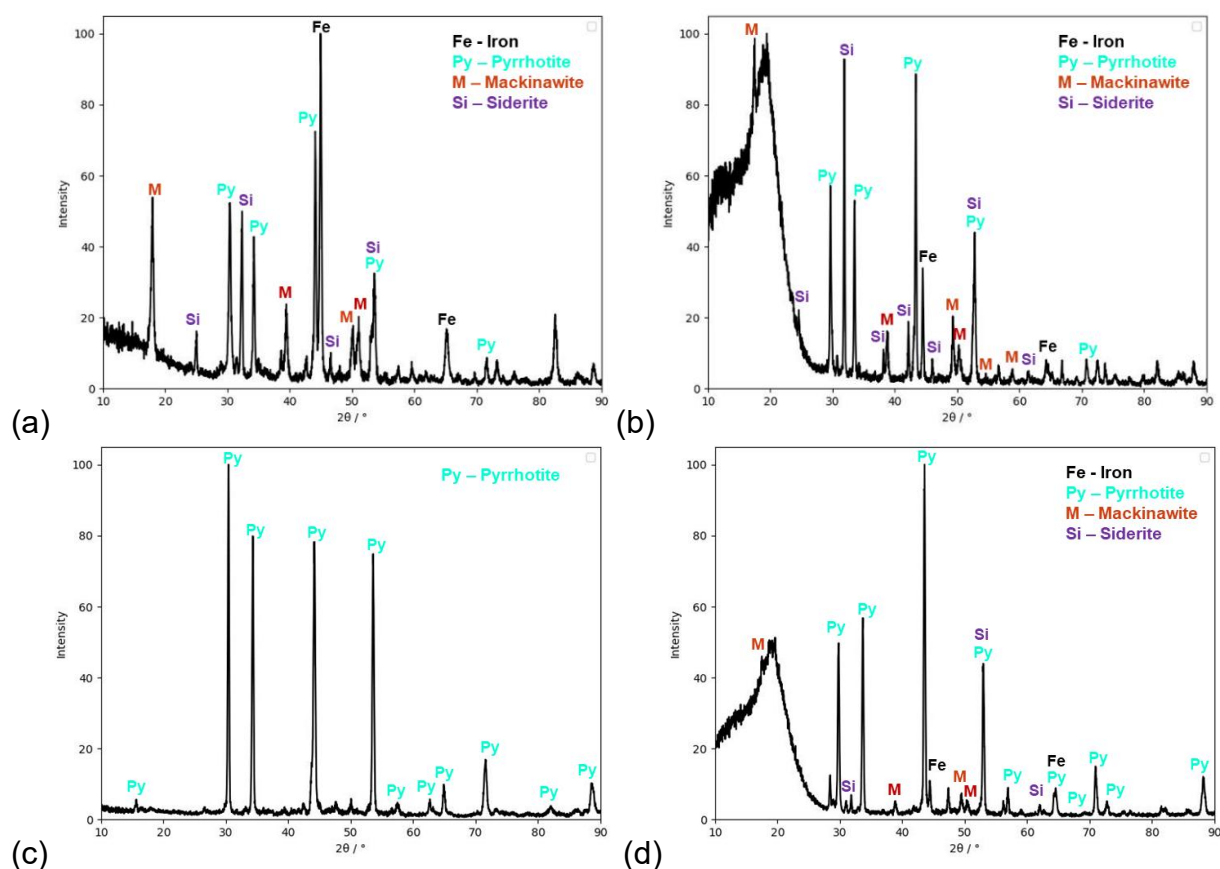


Figure 4. XRD analysis of the specimen exposed to H_2S environment for 4 days at 0.00385 M $[\text{H}_2\text{S}]_{\text{aq}}$ and 120 °C: (a) 0.009 M $[\text{CO}_2]_{\text{aq}}$, (b) 0.093 M $[\text{CO}_2]_{\text{aq}}$; 160 °C: (c) 0.009 M $[\text{CO}_2]_{\text{aq}}$, (d) 0.093 M $[\text{CO}_2]_{\text{aq}}$

