Kinetics of Corrosion Layer Formation. Part 2—Iron Sulfide and Mixed Iron Sulfide/Carbonate Layers in Carbon Dioxide/Hydrogen Sulfide Corrosion

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ABSTRACT

Glass cell experiments were conducted to investigate kinetics of iron sulfide and mixed iron sulfide/carbonate layer formation in carbon dioxide/hydrogen sulfide (CO$_2$/H$_2$S) corrosion of mild steel using the weight change method. Scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS), x-ray diffraction methodology (XRD), and x-ray photoelectron spectroscopy (XPS) were used to analyze the layer. The experimental results show that mackinawite is the predominant type of iron sulfide layer formed in short exposures in pure H$_2$S solutions. The type of layer formed in a CO$_2$/H$_2$S solution depends on the competitive mechanism of iron carbonate and mackinawite formation. At high H$_2$S concentration and low dissolved iron carbonate supersaturations, mackinawite was the predominant component in the layer; at low H$_2$S concentration and iron carbonate supersaturations, both iron carbonate and mackinawite may form on the steel surface. It was also found that the corrosion rate of mild steel in H$_2$S corrosion is affected by H$_2$S concentration, temperature, velocity, and the protectiveness of the layer.

KEY WORDS: hydrogen sulfide, iron carbonate, iron sulfide, kinetics, layer, mackinawite, solid state

INTRODUCTION

The internal carbon dioxide corrosion of mild steel in the presence of hydrogen sulfide (CO$_2$/H$_2$S corrosion) represents a significant problem for the oil and gas industry.[1-5] Although much higher cost corrosion-resistant alloys (CRA) were developed to resist the CO$_2$/H$_2$S corrosion, mild steel is still the most cost-effective material used in CO$_2$/H$_2$S corrosion.[4] The problems of CO$_2$/H$_2$S corrosion of mild steel were first recognized in the 1940s and have been investigated for more than 60 years.[5] However, until now, many of the key points discussed in the literature are still unclear and sometime contradictory.[5] On the other hand, it is very important to improve the prediction and control capability for CO$_2$/H$_2$S corrosion of mild steel.

In CO$_2$/H$_2$S corrosion of mild steel, both iron carbonate (FeCO$_3$) and iron sulfide layers can form on the steel surface. Studies have demonstrated that surface layer formation is one of the important factors governing the corrosion rate.[6-12] The surface layer can slow down the corrosion process by presenting a diffusion barrier for the species involved in the corrosion process and by covering up a part of the steel surface and impeding the underlying steel from further dissolution, especially as the layer grows in density and thickness. The growth of the layer is defined by the kinetics of layer formation. To better predict and control the CO$_2$/H$_2$S corrosion of mild steel, it is important to understand the kinetics of both iron carbonate and iron sulfide layer formation. It is noted that, compared to iron carbonate formation in pure CO$_2$ corrosion,

many types of iron sulfide may form in a H_2S environment. The complicated mechanisms of iron sulfide formation make it difficult to quantify the kinetics.

Smith and Joosten,[5] in their review paper, systematically describe most of the research work done in the area of CO_2/H_2S corrosion in the oilfield environments. It is mentioned there that most of the literature is still confusing and somewhat contradictory and the mechanism of CO_2/H_2S corrosion is still unclear. The mechanism of iron sulfide layer formation in H_2S corrosion was also reviewed by Lee in his recent Ph.D. dissertation.[13] Some of the key studies that address the mechanism of iron sulfide formation are Meyer, et al.,[2] and Shoesmith, et al.,[14-15] where it was suggested that a mackinawite layer formed on the steel surface by a solid-state reaction. Benning, et al.,[16] Anderko, et al.,[8-10] and Smith and coworkers[6-7,12,17-18] looked at thermodynamic arguments related to formation of various types of sulfides.

Clearly, many types of iron sulfides may form in H_2S environments, such as amorphous ferrous sulfide, mackinawite, cubic ferrous sulfide, smythite, greigite, pyrrhotite, troilite, and pyrite. However, there is no clear relationship established between the nature of the sulfide film and the underlying corrosion process. Among those iron sulfides, mackinawite is the prevalent iron sulfide that forms on the steel surface usually as a precursor to other types of sulfides and therefore needs to be quantified first.

Rickard[19] investigated the kinetics of iron(II) sulfide precipitation and described FeS precipitation rate as a function of Fe^{2+} concentration and H_2S concentration.

$$\frac{d[FeS]}{dt} = kc_{Fe^{2+}}c_{H_2S} \tag{1}$$

where k is the rate constant, $c_{Fe^{2+}}$ is the concentration of Fe^{2+} in the bulk of the solution, and c_{H_2S} is the concentration of H_2S in the bulk of the solution. In his paper, Rickard[19] did not mention whether FeS is the amorphous iron sulfide or mackinawite. However, it has been mentioned in his previously published related paper[20] that the precipitated iron sulfide was amorphous iron sulfide.

Harmandas and Koutsoukos[21] investigated the formation of iron sulfides in aqueous solutions and proposed Expression (2) to describe the kinetics of both amorphous iron sulfide and mackinawite formation.

$$R_P = k\sigma_S^m \tag{2}$$

where k is the rate constant, σ_S is the relative solution supersaturation with respect to the solid phase forming, and m is the apparent order of the reaction.

It should be noted that both expressions provided by Rickard[19] and Harmandas and Koutsoukos[21]

were obtained by using the ferrous ion concentration change measurements, a methodology that already has been addressed in a previous study[22] and found to be unreliable for quantifying the corrosion layer formation rate on the steel surface. Very few kinetics experiments have been conducted in a H_2S-purged corrosion system, which is more stable than the sulfide salt systems often used (without purging H_2S gas).

From the discussion above, it is clear that an improved understanding of the nature of surface layers formed in CO_2/H_2S corrosion of mild steel as well as their protective properties, and a better understanding of the mechanism and kinetics of mackinawite layer formation in the H_2S environments is needed as well.

OBJECTIVES

Based on the discussion above, the following objectives were set for the present research on kinetics of iron sulfide and mixed iron sulfide/carbonate layer formation in CO_2/H_2S corrosion:

—Quantify the kinetics of iron sulfide formation and the related corrosion rate of mild steel in a pure H_2S environment.

—Quantify the kinetics of mixed iron sulfide/carbonate formation and the related corrosion rate of mild steel in a CO_2/H_2S environment.

—Analyze the properties of the layer formed in pure H_2S and mixed CO_2/H_2S environments.

—Investigate the mechanism of the layer formation in the H_2S environment.

EXPERIMENTAL PROCEDURES

The present measurements were conducted in glass cells, as shown in Figure 1. The detailed view of the glass cell and the components within is given in the previous paper.[22] The concentration of H_2S was controlled by using gas mass flow rate controllers and a gas mixer. Each glass cell was filled with 2 L of distilled water with 1 wt% sodium chloride (NaCl). The solution was heated to a desired temperature and purged with N_2 or CO_2. After the solution was deoxygenated, the pH was adjusted to the desired value by adding a deoxygenated hydrogen chloride (HCl) or sodium hydroxide (NaOH) solution. Prior to immersion, the specimen surfaces were polished successively with 320-, 400-, and 600-grit silicon carbide (SiC) paper, rinsed with alcohol (C_2H_5OH), and degreased using acetone (CH_3COCH_3). Subsequently, the H_2S flow was turned on and the required amounts of Fe^{2+} were added in the form of a deoxygenated ferrous chloride salt ($FeCl_2 \cdot 4H_2O$) solution. Some of the experiments were repeated to test reproducibility. In one series of experiments, the effect of velocity was investigated by using a rotating cylinder electrode. X65 mild steel and
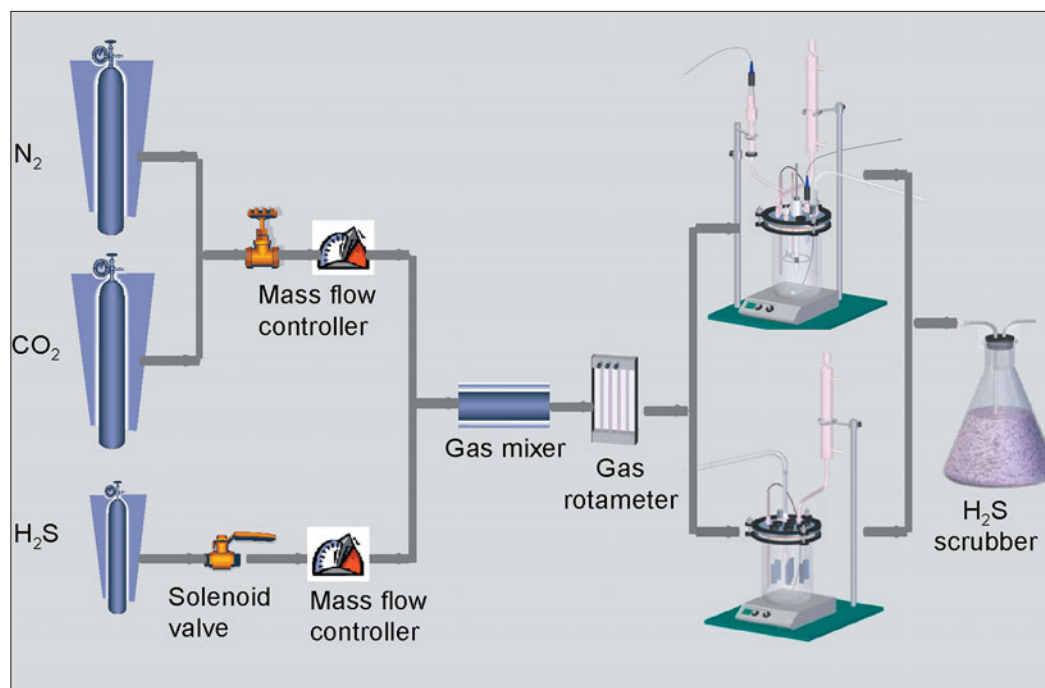
FIGURE 1. *Schematic of the test apparatus.*

TABLE 1
Chemical Composition of X65 (wt%)

C	Mn	Si	P	S	Cr	Cu	Ni	Mo	Al	Fe
0.050	1.32	0.31	0.013	0.002	0.042	0.019	0.039	0.031	0.0032	Bal.

