

# **KINETICS OF IRON SULFIDE AND MIXED IRON SULFIDE/CARBONATE SCALE PRECIPITATION IN CO<sub>2</sub>/H<sub>2</sub>S CORROSION**

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## **ABSTRACT**

Glass cell experiments were conducted to investigate kinetics of iron sulfide and mixed iron sulfide/carbonate scale precipitation in CO<sub>2</sub>/H<sub>2</sub>S corrosion. Weight gain/loss (WGL) method was used to investigate the scale formation using X65 carbon steel as substrates. Scanning Electron Microscopy (SEM/EDS), X-ray Diffraction methodology (XRD), X-ray Photoelectron Spectroscopy (XPS), and Electron Probe Micro-analyzer (EPMA) were used to analyse the scale. The experimental results show that the corrosion products formed in CO<sub>2</sub>/H<sub>2</sub>S system depend on the competitiveness of iron carbonate and mackinawite. At high H<sub>2</sub>S concentration and low Fe<sup>2+</sup> concentration, mackinawite was the predominant scale formed on the steel surface. At low H<sub>2</sub>S concentration and high Fe<sup>2+</sup> concentration, both iron carbonate and mackinawite form. It was also found that ferrous ions forming mackinawite scale mainly come from Fe<sup>2+</sup> released from the steel surface.

Keywords: kinetics, iron sulfide, iron carbonate, scale, precipitation, CO<sub>2</sub>/H<sub>2</sub>S corrosion

## **INTRODUCTION**

Internal CO<sub>2</sub> corrosion of mild steel in the presence of hydrogen sulfide (H<sub>2</sub>S) represents a significant problem for both upstream and downstream oil and gas facilities. In CO<sub>2</sub>/H<sub>2</sub>S corrosion, both iron carbonate and iron sulfide scale can form on the steel

surface<sup>1-5</sup>. Surface scale formation is one of the important factors governing the rate of corrosion. The scale slows down the corrosion process by presenting a diffusion barrier for the species involved in the corrosion process and by covering and preventing the underlying steel from further dissolution. The scale growth depends primarily on the kinetics of scale formation. The rate of precipitation is a function of iron carbonate supersaturation, the solubility, temperature, and surface area-to-volume ratio<sup>6, 7</sup>. Measurements of kinetics of scale formation via solution ferrous ion concentration lead to an overestimation of the precipitation rate as recently demonstrated<sup>8</sup>. Therefore, the weight gain/loss method (WGL) was used by Sun and Nescic<sup>8</sup> in order to more accurately define the kinetics of scale formation in CO<sub>2</sub> corrosion and have shown that the old data are one to two orders of magnitude too high.

For iron sulfides two different expressions exist for quantification of kinetics of iron sulfide formation in sulfide salt solutions (Rickard<sup>9</sup> in 1995 and Harmandas<sup>10</sup> in 1996). The expressions which apply to mackinawite are described as a function of Fe<sup>2+</sup> concentration, and sulfide species' concentration. However, both expressions were obtained by using ferrous ion concentration measurements which has recently proven to be unreliable to obtain the precipitation rate of scale on the steel surface<sup>8</sup>. Furthermore, no kinetics experiments have been conducted for an H<sub>2</sub>S purged corrosion system, which is more complex than the sulfide salt system (without purging H<sub>2</sub>S gas) because electrochemical corrosion, precipitation and solid state chemical reaction may occur on the steel surface simultaneously.

Finally, there are no expressions whatsoever that quantify the kinetics of scale formation in CO<sub>2</sub>/H<sub>2</sub>S solutions. The makeup of the surface scale under these conditions will not only depend on the chemistry of the brine and the respective solubility of iron carbonate and iron sulfides, but also on the competitive kinetics of the two scale formation mechanisms. It is important to note that in contrast to one single type of iron carbonate, many types of iron sulfides<sup>11, 12</sup> may form. Among those iron sulfides that form in CO<sub>2</sub>/H<sub>2</sub>S solutions, it is thought that mackinawite needs to be quantified first as it is prevalent and usually forms as a precursor to other types of sulfides.

From the brief introduction presented above it is clear that for an improved understanding of the nature of surface scales formed in CO<sub>2</sub>/H<sub>2</sub>S environments as well as their protective properties, a better understanding of the kinetics of scale formation in CO<sub>2</sub>/H<sub>2</sub>S environment is needed.

## **EXPERIMENTAL PROCEDURE**

The schematic diagrams of the experimental setup are shown in Figure 1. The flow rate of H<sub>2</sub>S, N<sub>2</sub>, and CO<sub>2</sub> gas was controlled by gas mass-flow controllers and then was mixed through a gas mixer to obtain a desired H<sub>2</sub>S concentration. Three glass cells were used to conduct the experiments at the same time.

Each glass cell was filled with 2 liters of distilled water with 1 wt% NaCl. The solution was heated to a desired temperature and purged with N<sub>2</sub> or CO<sub>2</sub>. H<sub>2</sub>S concentration of the inlet gas varied from 0.1%, 1%, to 10%. After the solution was deoxygenated, the pH was adjusted to the desired value by adding a deoxygenated hydrogen chloride solution, or sodium bicarbonate solution (for CO<sub>2</sub>/H<sub>2</sub>S testing) and sodium hydroxide solution (for N<sub>2</sub>/H<sub>2</sub>S testing). Later, the required amounts of Fe<sup>2+</sup> were added in the form of a deoxygenated ferrous chloride salt (FeCl<sub>2</sub>·4H<sub>2</sub>O) solution. Six X65 carbon steel specimens were inserted into the same glass cell as the substrate for scale formation. Prior to immersion, the specimen surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with alcohol, and degreased using acetone. Some of the experiments were repeated in order to obtain the reproducible results. The chemical composition of X65 steel used for all the experiments is shown in Table 1. Subsequently, a given amount of H<sub>2</sub>S was added into the system.

## RESULTS

Two sets of experiments were conducted in order to investigate both iron sulfide and mixed iron carbonate/sulfide scale formation.

- Kinetics experiments in H<sub>2</sub>S/N<sub>2</sub> environments
- Kinetics experiments in H<sub>2</sub>S/CO<sub>2</sub> environments

### **Kinetics experiments in H<sub>2</sub>S/N<sub>2</sub> environments**

The temperature at 80°C and H<sub>2</sub>S concentrations at 0.1%, 1% and 10%

A number of experiments were conducted to investigate iron sulfide scale formation in the solutions with H<sub>2</sub>S/N<sub>2</sub> at the temperature of 80°C. Figure 2 shows the precipitation rate of iron sulfide formed on the X65 carbon steel surface in the first hour under the conditions of initial Fe<sup>2+</sup> concentration of 0ppm, 10ppm and 50ppm, and H<sub>2</sub>S concentration of 0.1%, 1% and 10%. The corrosion rate of X65 in the first hour at different H<sub>2</sub>S concentrations and Fe<sup>2+</sup> concentrations is shown in Figure 3. As shown in Figure 2 and Figure 3, both the precipitation rate of iron sulfide scale and the corrosion rate of X65 increased with the increase of H<sub>2</sub>S concentration and did not alter much with the increase of Fe<sup>2+</sup> concentration. With the total reaction time increasing to 24 hours, both the precipitation rate and corrosion rate decreased, as illustrated in Figure 4 and Figure 5. The error bars represent the maximum and minimum measured the precipitation rates and the corrosion rates. Similar trends at different H<sub>2</sub>S concentrations and Fe<sup>2+</sup> concentrations in 24 hours were obtained as the experimental results in one hour.

Figure 6 to Figure 11 show the morphology of iron sulfide scale formed on the X65 carbon steel surface at different Fe<sup>2+</sup> concentrations of 0ppm and 50ppm, H<sub>2</sub>S concentrations of 0.1%, 1%, and 10%, and reaction time of 1 hour and one day. It is found that there is little iron sulfide scale formed on the steel surface at H<sub>2</sub>S concentration of 0.1% in the first hour, which is illustrated in Figure 6 (A) and Figure 7 (A). With the increase of the reaction time to approximately 24 hours, the steel surface is evenly

covered by the iron sulfide scale. Comparing the morphology of iron sulfide scale shown in Figure 6 and Figure 7,  $\text{Fe}^{2+}$  concentration does not affect the iron sulfide formation at the temperature of  $80^\circ\text{C}$  and  $\text{H}_2\text{S}$  concentration of 0.1%. While increasing  $\text{H}_2\text{S}$  concentration to 1%, the iron sulfide scale forms in the first one hour and evenly covers the steel surface, and then the scale becomes more protective in 23 hours, as shown in Figure 8 and Figure 9. No effect of  $\text{Fe}^{2+}$  concentration is identified at  $\text{H}_2\text{S}$  concentration of 1%. With the increase of  $\text{H}_2\text{S}$  concentration to 10%, even more iron sulfide scale forms on the steel surface in the first hour (Figure 10 and Figure 11).

The cross sections of the scale under different test conditions are shown in Figure 12. The thickness of the scale is approximately  $10\ \mu\text{m}$ . The figures show that there is a gap between the scale and the substrate. The reason is that the adherence of the scale is too weak to keep the scale attached on the substrate and resist the stress introduced during mounting in epoxy.

The XRD results of iron sulfide scale are shown in Figure 13 and Figure 14. Mackinawite is the only product formed on the X65 carbon steel surface under the test conditions. The XPS results (Figure 15) of iron sulfide scale formed on the steel surface under the conditions of  $T\ 80^\circ\text{C}$ ,  $\text{pH}\ 5$ ,  $\text{Fe}^{2+}\ 0\text{ppm}$ ,  $\text{H}_2\text{S}\ 10\%$ , and the reaction time 23 hours are in good agreement with the XRD results. FeS is the predominant product formed on the steel surface. Small amount of S element is detected because iron sulfide scale on the surface of the specimen gets oxidized while in air.