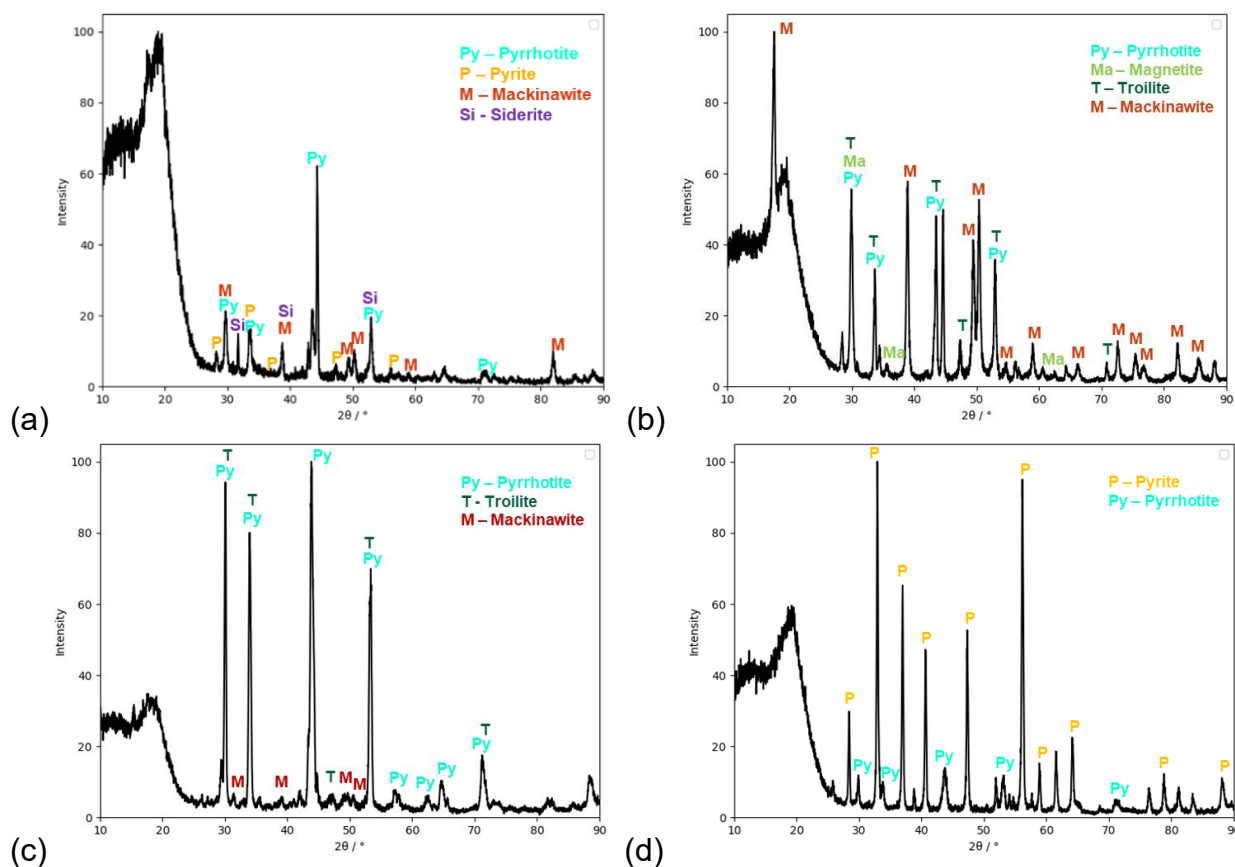


Figure 5. XRD analysis of the specimen exposed to H_2S environment for 4 days at $0.0385 \text{ M } [\text{H}_2\text{S}]_{\text{aq}}$ and 120°C : (a) $0.009 \text{ M } [\text{CO}_2]_{\text{aq}}$, (b) $0.093 \text{ M } [\text{CO}_2]_{\text{aq}}$; 160°C : (c) $0.009 \text{ M } [\text{CO}_2]_{\text{aq}}$, (d) $0.093 \text{ M } [\text{CO}_2]_{\text{aq}}$

Profilometry analysis was conducted on the surface of each WL specimen after removal of the corrosion product layer using a Clarke solution procedure¹⁶ (Figure 6). Pitting appeared in several cases, however, there was no clear trend between types of corrosion product layers and appearance of localized corrosion; this necessitates further investigation.