TABLE 2
Test Matrix of Experiments

Parameter	Description
Material	X65 mild steel and Type 316 SS
Solution	Deionized water with 1 wt% of NaCl, purged with N_2 or CO_2
Temperature (°C)	25, 60, 80
Total pressure (bar)	1
H_2S in the gas inlet (vol%)	0.0075, 0.015, 0.024, 0.04, 0.1, 1, and 10
pH	5 to 6.6

Type 316 (UNS S31600)[1] stainless steel were used as substrates to study the layer formation in H_2S environments. The chemical composition of X65 mild steel is shown in Table 1. The test matrix of the experiments is shown in Table 2.

Both the accumulation rate of the corrosion layer and the corrosion rate of the steel were measured by the weight change method using several identical rectangular samples with a surface area of 21 cm². Time-averaged (integral) corrosion layer accumulation rate (CLAR) was obtained by subtracting the weight of the coupon, which had the layer, and that after the layer was removed. Time-averaged (integral) corrosion rate (CR) was calculated by subtracting the weight of the coupon prior to running the experiments and that after removing the corrosion layer. In some experiments, linear polarization resistance (LPR) was also used to measure the corrosion rate using the cylindrical specimens with a surface area of 5.4 cm². A spectrophotometer was used to measure ferrous ion concentration in the solution. The specimens with the intact iron sulfide layer were analyzed using several surface analysis techniques, such as scanning electron microscopy/energy-dispersive microscopy (SEM/ EDS), x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS).

RESULTS AND DISCUSSION

The results obtained are presented below in the following manner:
- —baseline kinetics experiments in a pure H_2S solution at T = 80°C
- —baseline kinetics experiments in a CO_2/H_2S solution at T = 80°C
- —summary of all the baseline experiments

—summary of kinetics experiments considering the effects of H_2S concentration, temperature, flow rate, and the nature of substrate.

Baseline Kinetics Experiments in a Pure H_2S Solution at T = 80°C

To understand the kinetics of iron sulfide layer formation in a pure H_2S environment, experiments were conducted using X65 mild steel as the substrate in a stagnant solution through which a mixture of H_2S/N_2 gases was purged at a temperature of 80°C, initial Fe^{2+} concentration varied from 0 to 50 ppm, H_2S gas concentration varied from 0.1 vol% to 10 vol%, and the reaction time varied from 1 h to 1 day.

Figure 2 shows the retention rate of iron sulfide and the corrosion rate of X65 in the first hour expressed in molar units. The equivalent corrosion rate is about 1.5 mm/y to 3 mm/y. Both the retention rate of the iron sulfide layer and the corrosion rate of X65 increased with the increase of H_2S concentration; however, they did not change much with the change of initial Fe^{2+} concentration. This can be explained partly by the fact that the solubility of iron sulfide under these conditions is rather low, which led to rapid precipitation out of the solution.

With the total reaction time increasing to 24 h, similar trends were obtained as shown in Figure 3; however; the magnitude of both the CLAR and CR decreased when compared to a 1-h exposure. The average corrosion rate was less than 0.6 mm/y. The error bars in the figures represent the maximum and minimum measured values.

Figures 4 through 7 show the resulting morphology of the iron sulfide layer formed on the X65 mild steel surface. It is found that there is little iron sulfide layer formed on the steel surface at H_2S concentration of 0.1 vol% in the first hour, as illustrated in Figure 4. With the increase of the reaction time to 24 h, the steel surface is more evenly covered by the iron sulfide layer. Comparing the morphology of the iron sulfide layer shown in Figures 4 and 5, it is confirmed that dissolved Fe^{2+} concentration does not affect the iron sulfide formation. When H_2S concentration is increased from 0.1 vol% to 10 vol%, much more layer is formed in the first hour, and after 24 h the layer becomes more protective, as shown in Figures 6 and 7. No effect of Fe^{2+} concentration is identified at this H_2S concentration either. The cross sections of the layer formed under different test conditions are shown in Figure 8 for a 1-h exposure and Figure 9 for a 24-h exposure. In all cases the thickness of the layer is approximately 10 μm to 15 μm and the layer is delaminated.

An example of the XRD results of the iron sulfide layer is shown in Figure 10. It is found that mackinawite is the only product formed on the X65 steel surface under the test conditions. The XPS results (Figure 11) of the iron sulfide layer formed on the steel
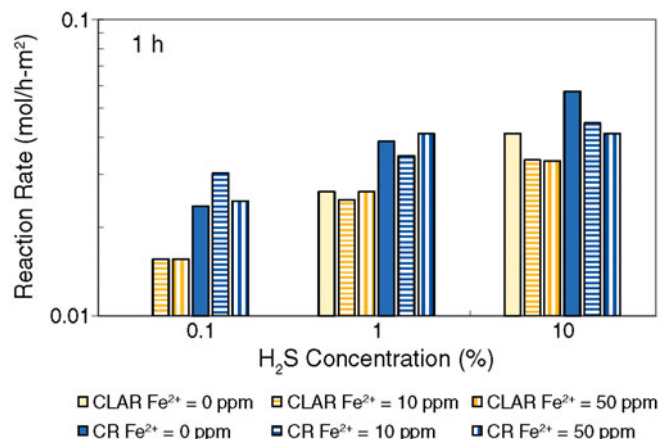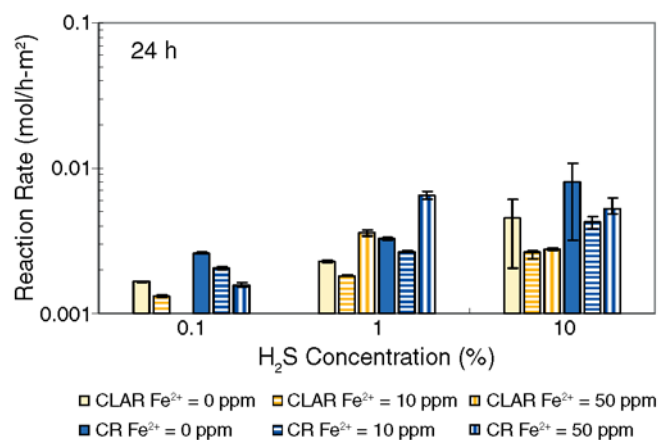

FIGURE 2. *The CLAR of iron sulfide formed on X65 steel surface and the CR of X65 steel in the same molar unit at different H_2S concentrations and initial Fe^{2+} concentrations in the solution with H_2S/N_2 at T = 80°C. The total reaction time was 1 h.*

FIGURE 3. *The CLAR of iron sulfide formed on X65 steel surface and the CR of X65 steel in the same molar unit at different H_2S concentrations and initial Fe^{2+} concentrations in the solution with H_2S/N_2 at T = 80°C. The total reaction time was 24 h.*

surface under these conditions show that FeS is the predominant product formed on the steel surface, which are in good agreement with the XRD results. A small amount of elemental sulfur is detected by XPS possibly because the iron sulfide layer might oxidize when exposed to air.