#### The temperature at $60^\circ\text{C}$ and $\text{H}_2\text{S}$ concentrations at 1% and 10%

Several experiments were performed at the temperature of  $60^\circ\text{C}$  under the conditions of  $\text{Fe}^{2+}$  concentration of 0ppm, 10ppm, and 50ppm, and  $\text{H}_2\text{S}$  concentrations of 1% and 10%. The precipitation rate of iron sulfide scale and the corrosion rate of X65 carbon steel in the first hour are shown in Figure 16 and Figure 17 respectively. Both the precipitation rate of iron sulfide scale and the corrosion rate of X65 increased with the increase of  $\text{H}_2\text{S}$  concentration, which are somewhat smaller than at the temperature of  $80^\circ\text{C}$  (Figure 2 and Figure 3). Figure 18 and Figure 19 show the precipitation rate of iron sulfide scale and the corrosion rate of X65 in approximately 20 hours, which are much lower than the reaction rates obtained in one hour.

Electron probe micro-analyzer (EPMA) was employed to analyze the specimen which is covered with iron sulfide scale under the conditions of the temperature of  $60^\circ\text{C}$ ,  $\text{H}_2\text{S}$  concentration of 10%,  $\text{Fe}^{2+}$  concentration of 50ppm, and the reaction time is 19 hours. Based on CASINO electron beam-Fe-S specimen interaction simulation, electron beam accelerated by 20 kV would have an interaction volume penetrating about 2-3  $\mu\text{m}$  into the scale. The slightly Fe enrichment could be related to the contribution of substrate Fe in the measurement. The EPMA result (65.36 wt.% of Fe and 32.795 wt.% of S, which can be normalized to 53.366 at.% of Fe and 46.635 at.% of S) proves that the scale is mackinawite, which correlates well with the XRD measurement.

## Kinetics experiments in H<sub>2</sub>S/CO<sub>2</sub> environments

### The temperature at 80°C and H<sub>2</sub>S concentrations at 0.1%, 1% and 10%

Experiments were conducted to investigate the scale formation in the solutions with H<sub>2</sub>S/CO<sub>2</sub> at the temperature of 80°C under the conditions of initial Fe<sup>2+</sup> concentrations of 0ppm, 10ppm and 50ppm, H<sub>2</sub>S concentrations of 0.1%, 1% and 10%, and the reaction times are one hour and one day. Figure 20 and Figure 21 show the precipitation rate of the scale and the corrosion rate of X65 carbon steel in the reaction time of one hour. Both precipitation rate and corrosion rate increase with the increase of H<sub>2</sub>S concentration in the first hour. Figure 22 and Figure 23 illustrate the precipitation rate and corrosion rate in the reaction time of 24 hours. Both precipitation rate and corrosion rate increase with H<sub>2</sub>S concentration increasing from 0.1% to 1% and then decrease from 1% to 10%. Ferrous ion concentration has no significant effects on precipitation rate and corrosion rate. It is noted that similar trends of precipitation rate and corrosion rate in H<sub>2</sub>S/CO<sub>2</sub> system were obtained as the experiments conducted in the solutions with H<sub>2</sub>S/N<sub>2</sub>.

However, the morphology (Figure 24 to Figure 32) of the scale formed in the solutions with H<sub>2</sub>S/CO<sub>2</sub> is not the same as the scale formed in the solutions of H<sub>2</sub>S/N<sub>2</sub>. Figure 24 to Figure 26 show the morphology of the scale formed at the temperature of 80°C under the conditions of pH 6.6, initial Fe<sup>2+</sup> concentrations of 0ppm, 10ppm, and 50ppm, and H<sub>2</sub>S concentrations of 0.1%, 1%, and 10%. There is only iron sulfide formed on the X65 carbon steel surface at H<sub>2</sub>S concentration of 0.1% and Fe<sup>2+</sup> concentrations of 0ppm and 10ppm (Figure 24 and Figure 25). While keeping H<sub>2</sub>S concentration 0.1% and increasing Fe<sup>2+</sup> concentration to 50ppm, both iron sulfide and iron carbonate scale formed on the steel surface. Figure 26 and Figure 27 show the morphology and EDS results of the scale formed on the steel surface individually. The results illustrate that both iron carbonate crystal and iron sulfide film formed on the steel surface under the test conditions. With the increase of H<sub>2</sub>S concentration to 1%, only iron sulfide formed on the steel surface at Fe<sup>2+</sup> concentrations of 0ppm and 10ppm (Figure 28 and Figure 29). Increasing Fe<sup>2+</sup> concentration to 50ppm, both iron carbonate and iron sulfide scale formed on the steel surface in the first hour, and then most products were iron sulfide after 24 hours (Figure 30). With the increase of H<sub>2</sub>S concentration to 10%, no iron carbonate formed on the steel surface at Fe<sup>2+</sup> concentrations of 0ppm and 50ppm, as shown in Figure 31 and Figure 32. Decreasing pH of the solutions from 6.6 to 5, several experiments were conducted at H<sub>2</sub>S concentration of 10%. It was found that pH did not greatly affect the precipitation rate under the test conditions; however pH did affect the morphology of the iron sulfide scale. The mackinawite scale is more clearly crystalline at pH 5 comparing to the scale formed in the solutions at pH 6.6.

The cross sections of the scale under different test conditions are shown in Figure 33. The thickness of the scale is less than 15 μm. The gap between the scale and the steel surface is induced because of weak adhesion of the scale during mounting. It is also noted that the scale formed under the conditions of Fe<sup>2+</sup> 50ppm and H<sub>2</sub>S 0.1% is much tighter and more protective because of uniform iron carbonate scale formation.

Figure 34 to Figure 36 show the XRD results of the scale formed on X65 carbon steel under the test conditions of H<sub>2</sub>S concentrations of 0.1%, 1%, and 10%, T 80°C, pH 6.6, Fe<sup>2+</sup> concentration of 50ppm, and the total reaction time is 24 hours. The XRD results are in good agreement with the SEM/EDS results (Figure 24 to Figure 32). Both iron carbonate and mackinawite formed on the X65 carbon steel surface at H<sub>2</sub>S concentration of 0.1%; only mackinawite formed at H<sub>2</sub>S concentration of 1% and 10%.

#### The temperature at 60°C and H<sub>2</sub>S concentrations at 1% and 10%

Several experiments were performed in the solutions with CO<sub>2</sub>/H<sub>2</sub>S at the temperature of 60°C under the conditions of Fe<sup>2+</sup> concentrations of 0ppm, 10ppm, and 50ppm, and H<sub>2</sub>S concentrations of 1% and 10%. The precipitation rate of the scale and the corrosion rate of X65 carbon steel in the reaction time of first hour are shown in Figure 37 and Figure 38 respectively. Both the precipitation rate and the corrosion rate increased with the increase of H<sub>2</sub>S concentration. Figure 39 and Figure 40 show the precipitation rate of the scale and the corrosion rate of X65 carbon steel in 24 hours. Similar trends in CO<sub>2</sub>/H<sub>2</sub>S experiments were obtained as in N<sub>2</sub>/H<sub>2</sub>S experiments.

#### Scaling tendency

The scaling tendency is obtained using the precipitation rate of the scale divided by the corrosion rate of X65 carbon steel, both in molar units. The scaling tendency is below 1 under all the test conditions, illustrating that the precipitation rate of the scale formed on the steel surface is smaller than the corrosion rate of the steel. Therefore, it is estimated that the entire amount of ferrous ions forming the scale in H<sub>2</sub>S environments come from the corrosion of the steel and the ferrous ions in the bulk of the solution have a negligible effect on the iron sulfide scale formation under the test conditions. This is in strong contrast with the pure CO<sub>2</sub> environments where both the dissolved bulk Fe<sup>2+</sup> and the Fe<sup>2+</sup> coming from the corrosion process are important in forming the iron carbonate scale.

## **CONCLUSIONS**

The primary findings are:

- The corrosion rate of X65 increases with the increase of H<sub>2</sub>S concentration and decreases with the increase of reaction time under the test conditions.
- The corrosion products formed in CO<sub>2</sub>/H<sub>2</sub>S system depend on the competitiveness of iron carbonate and mackinawite. Mackinawite is the predominant iron sulfide formed on the steel surface under the test conditions. The precipitation rate of the films increases with the increase of H<sub>2</sub>S concentration and decreases with the increase of reaction time.
- Only in one test condition, H<sub>2</sub>S concentration of 0.1% and Fe<sup>2+</sup> concentration of 50ppm, both iron carbonate and mackinawite scale formed.

- The corrosion rate of X65 carbon steel is higher than the precipitation rate of iron sulfide scale measured in the same molar units. Only a part of iron lost by the steel surface becomes iron sulfide scale. Iron sulfide scale is formed mainly by  $\text{Fe}^{2+}$  released from the steel surface by corrosion and not from  $\text{Fe}^{2+}$  in the bulk of the solution. Therefore the corrosion rate has a great effect on the precipitation rate of scale.