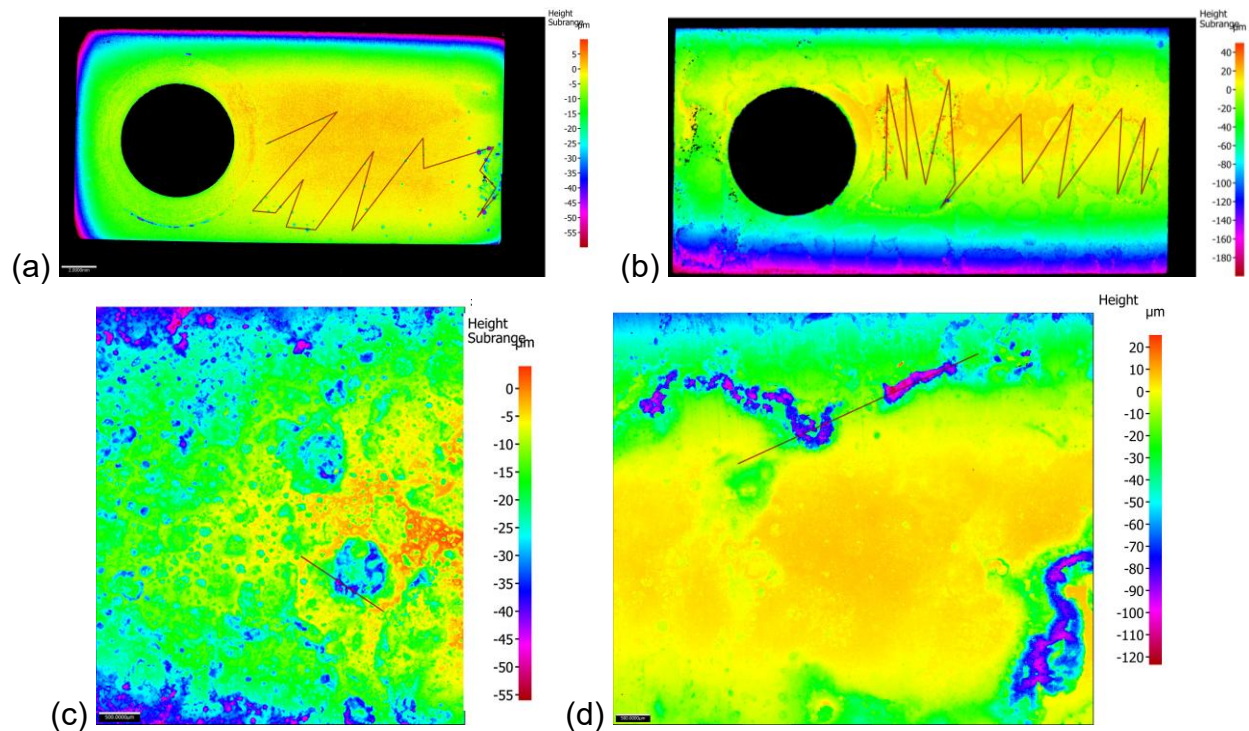


Figure 6. Profilometry analysis of the specimen exposed to H₂S environment for 4 days at (a) 0.00385 M [H₂S]_{aq}, 120 °C, 0.093 M [CO₂]_{aq}; (b) 0.0385 M [H₂S]_{aq}, 120 °C, 0.093 M [CO₂]_{aq}; (c) 0.0385 M [H₂S]_{aq}, 160 °C, 0.009 M [CO₂]_{aq}; (d) 0.0385 M [H₂S]_{aq}, 160 °C, 0.093 M [CO₂]_{aq}

Cross-sectional analysis of each specimen was done for each of the experiments (Figure 7-8). As can be seen from EDS mapping analysis, the corrosion product contained two separate layers: iron sulfide and iron oxide. The EDS line scans of each cross-section show distinct boundaries between these two layers based on sulfur and iron contents, consistent with the development of an iron sulfide layer and a magnetite layer, respectively. When the steel surface is reached via EDS line scan, there is no sulfur or oxygen present and iron content increases a maximum. The measured thicknesses of iron oxide layers are compared in Figure 10.