Baseline Kinetics Experiments in a CO_2/H_2S Solution at T = 80°C

To investigate the kinetics of mixed iron sulfide/carbonate formation, kinetics experiments were performed in a stagnant solution by purging with a mixture of CO_2/H_2S gas. Figure 12 shows the CLAR and the CR of X65 steel after a 1-h exposure. Both the CLAR and CR increase with the increased H_2S concentration and do not change much with dissolved Fe^{2+} concentration. The recalculated corrosion rates vary from 1.5 mm/y to 3 mm/y with the increase of
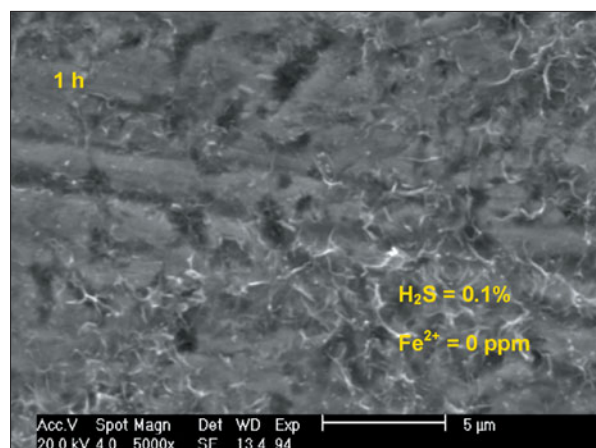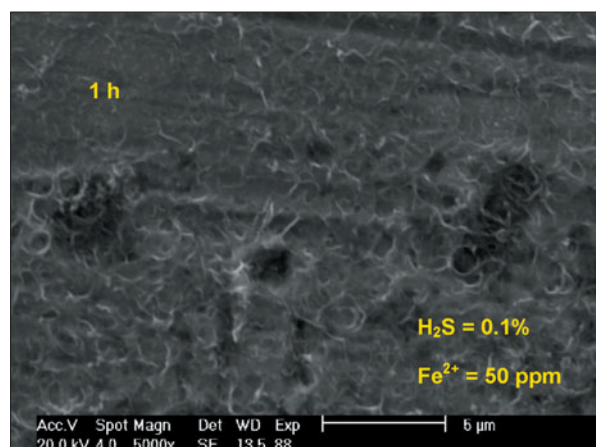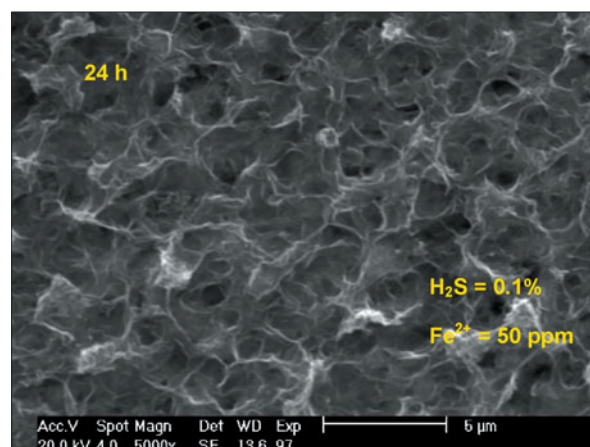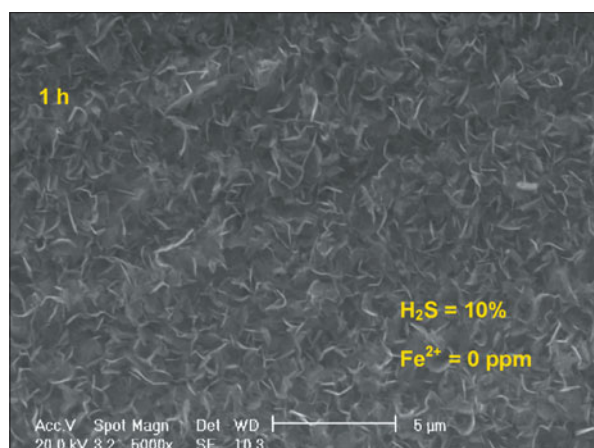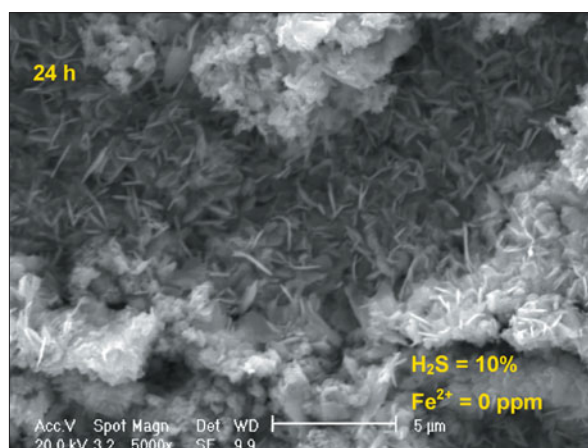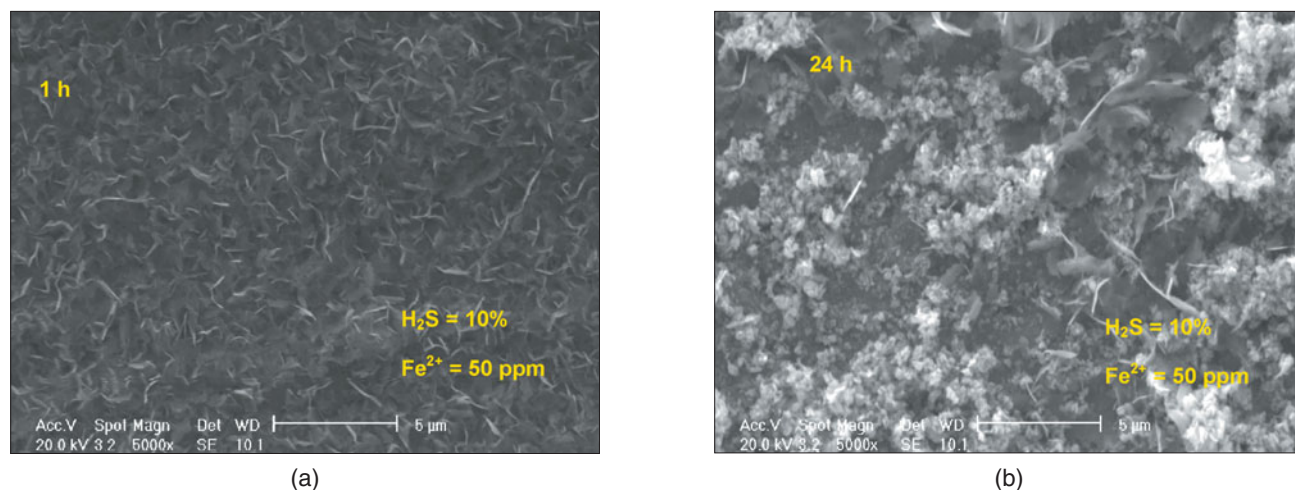
(a)
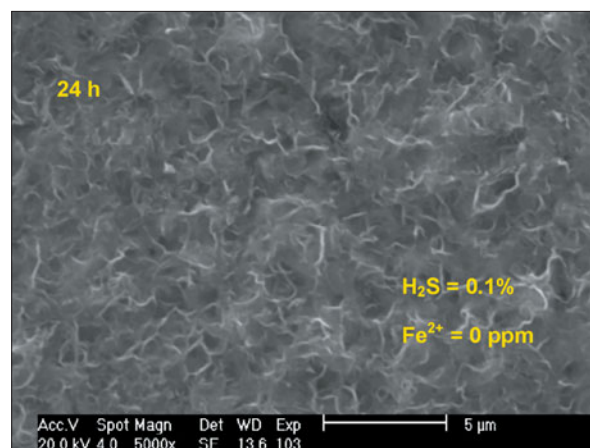
(b)

FIGURE 4. *The morphology (5,000X) of the iron sulfide layer formed on the X65 steel surface under the conditions of 0.1 vol% H₂S (H₂S/N₂ gas), T = 80°C, pH 5.5, and Fe²⁺ = 0 ppm. The total reaction time was: (a) 1 h and (b) 24 h.*

(a)

(b)

FIGURE 5. *The morphology (5,000X) of the iron sulfide layer formed on the X65 steel surface under the conditions of 0.1 vol% H₂S (H₂S/N₂ gas), T = 80°C, pH 5.5, and Fe²⁺ = 50 ppm. The total reaction time was (a) 1 h and (b) 24 h.*

(a)

(b)

FIGURE 6. *The morphology (5,000X) of the iron sulfide layer formed on the X65 steel surface under the conditions of 10 vol% H₂S (H₂S/N₂ gas), T = 80°C, pH 5.2, and Fe²⁺ = 0 ppm. The total reaction time was (a) 1 h and (b) 24 h.*

FIGURE 7. *The morphology (5,000X) of the iron sulfide layer formed on the X65 steel surface under the conditions of 10 vol% H_2S (H_2S/N_2 gas), T = 80°C, pH 5.2, and Fe^{2+} = 50 ppm. The total reaction time was: (a) 1 h and (b) 24 h.*
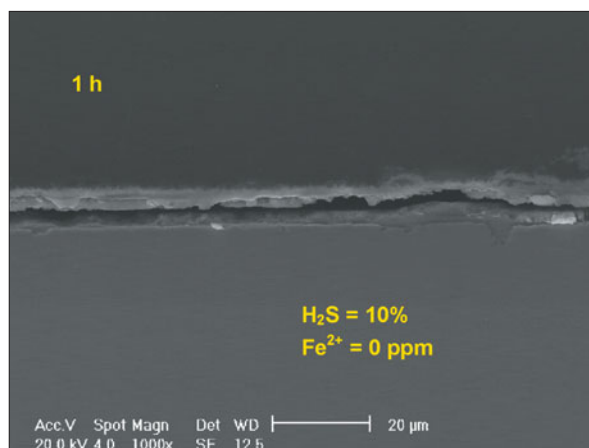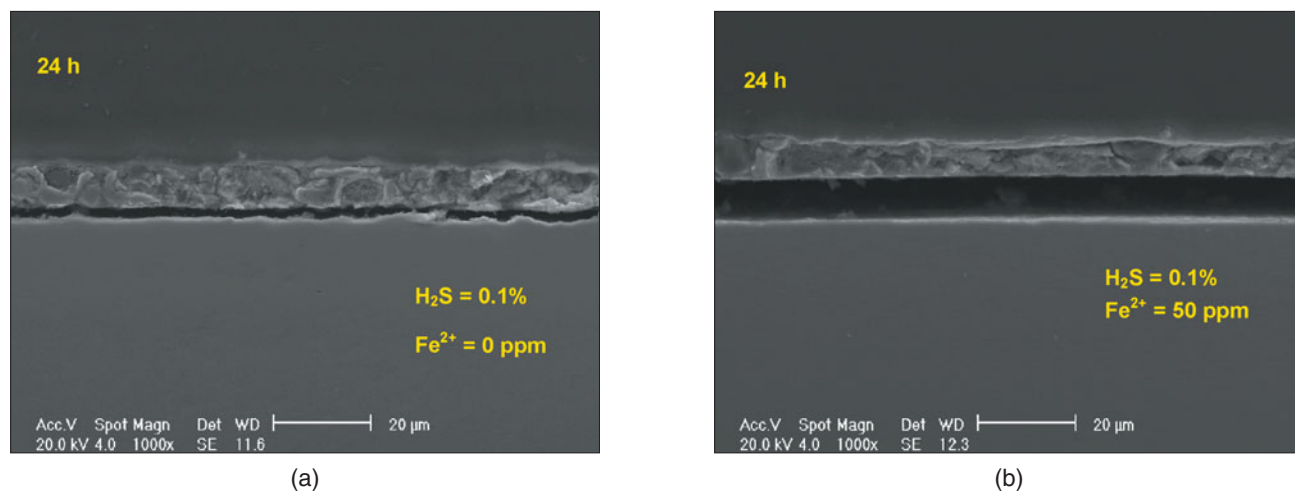