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## TABLES

TABLE 1. CHEMICAL COMPOSITION OF X65 (WT.%) (FE IS IN BALANCE)

Al	As	B	C	Ca	Co	Cr	Cu	Mn	Mo	Nb
0.0032	0.005	0.0003	0.050	0.004	0.006	0.042	0.019	1.32	0.031	0.046
Ni	P	Pb	S	Sb	Si	Sn	Ta	Ti	V	Zr
0.039	0.013	0.020	0.002	0.011	0.31	0.001	0.007	0.002	0.055	0.003



## FIGURES

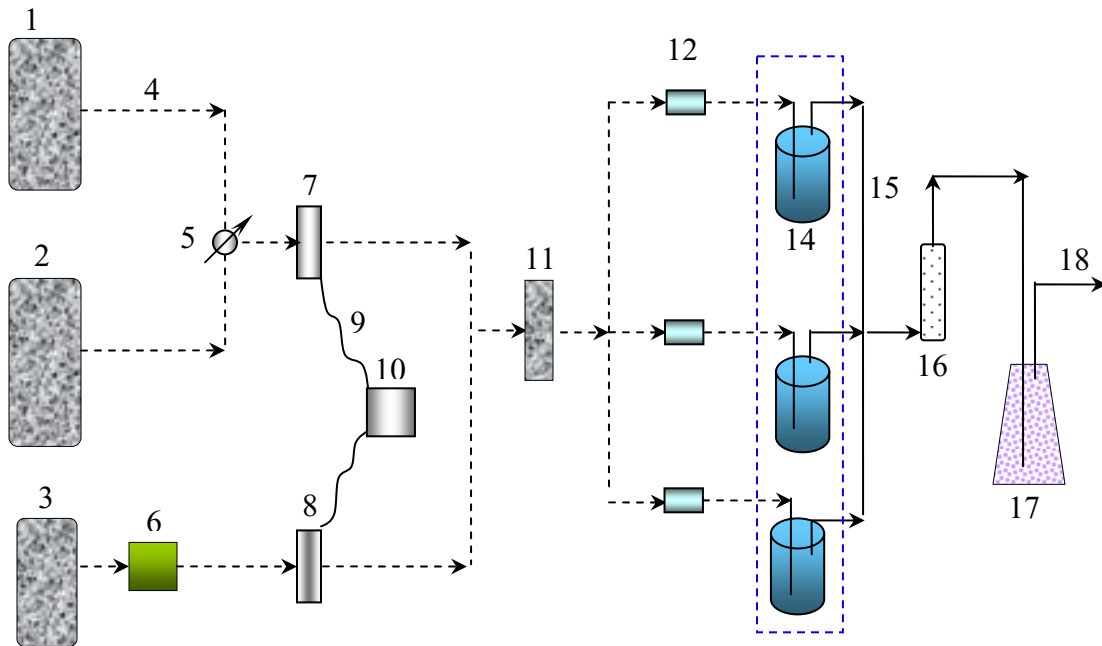


Figure 1. A schematic sketch of experiments: 1-N<sub>2</sub> cylinder, 2-CO<sub>2</sub> cylinder, 3-H<sub>2</sub>S cylinder, 4-Teflon tubing, 5-Three-way valve, 6-Solenoid valve, 7-Mass flow meter 1, 8-Mass flow meter 2, 9-Electronic wire, 10-Mass flow controller, 11-Gas mixer, 12-Gas rotameter, 13-Circulating bath heater, 14-Glass cells, 15-PVC tubing, 16-Condenser, 17-H<sub>2</sub>S scrubber (gas absorbent), 18-Gas outlet.

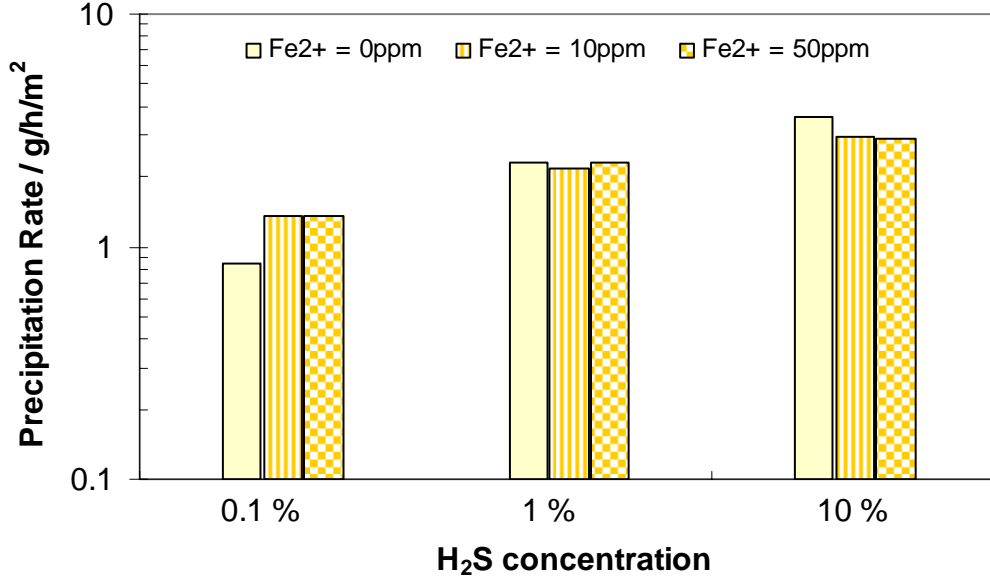


Figure 2. The precipitation rate of iron sulfide formed on the X65 carbon steel surface at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solution with H<sub>2</sub>S/N<sub>2</sub> under the conditions of T 80°C, the total reaction time is 1 hour.

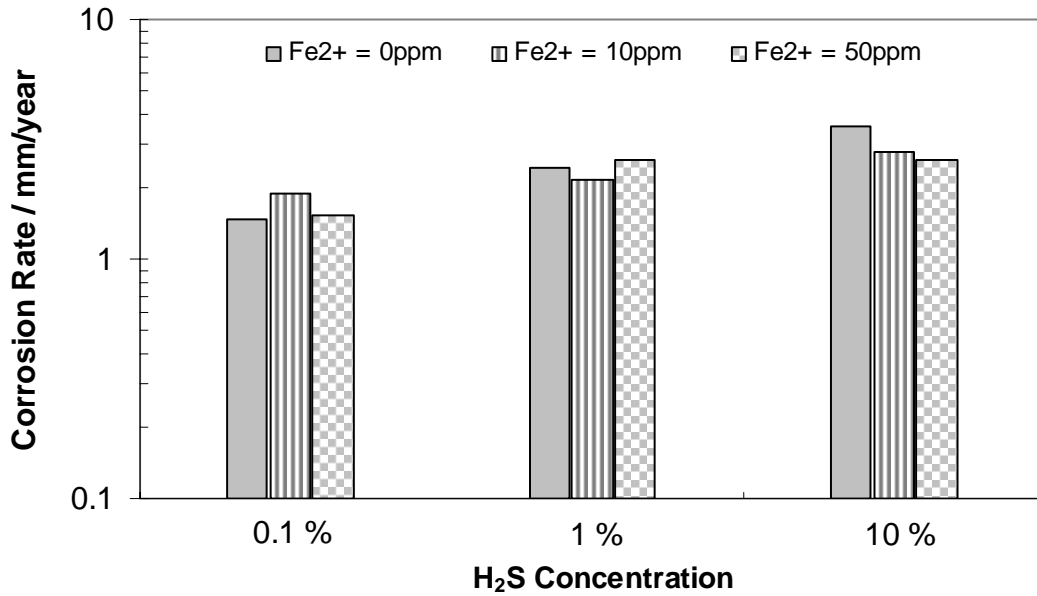


Figure 3. The corrosion rate of X65 carbon steel at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solution with H<sub>2</sub>S/N<sub>2</sub> under the conditions of T 80°C, the total reaction time is 1 hour.

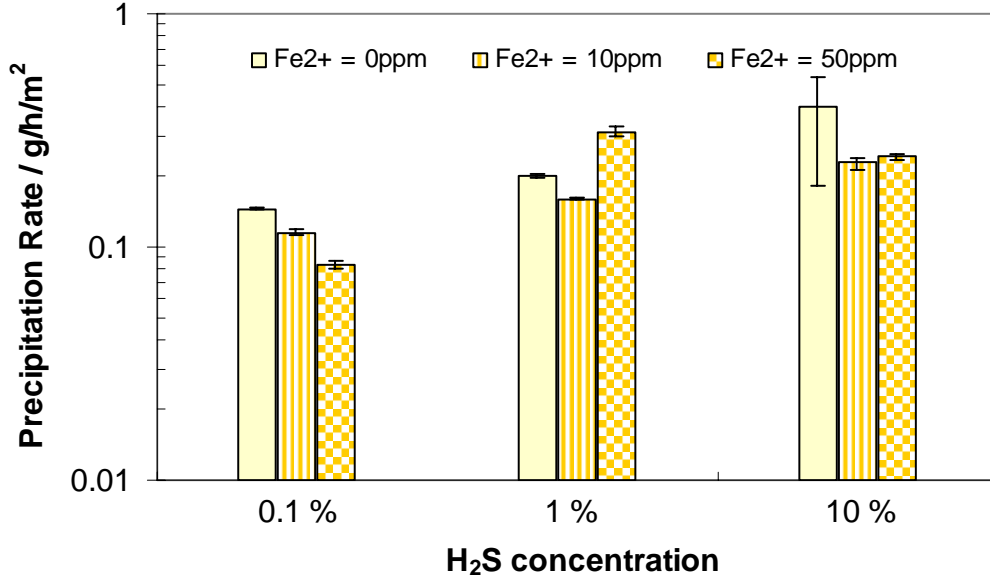


Figure 4. The precipitation rate of iron sulfide formed on the X65 carbon steel surface at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solution with H<sub>2</sub>S/N<sub>2</sub> under the conditions of T 80°C, the total reaction time is 24 hours.