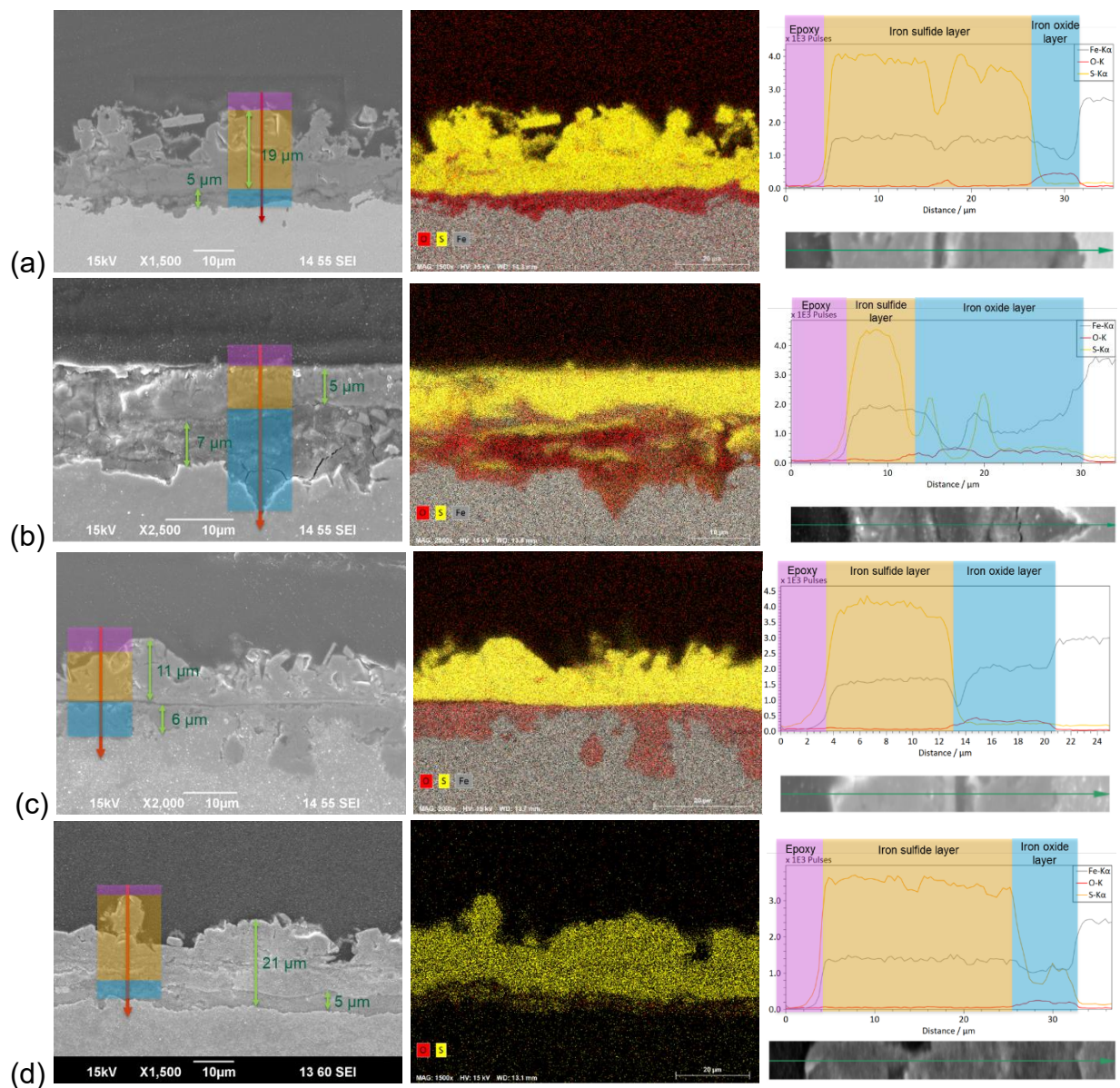


Figure 7. EDS mapping and line scan analysis of cross-section of the specimen exposed to H_2S environment for 4 days at $0.00385 \text{ M } [\text{H}_2\text{S}]_{\text{aq}}$ and 120°C : (a) $0.009 \text{ M } [\text{CO}_2]_{\text{aq}}$, (b) $0.093 \text{ M } [\text{CO}_2]_{\text{aq}}$; 160°C : (c) $0.009 \text{ M } [\text{CO}_2]_{\text{aq}}$, (d) $0.093 \text{ M } [\text{CO}_2]_{\text{aq}}$