FIGURE 8. *Cross section of the layer formed on the X65 steel surface (at 1,000X) under the conditions of 10 vol% H_2S (H_2S/CO_2 gas), T = 80°C, pH 5, and Fe^{2+} = 0 ppm. The total reaction time was 1 h.*

FIGURE 9. *Cross section of the layer formed on the X65 steel surface (at 1,000X) under the conditions of 0.1 vol% H_2S (H_2S/N_2 gas), T = 80°C, pH 5, (a) Fe^{2+} = 0 ppm, and (b) Fe^{2+} = 50 ppm. The total reaction time was 24 h.*
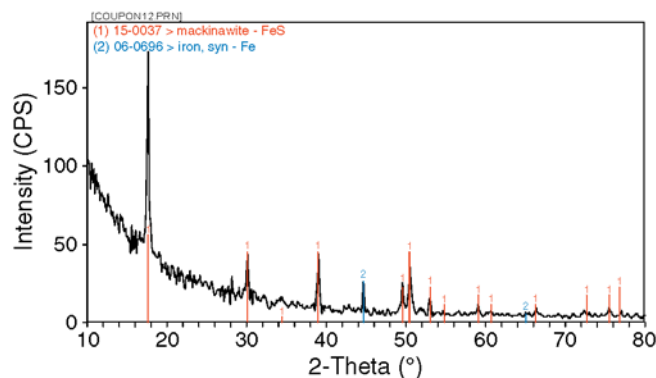
FIGURE 10. *XRD results of the iron sulfide layer formed on the X65 steel surface under the conditions of 10 vol% H_2S (H_2S/N_2 gas), T = 80°C, pH 5.2, and Fe^{2+} = 10 ppm. The total reaction time was 24 h.*
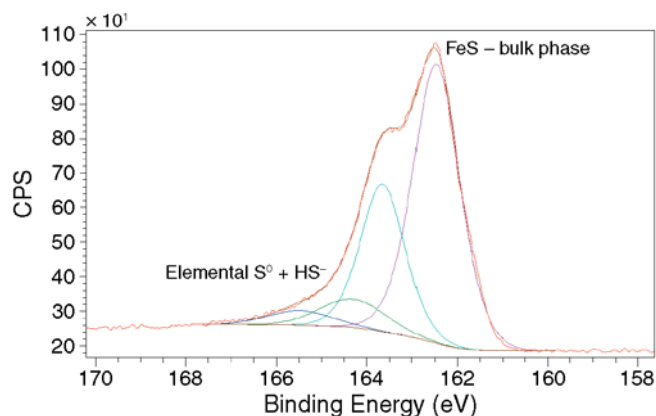

FIGURE 11. *XPS multiplex S2p spectrum recorded following a 100-Å ion etch for the specimen under the conditions of T = 80°C, pH 5, 0 ppm Fe^{2+}, and 10 vol% H_2S. The reaction time was 24 h.*
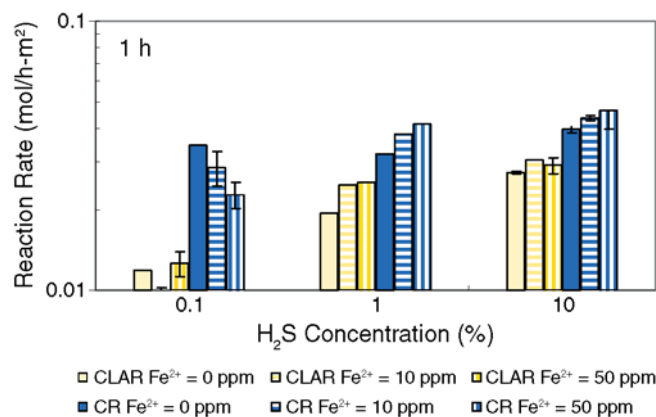

FIGURE 12. *The CLAR of iron sulfide formed on the X65 steel surface and the CR of X65 steel in the same molar unit at different H_2S concentrations and initial Fe^{2+} concentrations in the solution with CO_2/H_2S under the conditions of T = 80°C. The total reaction time was 1 h.*
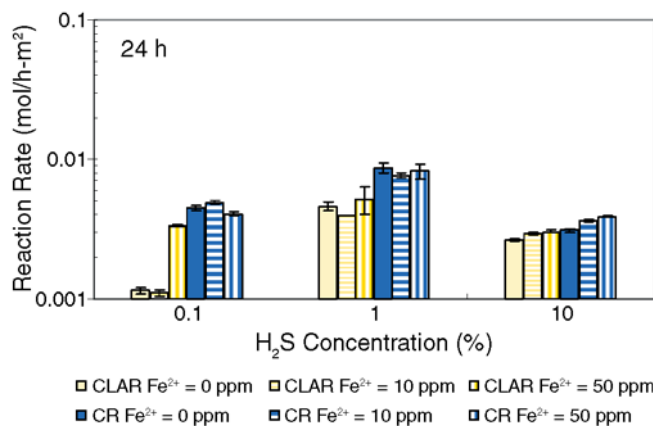

FIGURE 13. *The CLAR of iron sulfide formed on X65 steel surface and the CR of X65 steel in the same molar unit at different H_2S concentrations and initial Fe^{2+} concentrations in the solution with CO_2/H_2S under the conditions of T = 80°C. The total reaction time was 24 h.*

H_2S concentration from 0.1 vol% to 10 vol%. Figure 13 illustrates the same information collected after a 24-h exposure. The CLAR and CR increase with H_2S concentration changing from 0.1 vol% to 1 vol% and then decrease as the H_2S concentration changes from 1 vol% to 10 vol%. Compared to the values obtained in a 1-h exposure, it is found that both CLAR and CR are significantly lower after a 24-h exposure. For example, the CR after a 24-h exposure is in the range from 0.2 mm/y to 0.5 mm/y. The reduction in the corrosion rate over time illustrates that the corrosion layer formed on the steel surface becomes gradually more protective. Overall, similar trends in the CLAR and CR in a CO_2/H_2S system were obtained as in a pure H_2S system.

The morphology of the layer formed under the conditions discussed above was studied using SEM. At a H_2S concentration of 0.1 vol%, it is found that when Fe^{2+} concentrations were 0 ppm and 10 ppm,

only an iron sulfide layer formed on the X65 steel surface. Increasing Fe^{2+} concentration to 50 ppm (Figure 14) resulted in a iron sulfide layer with dispersed iron carbonate crystals. With the increase of H_2S concentration to 1 vol%, there was no iron carbonate on the steel surface at Fe^{2+} concentrations of 0 ppm and 10 ppm. Increasing Fe^{2+} concentration to 50 ppm resulted in iron carbonate appearing on the steel surface in the first hour; however, no iron carbonate could be found after a 24-h exposure (Figure 15). When H_2S concentration was increased further to 10 vol%, no iron carbonate formed on the steel surface, even at high initial Fe^{2+} concentrations (50 ppm), as shown in Figure 16.