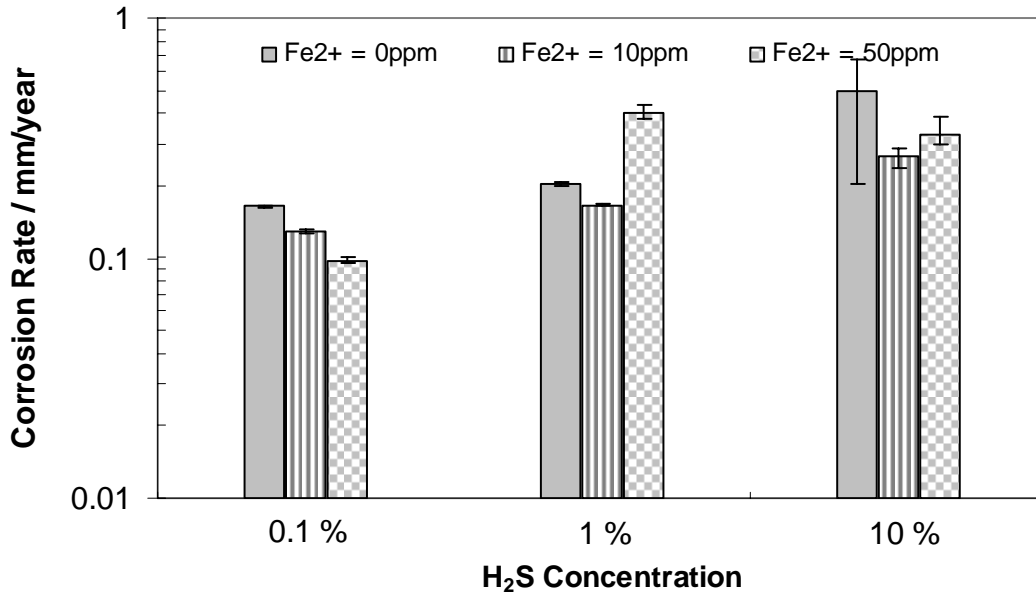
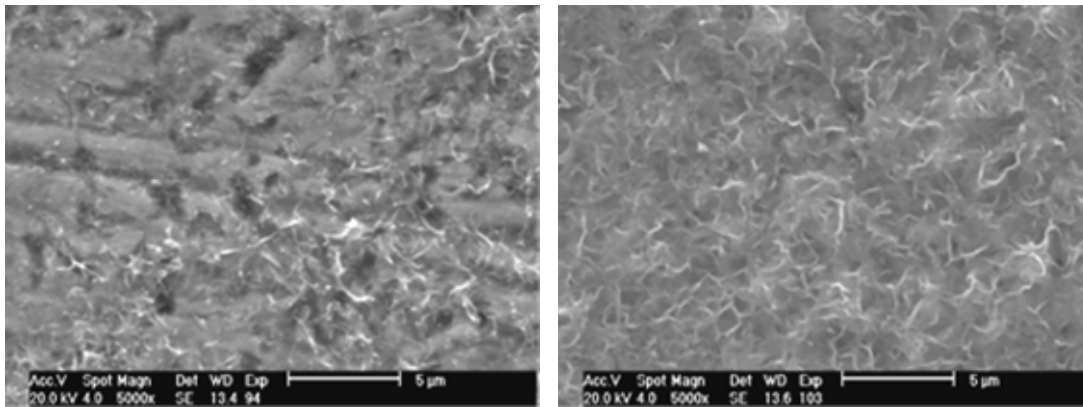


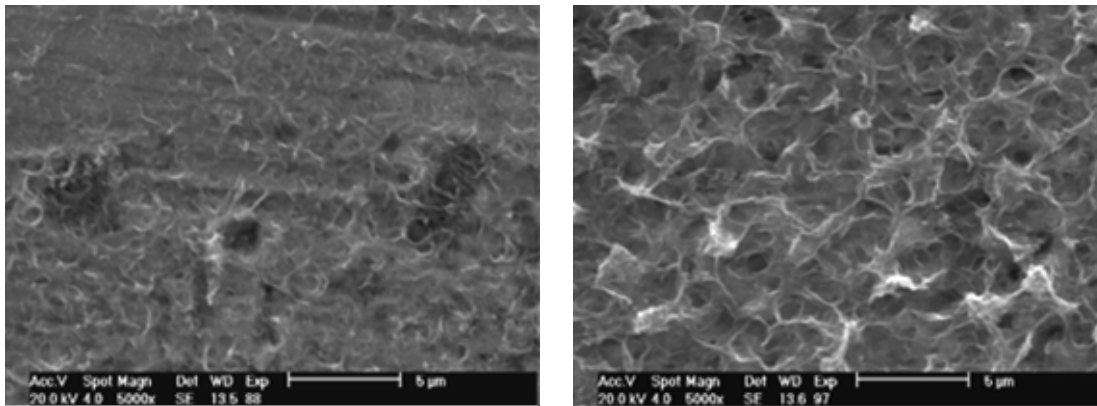
Figure 5. The corrosion rate of X65 carbon steel at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solution with H<sub>2</sub>S/N<sub>2</sub> under the conditions of T 80°C, the total reaction time is 24 hours.



(A)

(B)

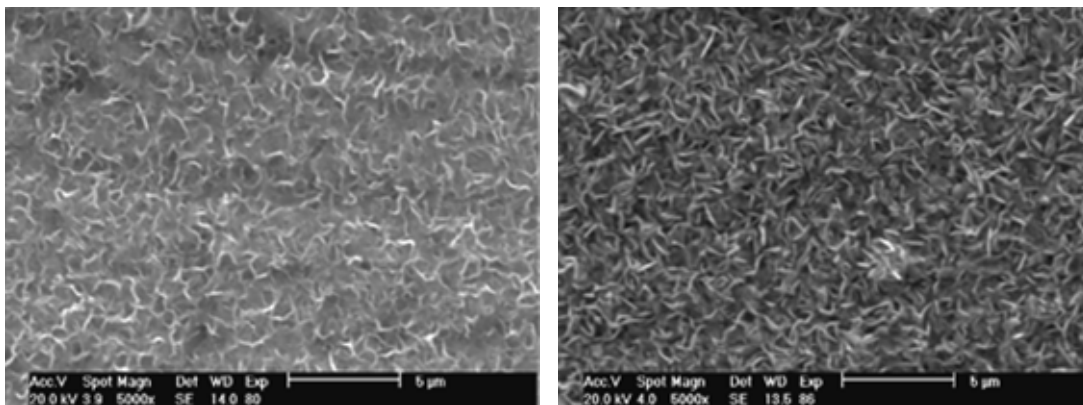
Figure 6. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5.5, Fe<sup>2+</sup> = 0ppm, the total reaction time is (A) 1 hour, (B) 25.5 hours.



(A)

(B)

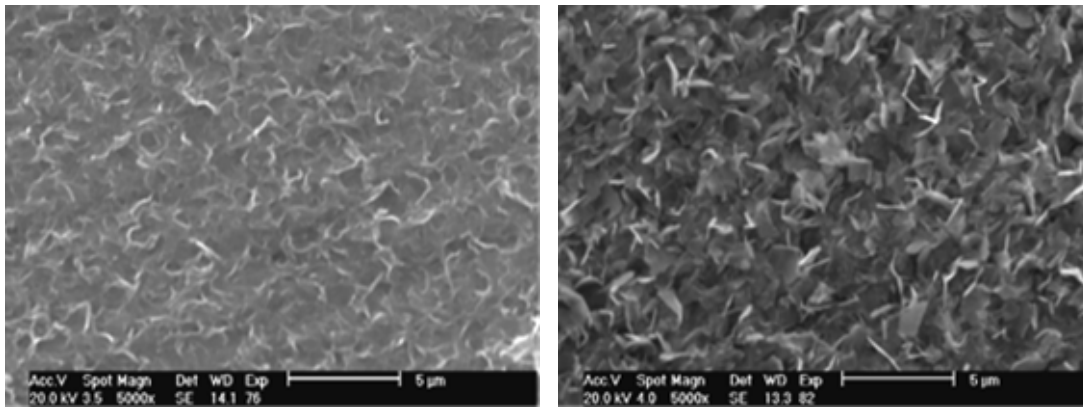
Figure 7. The morphology (at 1000X and 5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5.5, Fe<sup>2+</sup> = 50ppm, the total reaction time is (A) 1 hour, (B) 25.5 hours.



(A)

(B)

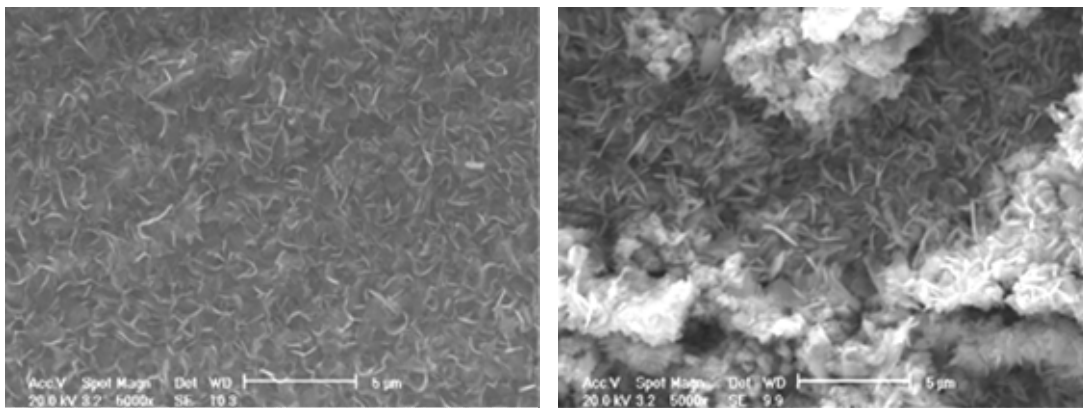
Figure 8. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 1% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5.5, Fe<sup>2+</sup> = 0ppm, the total reaction time is (A) 1 hour, (B) 23 hours.