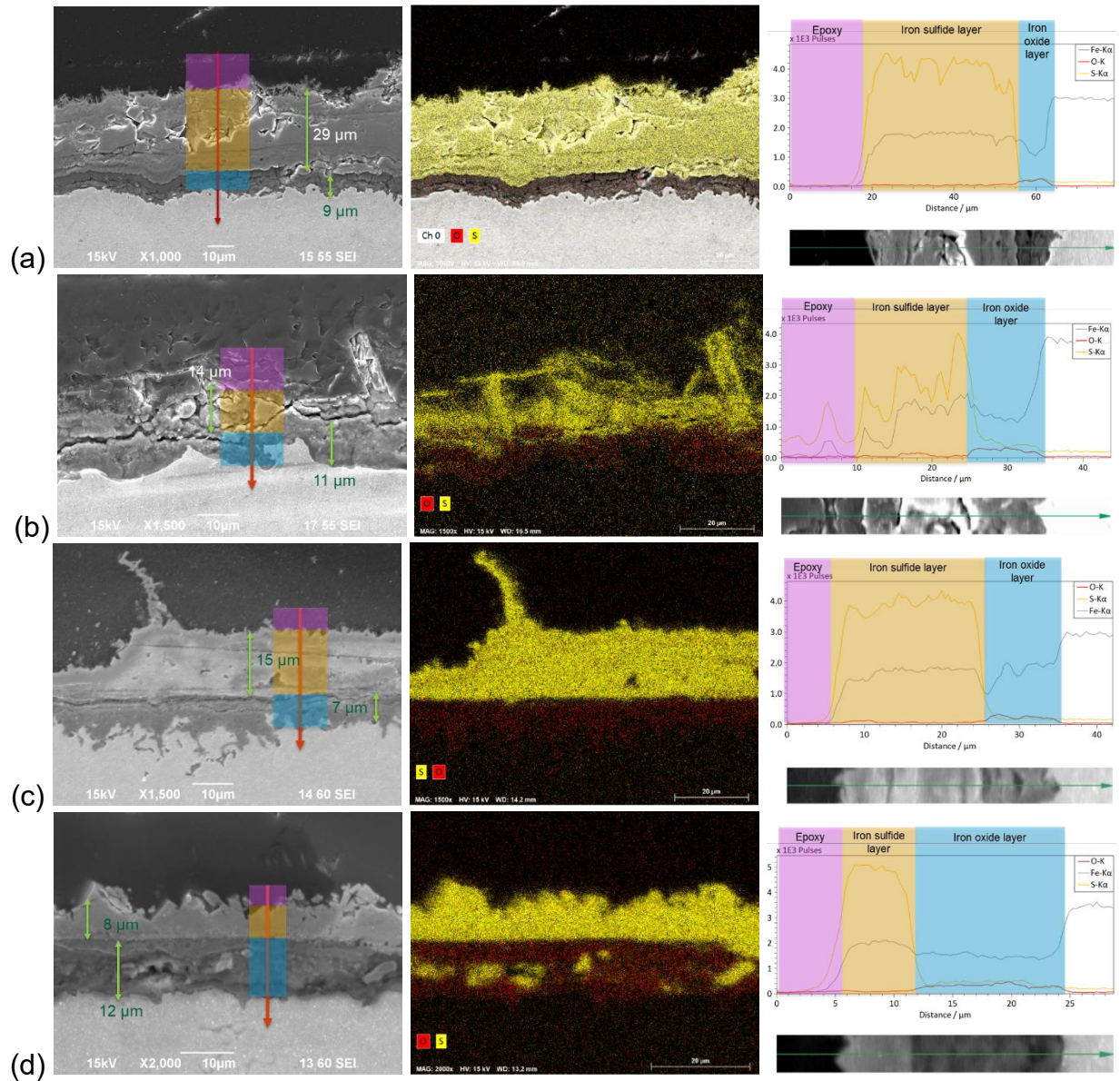


Figure 8. EDS mapping and line scan analysis of cross-section of the specimen exposed to H_2S environment for 4 days at $0.0385 \text{ M } [\text{H}_2\text{S}]_{\text{aq}}$ and 120°C : (a) $0.009 \text{ M } [\text{CO}_2]_{\text{aq}}$, (b) $0.093 \text{ M } [\text{CO}_2]_{\text{aq}}$; 160°C : (c) $0.009 \text{ M } [\text{CO}_2]_{\text{aq}}$, (d) $0.093 \text{ M } [\text{CO}_2]_{\text{aq}}$

Weight Loss and Cross-Section Measurements

Figure 9 shows the comparison between weight loss (WL) measurements over all sets of conditions. At 120°C , the corrosion rate in pure CO_2 environment is much higher than in other cases due to the formation of an iron carbonate layer and the absence of magnetite, whereas at 160°C a magnetite layer forms instead, and no iron carbonate is