The cross sections of the layer under the different test conditions are shown in Figures 17 and 18. Figure 17 shows the cross section of the layer formed at the H_2S concentration of 0.1 vol% and various Fe^{2+} concentrations. It is noted that at 0 ppm
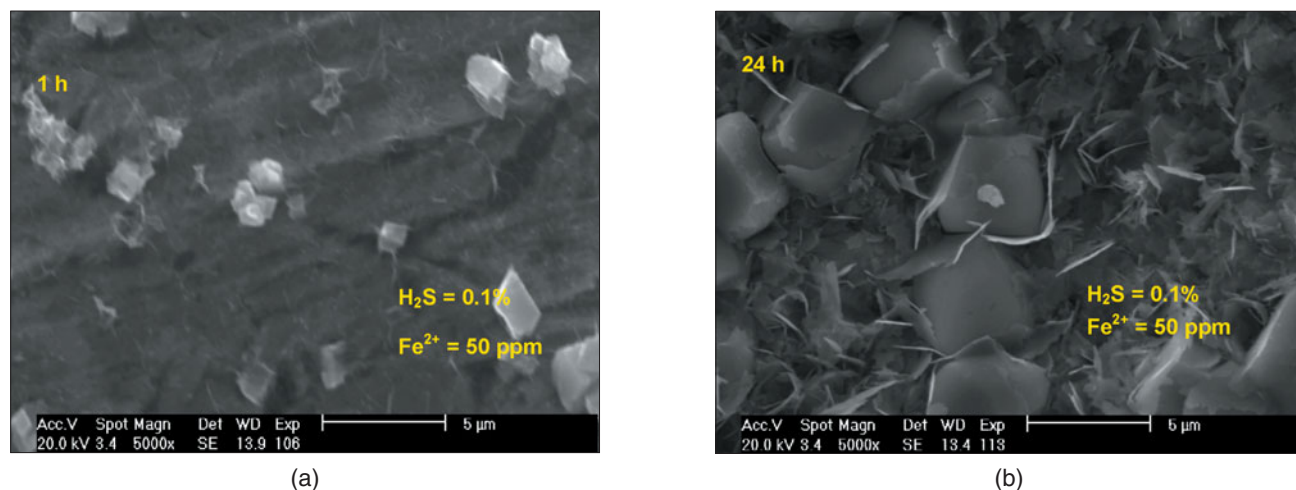
FIGURE 14. *The morphology of the layer formed on the X65 steel surface under the conditions of 0.1 vol% H_2S (H_2S/CO_2 gas), T = 80°C, pH 6.5~6.6, and Fe^{2+} = 50 ppm. The total reaction time was (a) 1 h and (b) 24 h.*
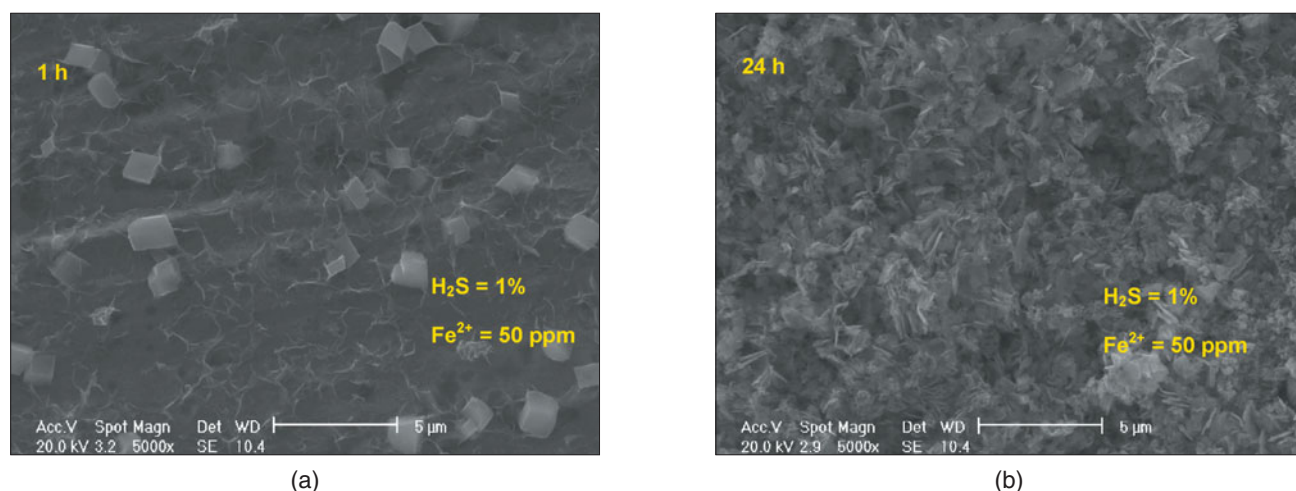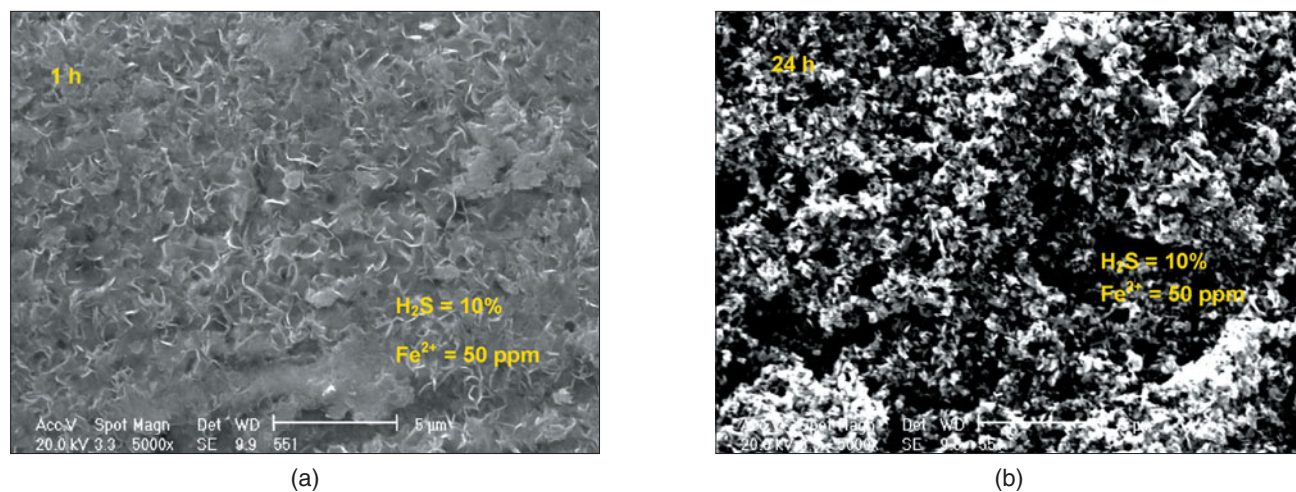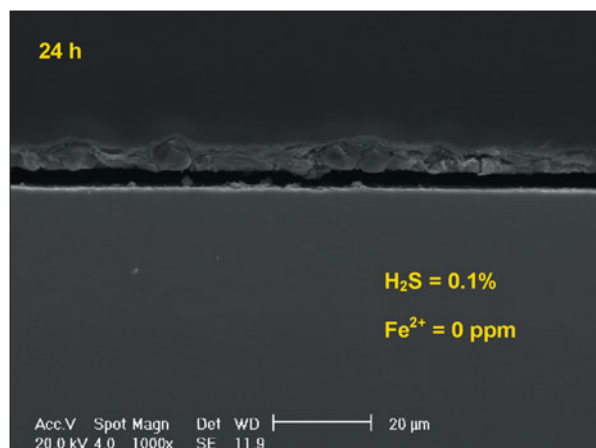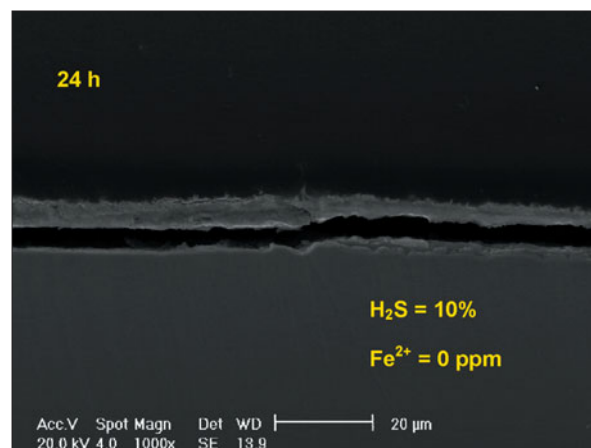

FIGURE 15. *The morphology (5,000X) and EDS results of the layer formed on the X65 steel surface under the conditions of 1 vol% H_2S (CO_2/H_2S gas), T = 80°C, pH 6.5~6.6, and Fe^{2+} = 50 ppm. The total reaction time was (a) 1 h and (b) 24 h.*
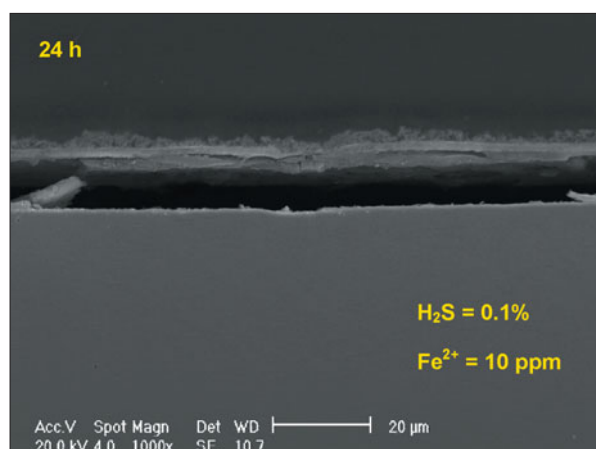

FIGURE 16. *The morphology (5,000X) and EDS results of the layer formed on the X65 steel surface under the conditions of 10 vol% H_2S (CO_2/H_2S gas), T = 80°C, pH 6.5~6.6, and Fe^{2+} = 50 ppm. The total reaction time was (a) 1 h and (b) 24 h.*
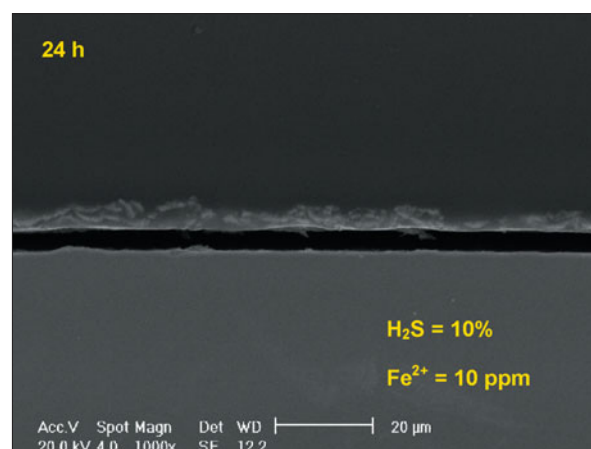
(a)

(b)

(c)