(A)

(B)

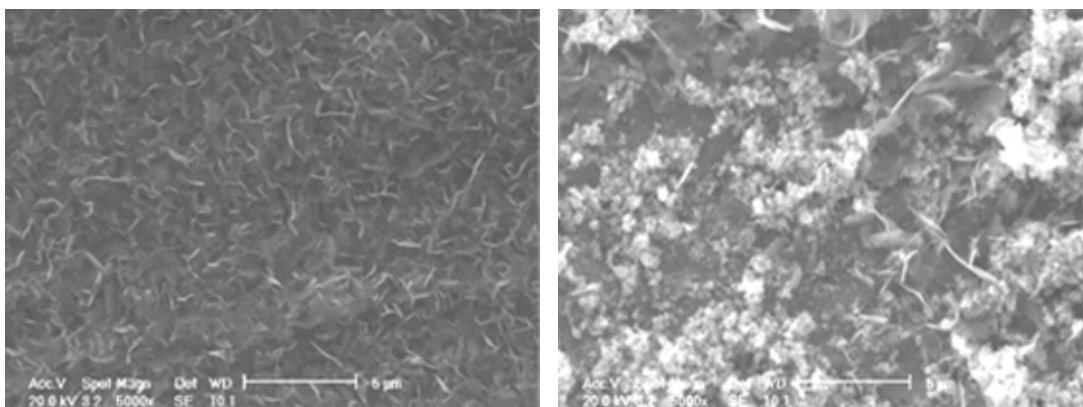
Figure 9. The morphology (at 5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 1% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5.5, Fe<sup>2+</sup> = 50ppm, the total reaction time is (A) 1 hour, (B) 23 hours.



(A)

(B)

Figure 10. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 10% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5.2, Fe<sup>2+</sup> = 0ppm, the total reaction time is (A) 1 hour, (B) 24 hours.



(A)

(B)

Figure 11. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 10% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5.2, Fe<sup>2+</sup> = 50ppm, the total reaction time is (A) 1 hour, (B) 24 hours.

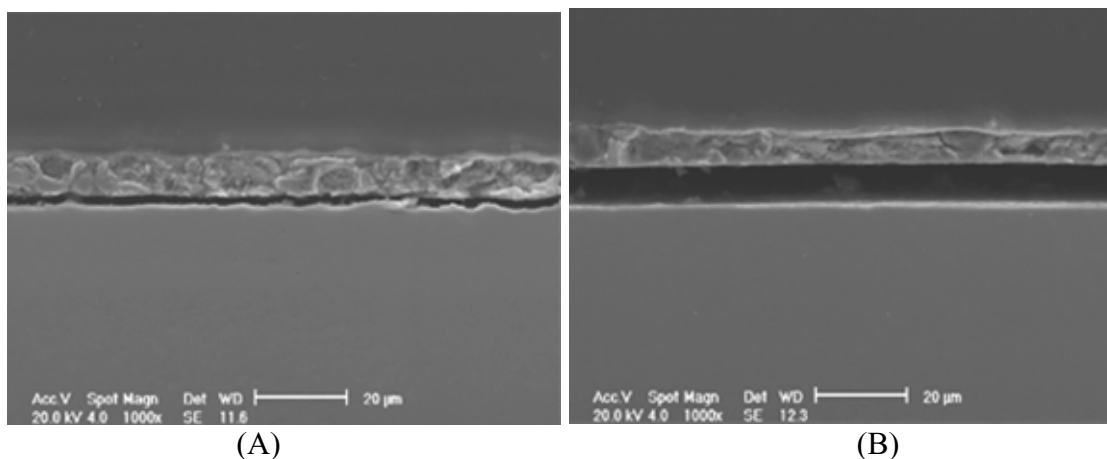


Figure 12. Cross section of the films formed on the X65 carbon steel surface (at 1000X) under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5, (A)  $Fe^{2+}=0ppm$ , (B)  $Fe^{2+}=50ppm$ , the total reaction time is 24 hours.

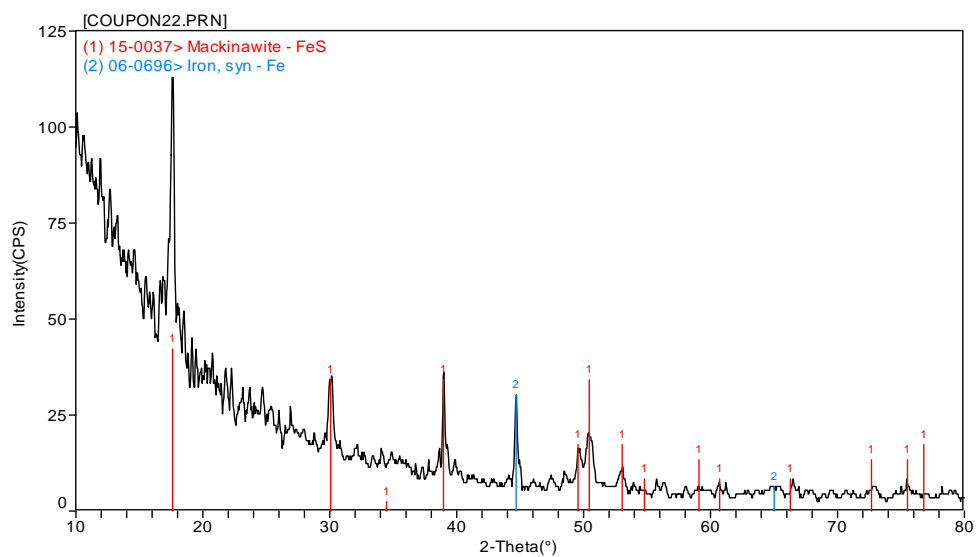


Figure 13. XRD results of iron sulfide films formed on the X65 carbon steel surface under the conditions of 1% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5.5,  $Fe^{2+} = 10ppm$ , the total reaction time is 23 hours.

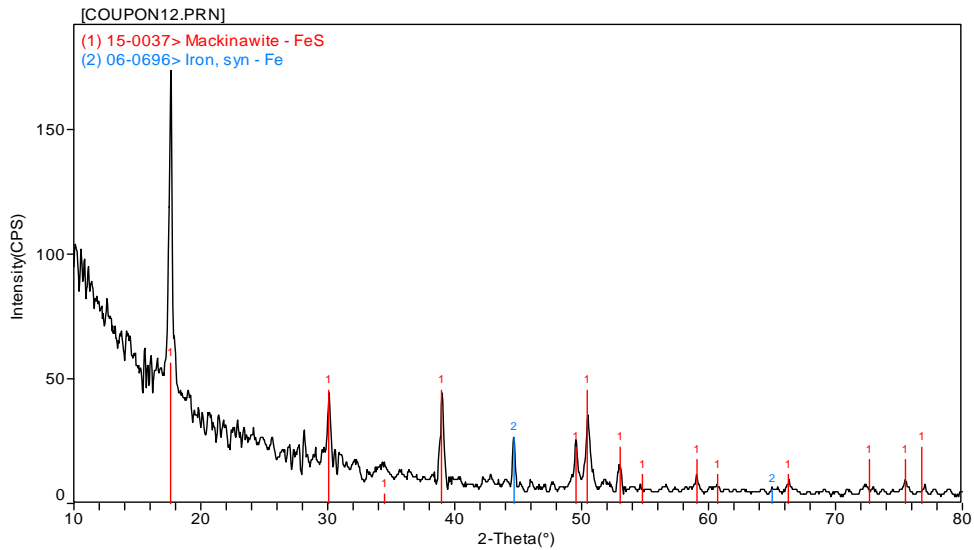


Figure 14. XRD results of iron sulfide films formed on the X65 carbon steel surface under the conditions of 10% H<sub>2</sub>S (H<sub>2</sub>S/N<sub>2</sub> gas), T 80°C, pH 5.2, Fe<sup>2+</sup> = 10ppm, the total reaction time is 24 hours.

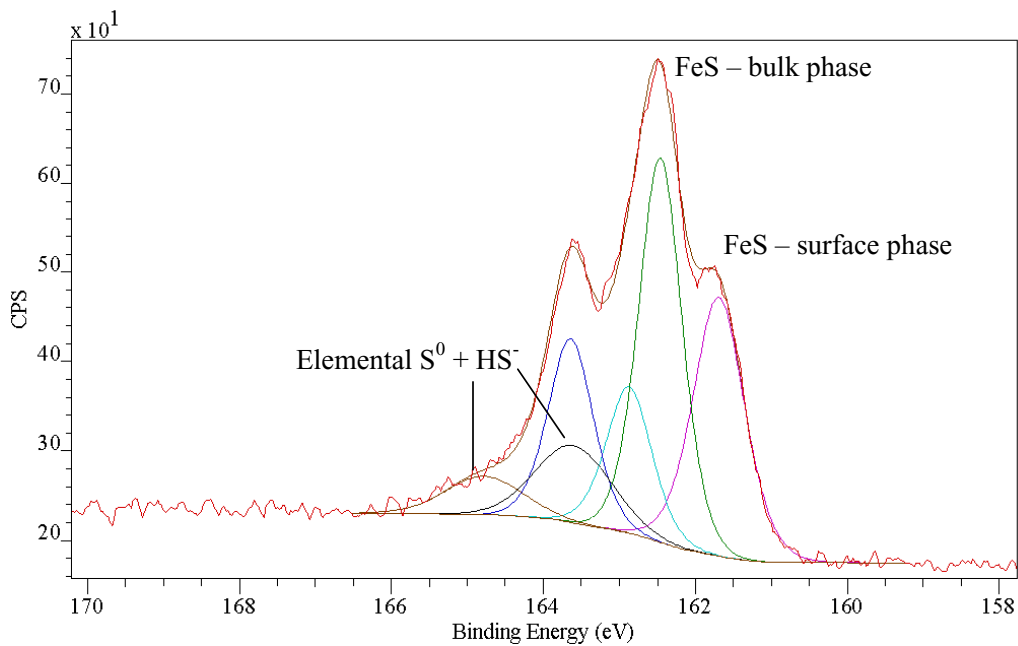


Figure 15. XPS multiplex S2p spectrum recorded at the surface of specimen under the conditions of T 80°C, pH 5, Fe<sup>2+</sup> 0ppm, H<sub>2</sub>S 10%, and reaction time 23 hours.