present. Since iron carbonate is less protective than magnetite, the corrosion rate is highest under these conditions. It is observed that the addition of H_2S to the system decreases the corrosion rates, and the corrosion rates in all tested conditions are relatively close, within the margin of error, due to the formation of an inner iron oxide layer in each case.

Nevertheless, there is a slight increase in corrosion rate as CO₂ concentration in the aqueous phase is increased at the lower H₂S content. At higher H₂S concentrations, the effect of CO₂ on corrosion rate is insignificant, possibly due to dominance of H₂S in the system.

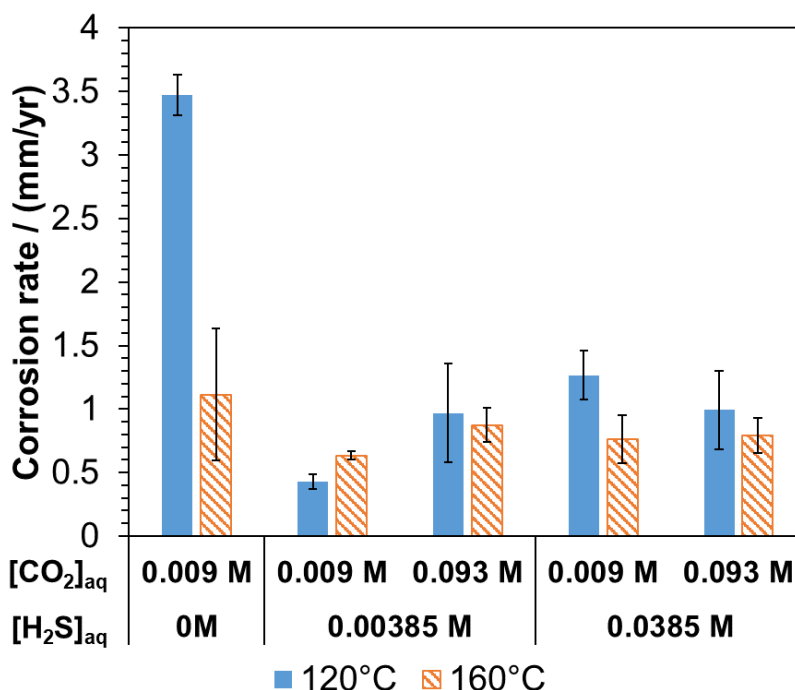


Figure 9. Comparison of WL corrosion rates over time at 120 °C and 160 °C over a range of [CO₂]_{aq} and [H₂S]_{aq} using WL measurements