FIGURE 17. *Cross section of the layer formed on the X65 steel surface (at 1,000X) under the conditions of 0.1 vol% H_2S (CO_2/H_2S gas), T = 80°C, pH 6.5~6.6, (a) Fe^{2+} = 0 ppm, (b) Fe^{2+} = 10 ppm, and (c) Fe^{2+} = 50 ppm. The total reaction time was 24 h.*
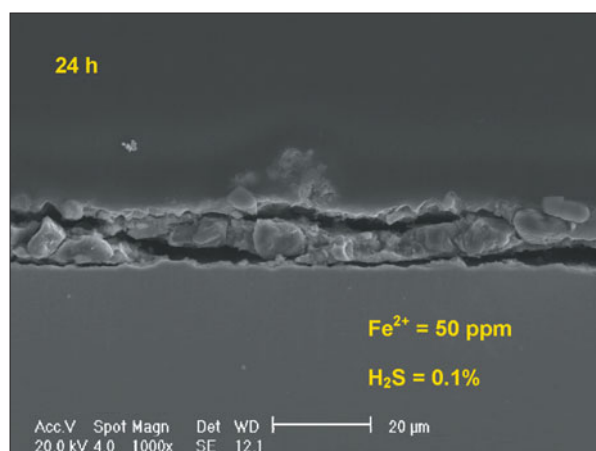

(a)

(b)

FIGURE 18. *Cross section of the layer formed on the X65 steel surface (at 1,000X) under the conditions of 10 vol% H_2S (CO_2/H_2S gas), T = 80°C, pH 6.5~6.6, (a) Fe^{2+} = 0 ppm, and (b) Fe^{2+} = 10 ppm. The total reaction time was 24 h.*

carbonate layer formation. When H_2S concentration is increased to 10 vol%, the cross section of the layer shows that the thickness of the layer does not change, it is 10 μm to 15 μm (Figure 18), which is similar to the thickness of the layer observed at 0.1 vol% H_2S.

Figures 19 through 21 show the XRD results of the layer formed on the X65 steel surface under the test conditions discussed above. The XRD results show that mackinawite is the predominant iron sulfide formed on the steel surface. It is also found that both iron carbonate and mackinawite formed on the steel surface at a H_2S concentration of 0.1 vol%, while only mackinawite layer formed at H_2S concentrations of 1 vol% and 10 vol%. The XRD results are in good agreement with the SEM results (Figures 14 through 16).

Summary of the Baseline Experiments

In the experiments discussed above, it was observed that in the pure H_2S corrosion of mild steel

and 10 ppm Fe^{2+} concentration, the thickness of the layer is similar (10 μm to 15 μm) and is composed of pure iron sulfide. At 50 ppm, the layer is not much thicker; however, it is more protective due to the iron

there was no significant effect of dissolved Fe^{2+} concentration on either the CR or on the iron sulfide CLAR. This was in sharp contrast with pure CO_2 corrosion where the iron carbonate layer formation rate is a strong function of dissolved Fe^{2+} concentration, i.e., it depends heavily on iron carbonate supersaturation, which is a major driving force for iron carbonate layer formation by precipitation.[22] Actually, it has been known for a long time that an iron sulfide layer forms even in solutions that are well undersaturated,[14] i.e., at pH much lower than pH 5.0 to 5.5, which was used in this study. In addition, the structure and morphology of the iron sulfide layer formed in H_2S corrosion (which was identified primarily as mackinawite) is very different from the iron carbonate layer formed in CO_2 corrosion. One observes a layered crystalline iron sulfide layer, with cracks and delaminations, often with the imprint of the underlying metal surface clearly visible even after long exposures.[23] Therefore, it is hypothesized here that the iron sulfide layer observed in the experiments formed primarily by a direct heterogeneous chemical reaction between H_2S and iron at the steel surface (often referred to as a "solid-state reaction").[(2)] This hypothesis does not exclude the possibility of iron sulfide layer forming by precipitation over long periods of time; however, in the relatively short duration experiments, the main mechanism of iron sulfide formation is the direct chemical reaction between H_2S and the steel surface. Even more importantly, it is thought that the thin and tight iron sulfide layer formed in this way is one of the most important controlling factors in H_2S corrosion.

Another important observation is that the results obtained in pure H_2S experiments are rather similar to the equivalent ones obtained in the mixed CO_2/H_2S experiments, suggesting that within the range of partial pressures covered in this study the dominant corrosion species is H_2S, i.e., the effect of CO_2 on layer formation is not significant.

Summary of Kinetics Experiments Considering the Effects of Other Parameters

A large number of detailed experiments were conducted where parameters such as H_2S, temperature, flow rate, etc., were varied; however, showing the full set of data exceeds the scope of this paper. For these, the reader is directed to the source document.[24] In the text below, only the summary of the key effects is presented.

Effect of H_2S Concentration — A number of experiments were conducted to investigate the effect of H_2S gas concentration on the mackinawite layer formation in pure H_2S solutions at 80°C. Figure 22 shows the comparison of CR and CLAR expressed in the same
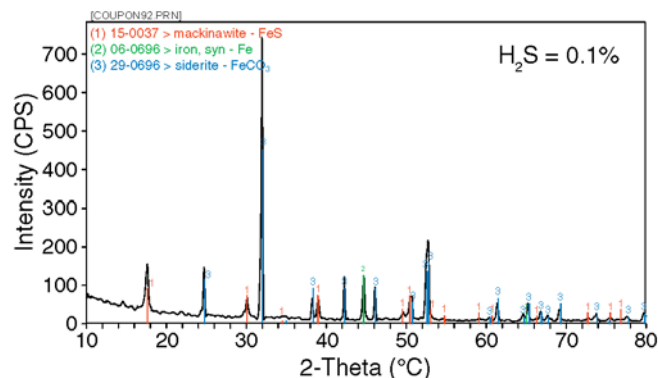
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(2) This hypothesis is not entirely new. It has been mentioned in various publications on H_2S corrosion of steel.[6-7,14-15]

FIGURE 19. *XRD results of the layer formed on the X65 steel surface under the conditions of 0.1 vol% H_2S (CO_2/H_2S gas), T = 80°C, pH 6.5~6.6, and Fe^{2+} = 50 ppm. The total reaction time was 24 h.*

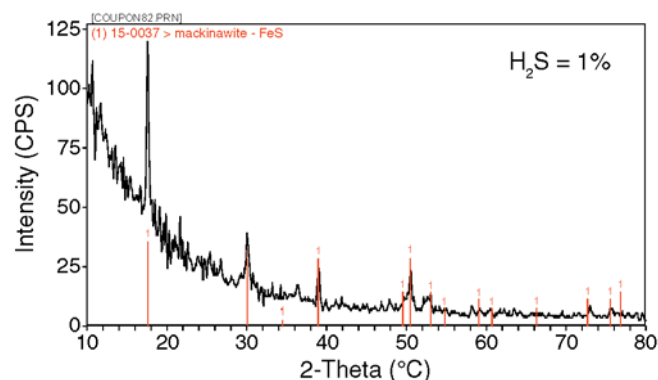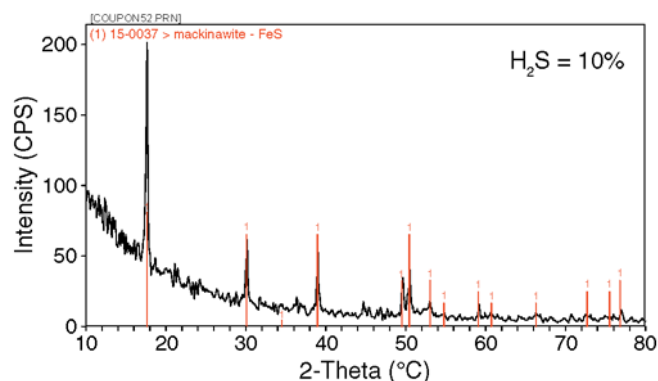**FIGURE 20.** *XRD results of the layer formed on the X65 steel surface under the conditions of 1 vol% H_2S (CO_2/H_2S gas), T = 80°C, pH 6.5~6.6, and Fe^{2+} = 50 ppm. The total reaction time was 24 h.*

FIGURE 21. *XRD results of the layer formed on the X65 steel surface under the conditions of 10 vol% H_2S (CO_2/H_2S gas), T = 80°C, pH 6.5~6.6, and Fe^{2+} = 50 ppm. The total reaction time was 24 h.*

molar units vs. H_2S gas concentration after a 1-h exposure. The value for the scaling tendency, which is the ratio of the two rates, is also shown. The comparison indicates that both the CR and CLAR increase with the increase of H_2S gas concentration; however, the CR is always higher than the CLAR. The scal-
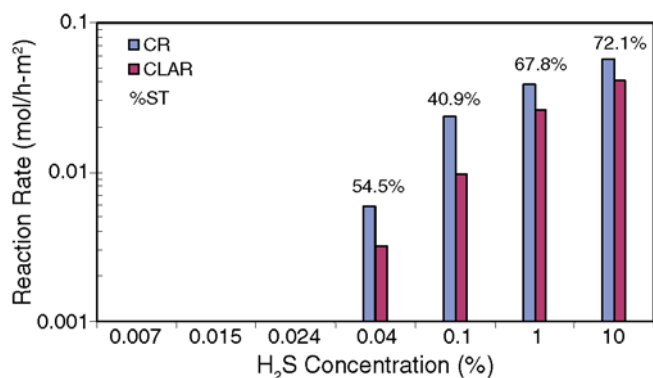
FIGURE 22. *The comparison of CR and CLAR in the same molar units as a function of H_2S gas concentration; ST = CLAR/CR stands for scaling tendency; total pressure: p = 1 bar, T = 80°C, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0 to 5.5, reaction time: 1 h.*
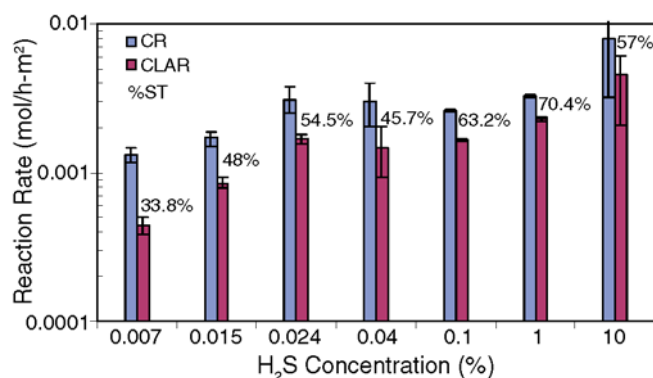