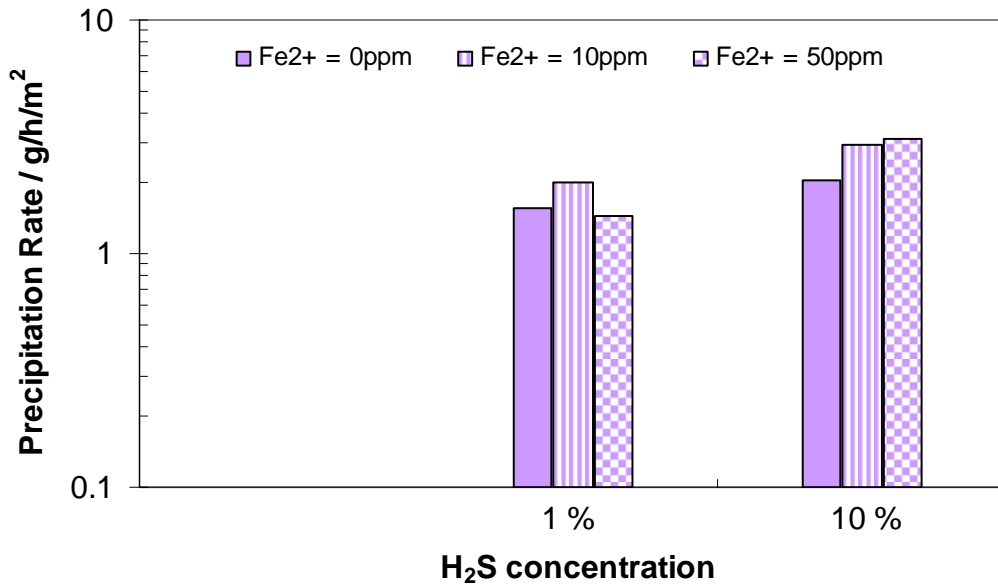


Figure 16. The precipitation rate of iron sulfide formed on the X65 carbon steel surface at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solution with H<sub>2</sub>S/N<sub>2</sub> under the conditions of T 60°C, the total reaction time is 1 hour.

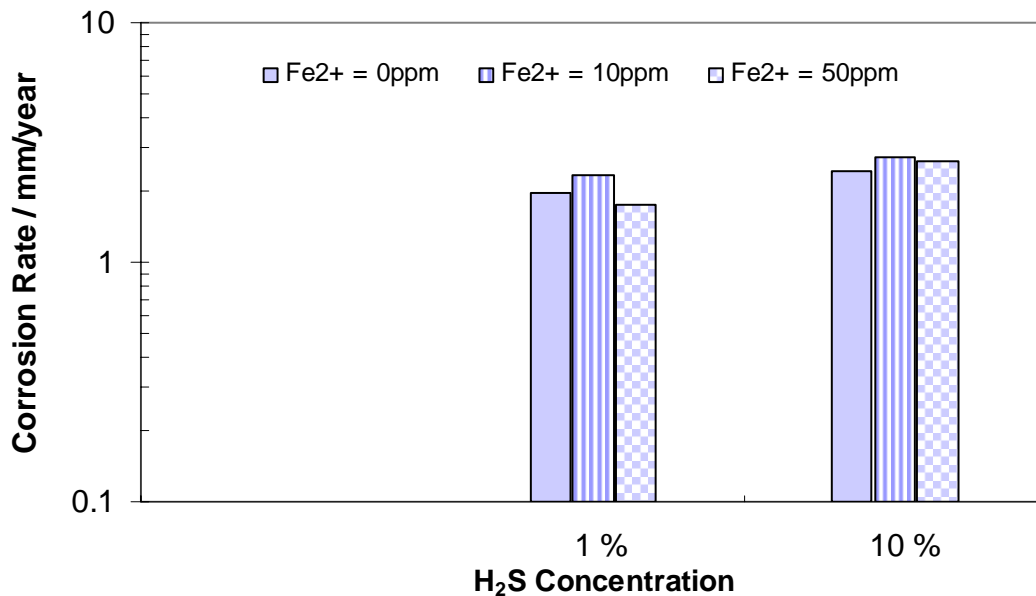


Figure 17. The corrosion rate of X65 carbon steel at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/N<sub>2</sub> under the condition of T 60°C, the total reaction time is 1 hour.



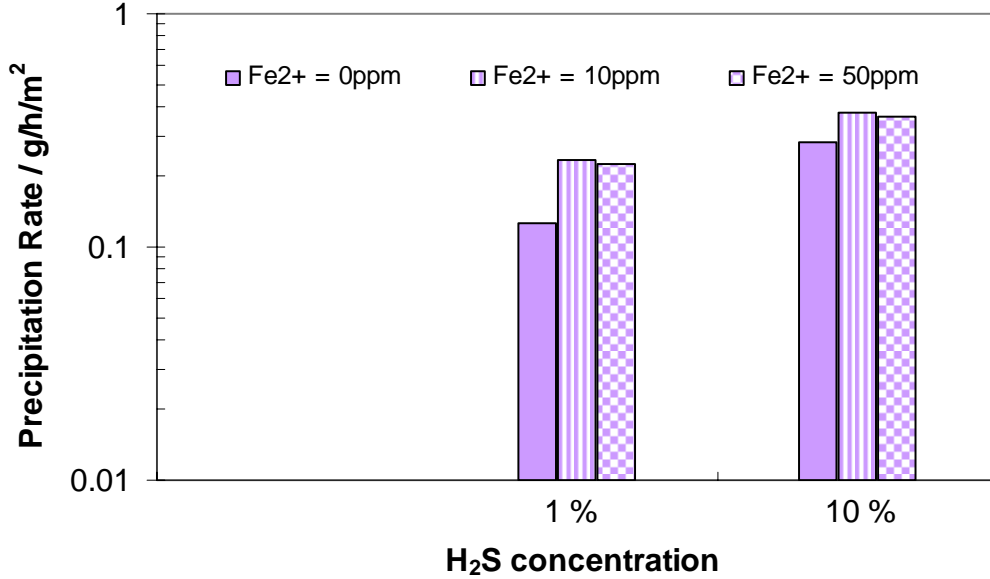


Figure 18. The precipitation rate of iron sulfide formed on the X65 carbon steel surface at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solution with H<sub>2</sub>S/N<sub>2</sub> under the conditions of T 60°C, the total reaction time is approximately 20 hours.

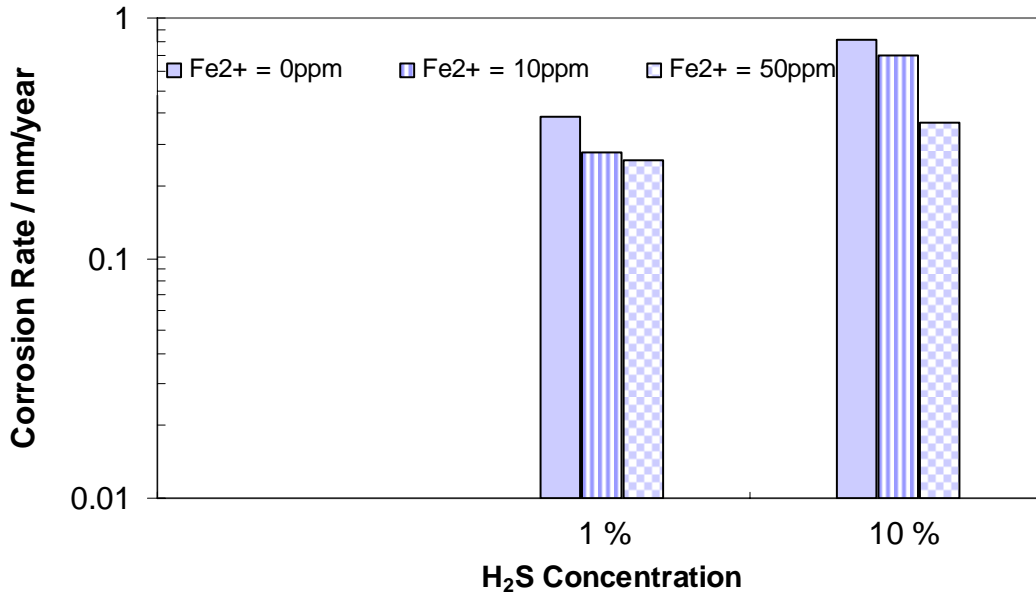


Figure 19. The corrosion rate of X65 carbon steel at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/N<sub>2</sub> under the condition of T 60°C, the total reaction time is approximately 20 hours.