The analysis of the cross-sections from Figure 8 enables the measurement of the thickness of the magnetite layers for each condition, as shown in Figure 10. The error bars represent the standard deviation of the measured thickness values. The measured magnetite layer thickness ranges from 2 to 20 µm across the different test conditions. However, the values are not statistically distinguishable due to overlapping error bars. Additional experimental conditions must be examined to determine whether a meaningful correlation exists between magnetite thickness and corrosion rate.

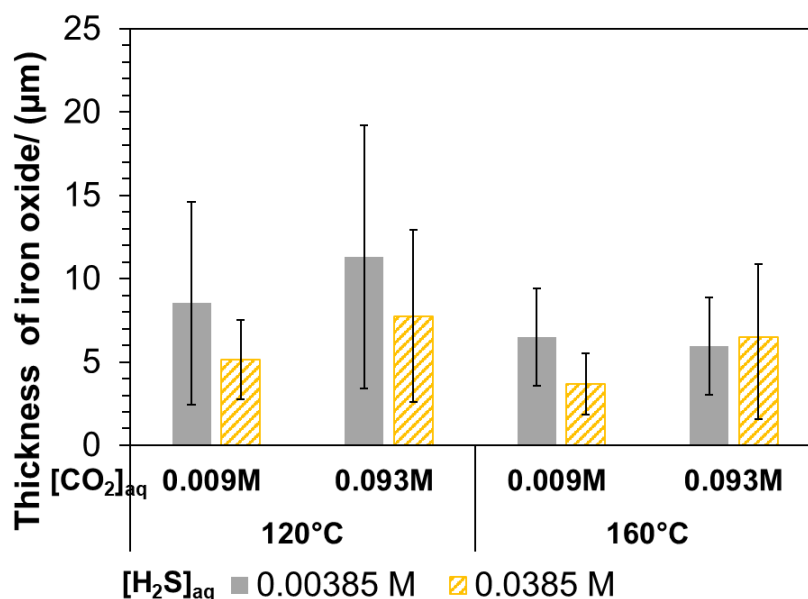


Figure 10. Comparison of iron oxide thickness at 120 °C and 160 °C over a range of CO₂ aqueous concentrations at 0.00385-0.0385 M [H₂S]_{aq} retrieved from SEM/EDS analysis

CONCLUSIONS

The effects of varying CO₂ and H₂S concentrations and the impact of high temperatures were examined. The corrosion rate decreased with time for both temperatures as expected but remained relatively high due to corrosion product layers being unprotective. The values of corrosion rates at 120 and 160 °C and at different concentrations of CO₂ and H₂S were essentially the same, within error, with surface analysis confirming a combination of various iron sulfides (pyrrhotite, mackinawite, pyrite, troilite) found in the outer corrosion product layer and magnetite as an inner corrosion product layer. Localized corrosion was observed on specimens from select cases which was not clearly related to specific iron sulfides but was due to heterogeneity of the layer, as stated in the literature. Further investigation is needed to determine whether a correlation exists between magnetite thickness and corrosion rate.

ACKNOWLEDGEMENTS

The author would like to thank the following companies for their financial support: Ansys, Baker Hughes, ChampionX LLC, Chevron Energy Technology, Coastal Chemical Co., ConocoPhillips, Equity Engineering Group, ExxonMobil, SLB, Occidental Oil Company, Pertamina, Saudi Aramco, Shell Global Solutions and TotalEnergies.