FIGURE 23. *The comparison of CR and CLAR in the same molar units as a function of H_2S gas concentration; ST = CLAR/CR stands for scaling tendency; total pressure: p = 1 bar, T = 80°C, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0 to 5.5, reaction time: 24 h.*

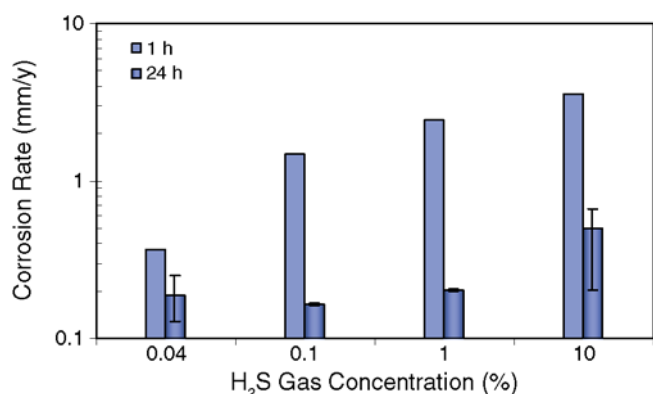**FIGURE 24.** *The CR vs. H_2S gas concentration after 1-h and 24-h exposures at total pressure p = 1 bar, T = 80°C, initial Fe^{2+} aqueous concentration: 0 ppm, and pH 5.0 to 5.5.*
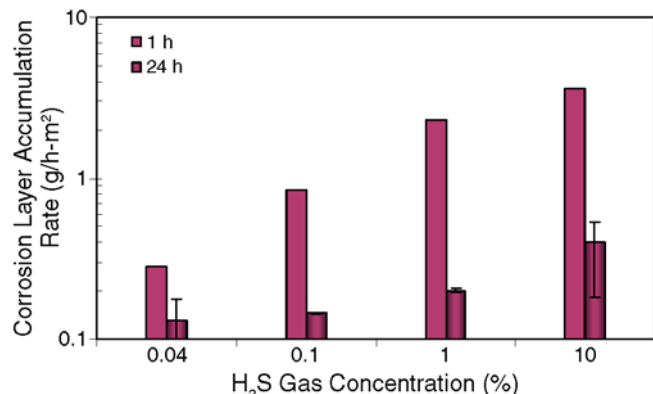

FIGURE 25. *The CLAR vs. H_2S gas concentration after 1-h and 24-h exposures at total pressure, p = 1 bar, T = 80°C, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0 to 5.5.*

ing tendency under the test conditions indicates that between 40% and 72% of the iron consumed by corrosion ended up as iron sulfide on the steel surface, with the balance lost to the solution. A very small increase in the dissolved Fe^{2+} was measured in the solution, and "black powder" was noticed at the bottom of the cell. It was concluded that some of the iron sulfide layer that formed on the steel spalled off in a spontaneous process, probably caused by intrinsic growth stresses. No flow was present in these experiments that would impose extrinsic hydrodynamic stresses. In Figure 23, the same kind of data is presented for a 24-h exposure where a broader range of H_2S gas concentrations was used: 0.0075 vol% to 10 vol%. The same conclusions apply as for the 1-h exposure with the exception that the magnitude of both the CR and CLAR are almost an order lower after 24 h. Interestingly, the scaling tendency remains in approximately the same range, 33% to 70%, suggesting that between one- and two-thirds of the iron sulfide that is formed by the corrosion process is lost to the solution by spalling.

The reduction in the rates with time is accentuated by the direct comparison of the 1-h and 24-h CR, as illustrated in Figure 24, and CLAR, as illustrated in Figure 25, at different H_2S gas concentrations. Clearly, the iron sulfide layer that is retained on the surface over time becomes gradually more protective.

Effect of Temperature — The effect of temperature on both the CR and the CLAR is shown in Figure 26 for a 1-h exposure and in Figure 27 for a 24-h exposure at 1 vol% H_2S gas concentration. Very weak temperature dependence is observed even for the shorter-term exposure, which all but disappears for the longer exposure times. The same is obtained in experiments at H_2S gas concentrations of 10 vol%, as shown in Figures 28 and 29. This seems to suggest that the CR is predominantly controlled by the presence of the iron sulfide layer, with the effect increasing over time.

Effect of Flow Rate — The effect of flow rate has been investigated by varying the rotation rate of the cylindrical working electrode up to 8,000 rpm, which
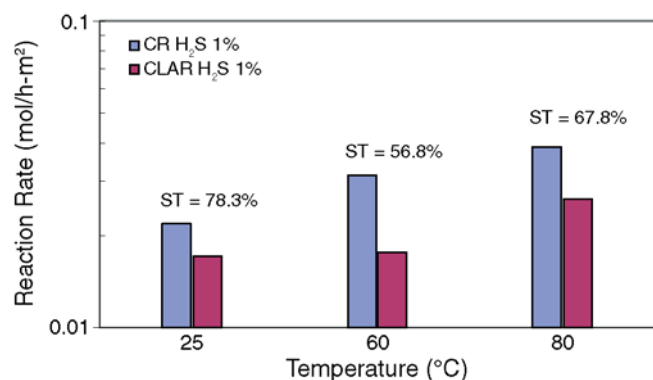
FIGURE 26. *The CR and CLAR vs. temperature, ST = CLAR/CR stands for scaling tendency, total pressure: p = 1 bar, H_2S gas concentration: 1 vol%, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0 to 5.5, and reaction time: 1 h.*
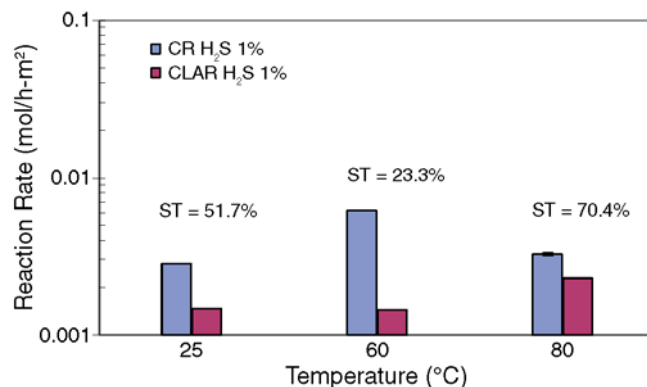

FIGURE 27. *The CR and CLAR vs. temperature, ST = CLAR/CR stands for scaling tendency, total pressure: p = 1 bar, H_2S gas concentration: 1 vol%, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0 to 5.5, and reaction time: 24 h.*
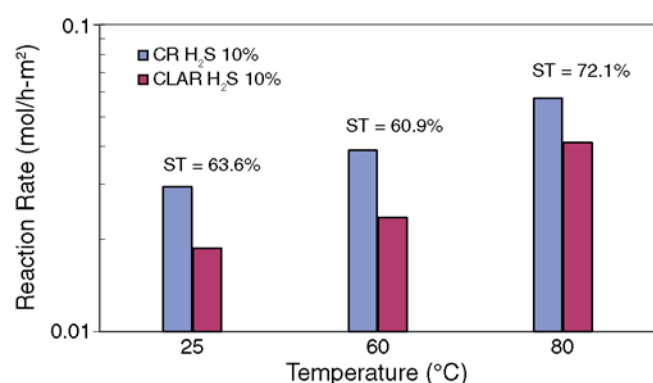

FIGURE 28. *The CR and CLAR vs. temperature, ST = CLAR/CR stands for scaling tendency, total pressure: p = 1 bar, H_2S gas concentration: 10 vol%, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0 to 5.5, and reaction time: 1 h.*
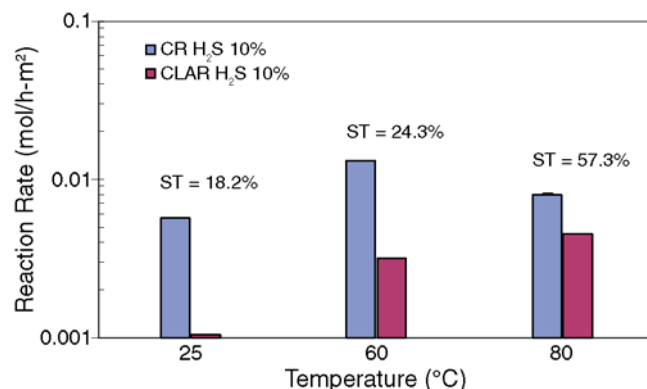

FIGURE 29. *The CR and CLAR vs. temperature, ST = CLAR/CR stands for scaling tendency, total pressure: p = 1 bar, H_2S gas concentration: 10 vol%, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0 to 5.5, and reaction time: 24 h.*

corresponds to a peripheral velocity of approximately 4 m/s and a wall shear stress of 57 Pa. The CR as a function of reaction time at different velocities is shown in Figure 30 for experiments performed with 0.04 vol% H_2S in the gas phase. The CR clearly increases with velocity and the effect is much more pronounced for shorter exposure times. For longer exposures in flowing conditions, the CR decrease significantly just as they did in experiments conducted under stagnant conditions, as a result of a buildup of a protective iron sulfide layer. However, as illustrated in Figure 31, the scaling tendency, which is on average 50% in stagnant conditions, decreases to below 20% under flowing conditions. This decrease suggests that a much larger fraction of the iron sulfide layer formed in the corrosion process is lost to the solution as a consequence of the hydrodynamic stresses induced by the flow. Iron sulfide layer dissolution could be excluded as a reason for losing the layer as a result of a slight supersaturation of the solution with respect to mackinawite.