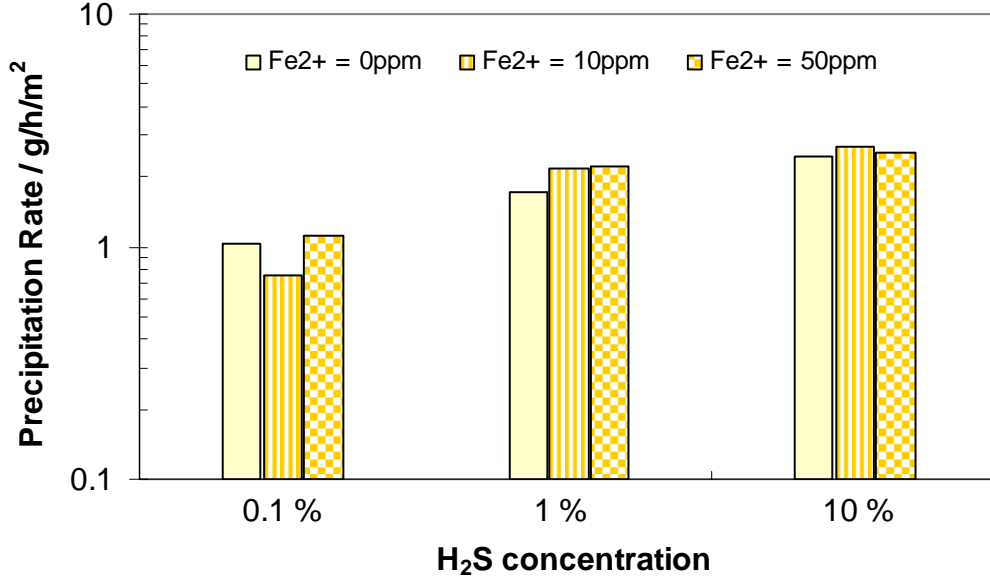


Figure 20. The precipitation rate of films formed on the X65 carbon steel surface at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/CO<sub>2</sub> under the conditions of T 80°C, pH 6.5~6.6, the total reaction time is 1 hour.

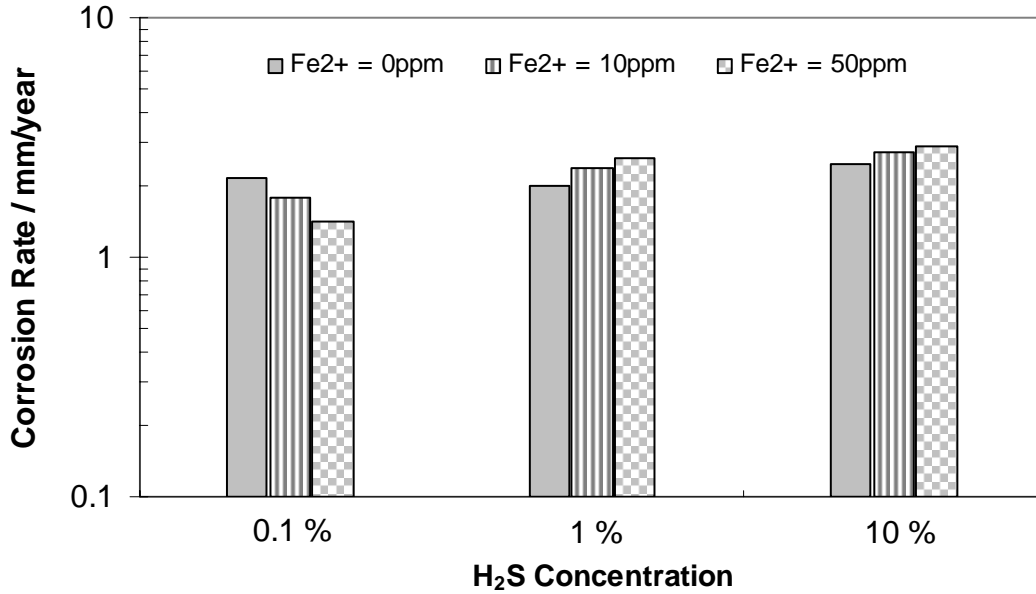


Figure 21. The corrosion rate of X65 carbon steel at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/CO<sub>2</sub> under the conditions of T 80°C, pH 6.5~6.6, the total reaction time is 1 hour.

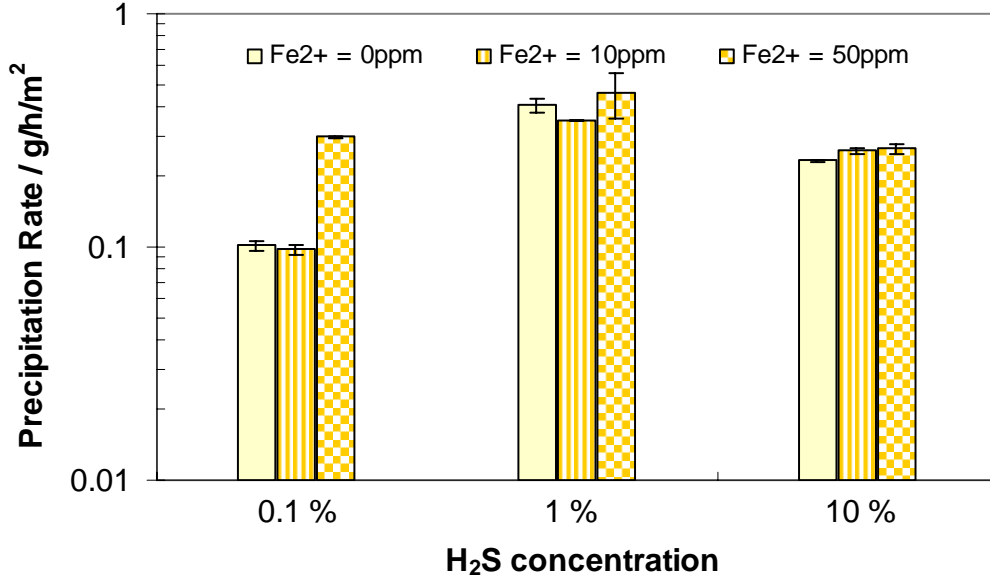


Figure 22. The precipitation rate of films formed on the X65 carbon steel surface at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/CO<sub>2</sub> under the conditions of T 80°C, pH 6.5~6.6, the total reaction time is 24 hours.

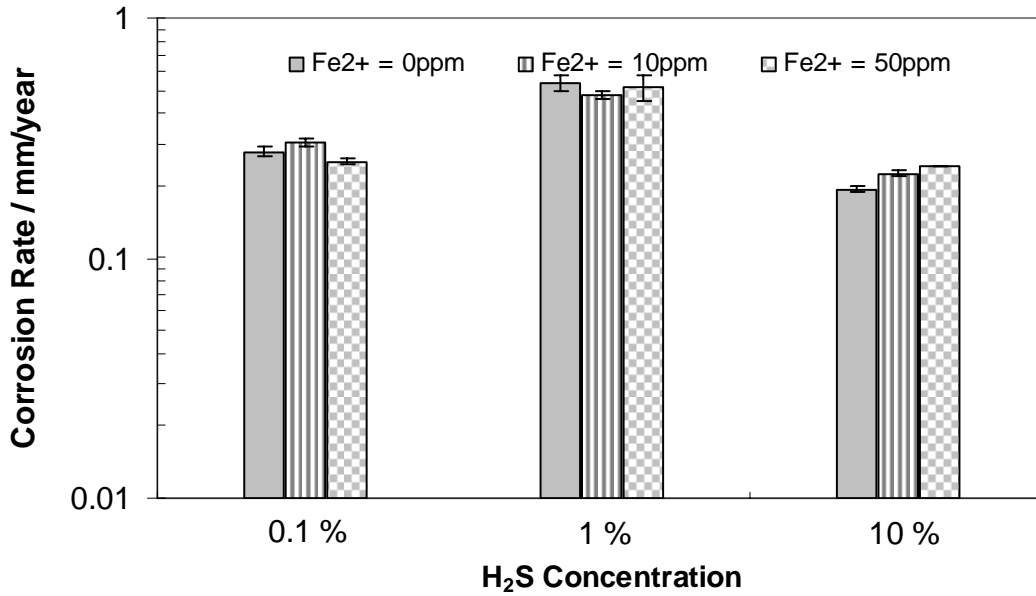


Figure 23. The corrosion rate of X65 carbon steel at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/CO<sub>2</sub> under the conditions of T 80°C, pH 6.5~6.6, the total reaction time is 24 hours.

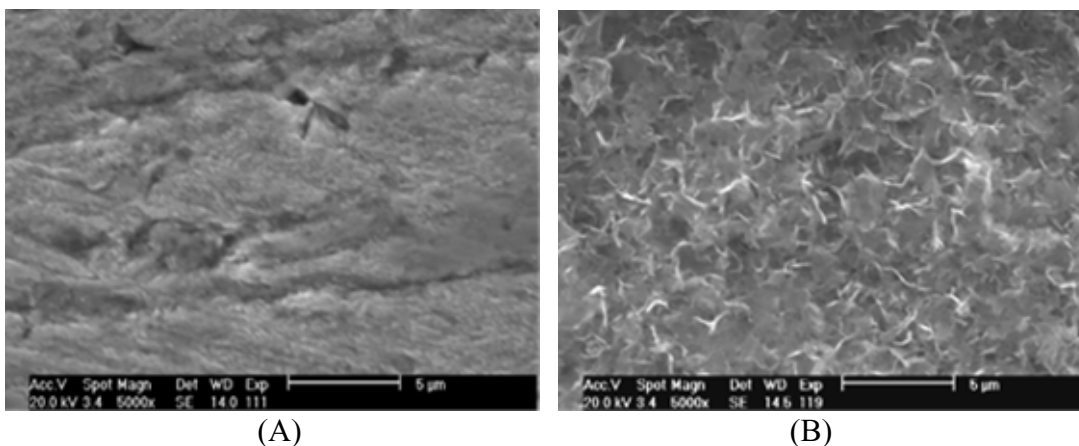


Figure 24. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 0ppm, the total reaction time is (A) 1 hour, (B) 24 hours.