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APPENDIX A

When steel is exposed to an acidic aqueous environment containing H₂S, the corrosion process can be described by the following reactions. First, H₂S dissolves in water via reaction:



$$K_{sol,H_2S} = \frac{c_{H_2S}}{p_{H_2S}} \quad (10)$$

Then, aqueous H₂S dissociates in two steps. Dissociation of hydrogen sulfide:



$$K_{a,1} = \frac{c_{HS^-} \times c_{H^+}}{c_{H_2S}} \quad (12)$$

Dissociation of hydrogen sulfide ion:



$$K_{a,2} = \frac{c_{S^{2-}} \times c_{H^+}}{c_{HS^-}} \quad (14)$$

Solubility constant for H₂S dissolution in reaction (9) was proposed by Suleimenov and Krupp ¹⁷ demonstrated in Equation (15). This equation doesn't account for non-ideality of solution as was mentioned by Ma ¹⁴, however, the solution in these experiments being 1 wt.% NaCl is close to the ideal conditions such that the following equation can be used for calculating dissolved H₂S concentrations:

$$K_{sol,H_2S} = 10^{-\left(634.27 + 0.2709 T_k - 0.0001132 T_k^2 - \frac{16719}{T_k} - 261.9 \log T_k\right)} \quad (15)$$

Dissociation constant of H₂S proposed by Suleimenov and Seward ¹⁸:

$$K_{a,1} = 10^{782.43945 + 0.36126 T_k - 0.00016722 T_k^2 - \frac{20565.7315}{T_k} - 142.7417222 \ln T_k} \quad (16)$$

Dissociation constant of HS⁻ proposed by Kharaka et al. ¹⁹:

$$K_{a,2} = 10^{-(23.93 + 0.030446 T_k - 2.4831 \times 10^{-5} T_k^2)} \quad (17)$$

The corrosion mechanism in the presence of CO₂ undergoes similar paths. First, CO₂ in gaseous state dissolves in water:



$$K_{sol,CO_2} = \frac{c_{CO_2}}{p_{CO_2}} \quad (19)$$

Once carbon dioxide dissolves in water via reaction (18), a hydration reaction and two dissociation reactions occur:



$$K_{hyd} = \frac{c_{H_2CO_3}}{c_{CO_2}} \quad (21)$$



$$K_{ca} = \frac{c_{HCO_3^-} \times c_{H^+}}{c_{H_2CO_3}} \quad (23)$$



$$K_{bi} = \frac{c_{CO_3^{2-}} \times c_{H^+}}{c_{HCO_3^-}} \quad (25)$$

Oddo and Tomson ²⁰ provided the following equilibrium constants for the reactions (18) and (24):

$$K_{sol,CO_2} = \frac{14.5}{1.00258} \times 10^{-(2.27 + 5.65 \times 10^{-3} T_f - 8.06 \times 10^{-6} T_f^2 + 0.075 I)} \quad (26)$$

$$K_{bi} = 10^{-(10.61 - 4.97 \times 10^{-3} T_f + 1.331 \times 10^{-5} T_f^2 - 2.624 \times 10^{-5} p_{CO_2} - 1.166 I^{1/2} + 0.3466 I)} \quad (27)$$

Ma ¹⁴ adapted equation for K_{ca} originally proposed by Oddo and Tomson ²⁰ for a wider range of salt concentrations and developed following equation:

$$K_{ca} = 387.6 \times 10^{-(6.41 - 1.594 \times 10^{-3} T_f + 8.52 \times 10^{-6} T_f^2 - 3.07 \times 10^{-5} p_{CO_2} - 0.4772 I^{1/2} + 0.11807 I)} \quad (28)$$

Water dissociation constant is proposed by Kharaka et al. ¹⁹:

$$K_{wa} = 10^{-(29.3868 - 0.0737549 T_k + 7.47881 \times 10^{-5} T_k^2)} \quad (29)$$

Palmer and van Eldik ²¹ developed expression for K_{hyd} :

$$K_{hyd} = 2.58 \times 10^{-3} \text{ at } 25^\circ \text{C} \quad (30)$$

APPENDIX B

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