The morphology of the layer formed on the steel surface at different velocities is shown in Figure 32. At 100 rpm, a porous iron sulfide layer can be observed on the steel surface; while at 8,000 rpm, most of the porous layer is removed.

Effect of Steel Substrate — In all the experiments discussed above, the CR was closely correlated with the iron sulfide CLAR, suggesting that the main iron source in the layer is the underlying corroding steel substrate. To investigate this point further, a number of experiments were conducted using the much more corrosion-resistant stainless steel as the substrate under the similar test conditions as were used for the X65 mild steel. The CR of stainless steel was measured to be less than 0.04 mm/y under these test conditions. Compared to the X65 mild steel (shown in Figures 4 through 7), little iron sulfide layer formed on the stainless steel surface (Figure 33). However, iron carbonate crystals did form in the CO_2/H_2S environment in iron carbonate supersaturated solutions (Figure 34).
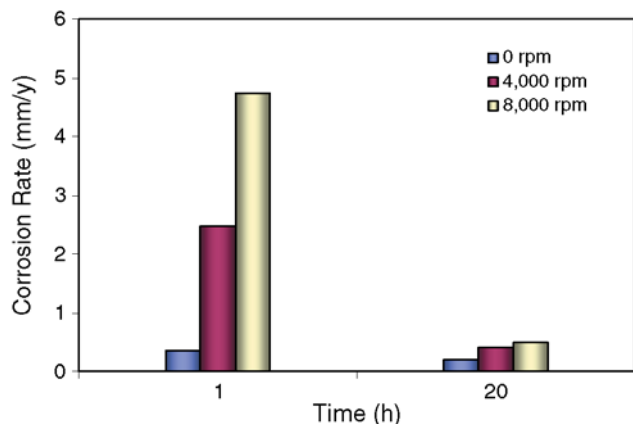
FIGURE 30. *The CR vs. time for different rotational speeds; conditions: total pressure: p = 1 bar, T = 25°C, H₂S gas concentration: 0.04 vol%, initial Fe²⁺ aqueous concentration: 0 ppm, and pH 5.0 to 5.5.*
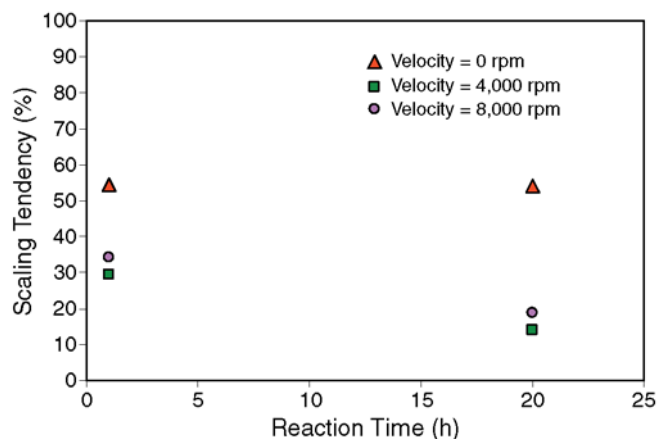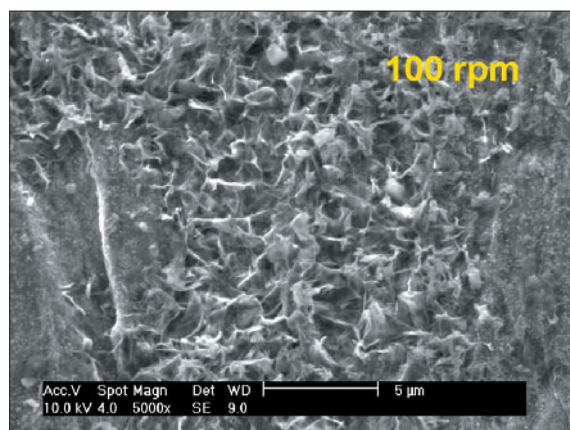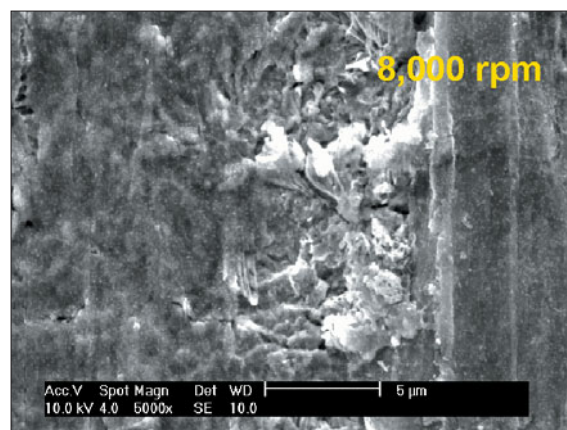

FIGURE 31. *The comparison of scaling tendency vs. reaction time under the conditions of total pressure: p = 1 bar, T = 25°C, H₂S gas concentration: 0.04 vol%, initial Fe²⁺ aqueous concentration: 0 ppm, and velocity: 0, 4,000, and 8,000 rpm.*

(a)

(b)

FIGURE 32. *The morphology (5,000X) of the layer on the X65 steel surface under the conditions of 0.04 vol% H₂S (H₂S/N₂ gas), T = 80°C, pH 5, the total reaction time: 20 h at: (a) 100 rpm and (b) 8,000 rpm.*
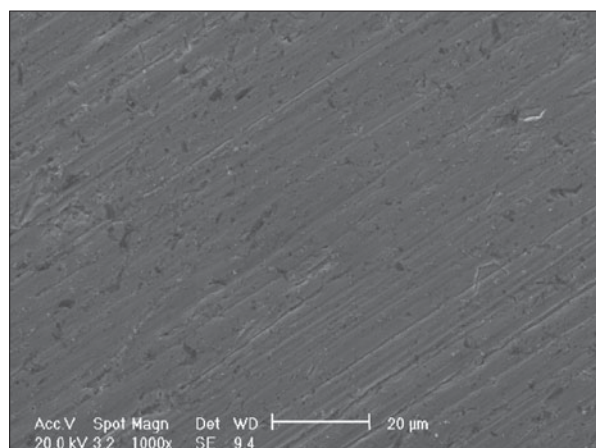

FIGURE 33. *The morphology (1,000X) of a Type 316 stainless steel surface in H₂S/N₂ solution under the conditions of total pressure: p = 1 bar, Fe²⁺ 50 ppm, H₂S gas concentration: 0.1 vol%, T = 80°C, reaction time: 24 h, pH 5.0 to 5.5, and velocity: 0 rpm.*

CONCLUSIONS

❖ Mackinawite is the predominant type of iron sulfide formed on the steel surface under the test conditions. Only in one test condition, H₂S concentration of 0.1 vol% and initial Fe²⁺ concentration of 50 ppm, both iron carbonate and mackinawite layer formed. Little mackinawite forms on the Type 316 stainless steel surface compared to X65 mild steel.

❖ The CR of X65 steel is higher than the mackinawite CLAR. Only a part of iron corroded from the steel surface is retained as the iron sulfide layer. Ferrous ions forming the layer mainly come from the iron in the steel and not from dissolved Fe²⁺ in the bulk of the solution. Therefore, the CR is directly correlated with the iron sulfide layer formation rate.

❖ The CR of mild steel in H₂S corrosion is affected primarily by the protectiveness of the iron sulfide layer, H₂S concentration, velocity, and temperature

in the order of importance. With longer exposure, the iron sulfide film becomes more protective, and both the CR and the CLAR diminish.

ACKNOWLEDGMENTS

FIGURE 34. *The morphology (1,000X) of Type 316 stainless steel surface in a H_2S/CO_2 solution under the conditions of total pressure: p = 1 bar, Fe^{2+} 50 ppm, H_2S gas concentration: 0.1 vol%, T = 80°C, reaction time: 24 h, pH 6.6, and velocity: 0 rpm.*

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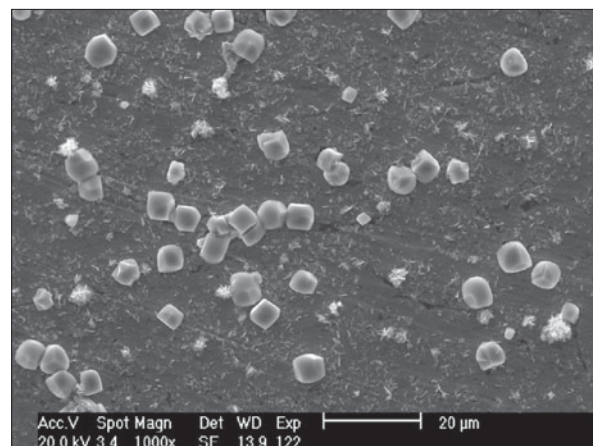24. W. Sun, "Kinetics of Iron Carbonate and Mixed Iron Carbonate/Sulfide Layer Formation in CO_2/H_2S Corrosion" (Ph.D. diss., Ohio University, 2006).