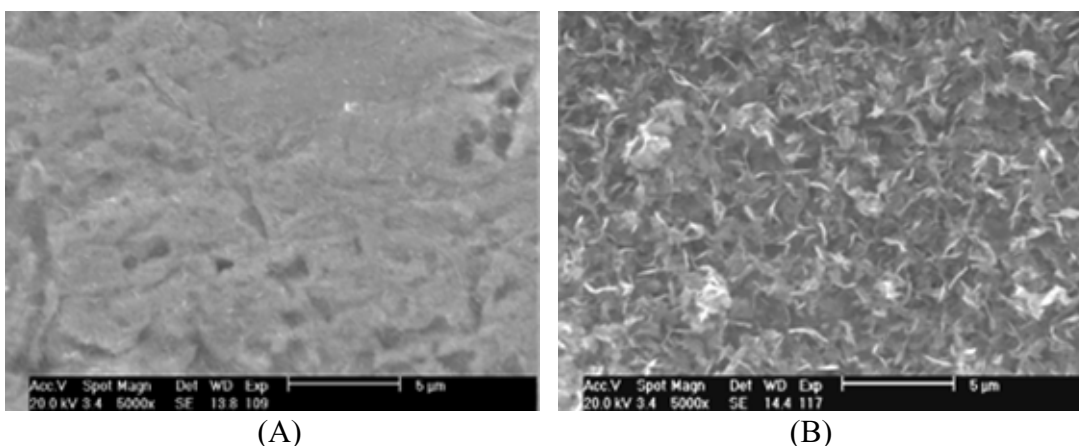


Figure 25. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 10ppm, the total reaction time is (A) 1 hour, (B) 24 hours.

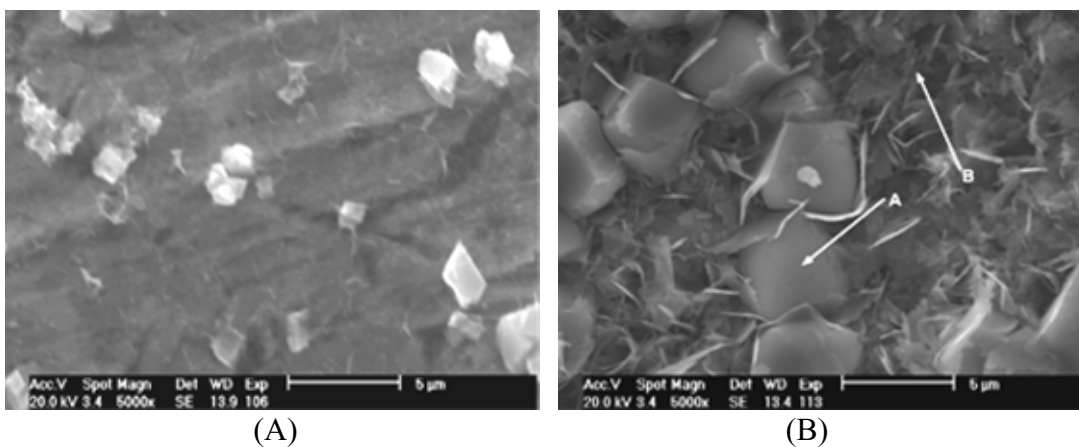


Figure 26. The morphology (5000X) of films formed on the X65 carbon steel surface under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 50ppm, the total reaction time is (A) 1 hour, (B) 24 hours.

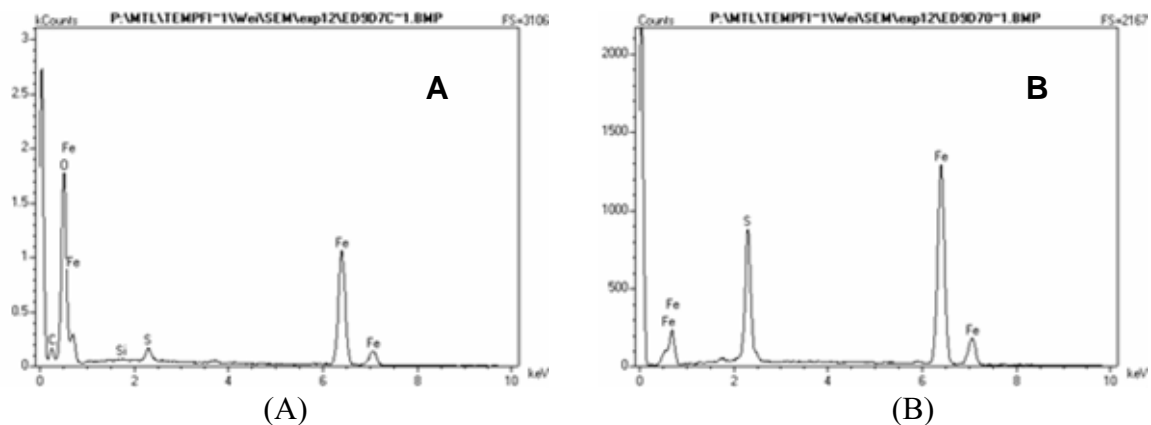


Figure 27. The EDS results of films (Part A and Part B in Figure 26) formed on the X65 carbon steel surface under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 50ppm, the total reaction time is 24 hour.

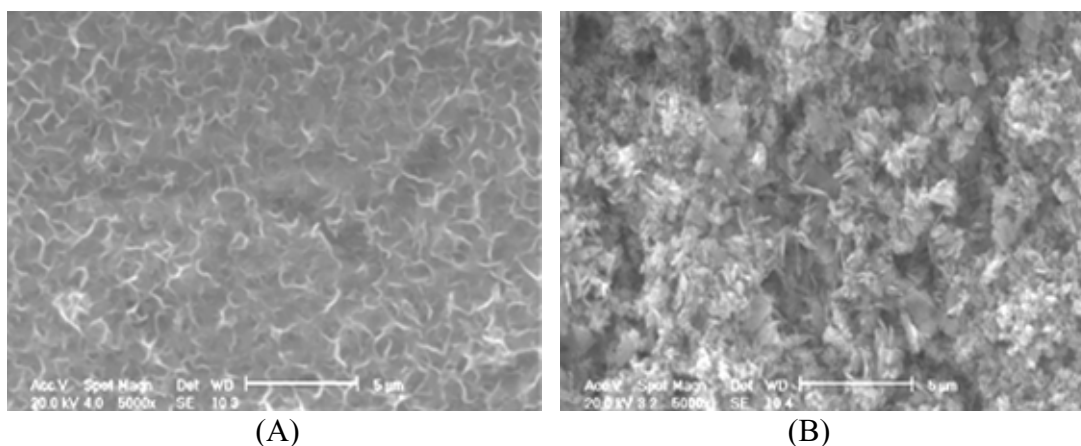


Figure 28. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 0ppm, the total reaction time is (A) 1 hour, (B) 24 hours.

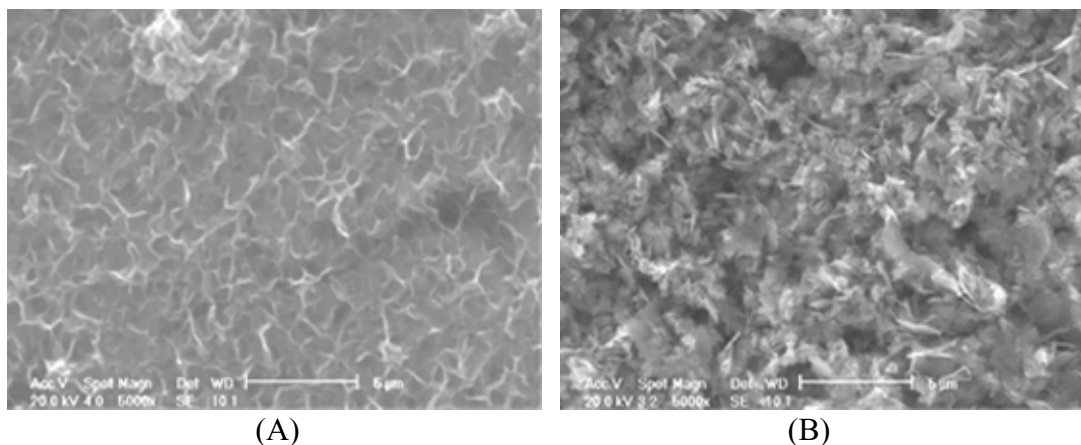


Figure 29. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 10ppm, the total reaction time is (A) 1 hour, (B) 24 hours.

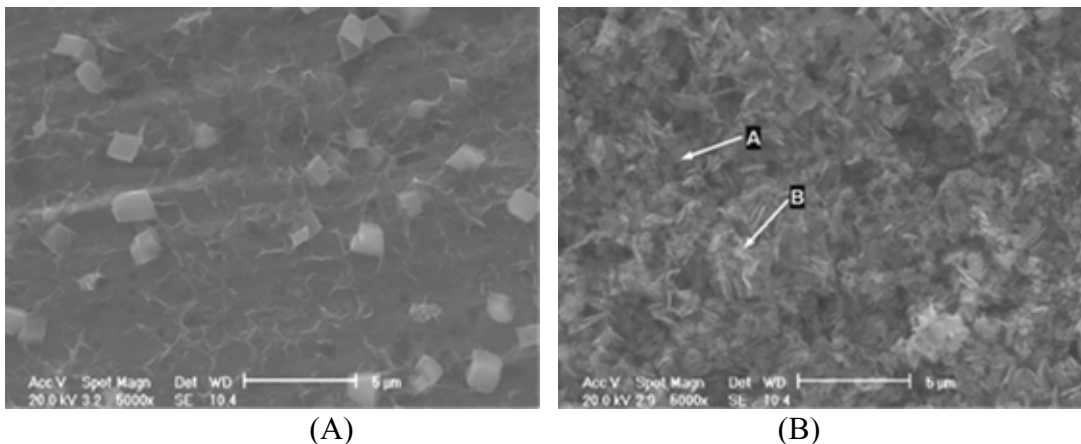


Figure 30. The morphology (5000X) of films formed on the X65 carbon steel surface under the conditions of 1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 50ppm, the total reaction time is (A) 1 hour, (B) 24 hours.

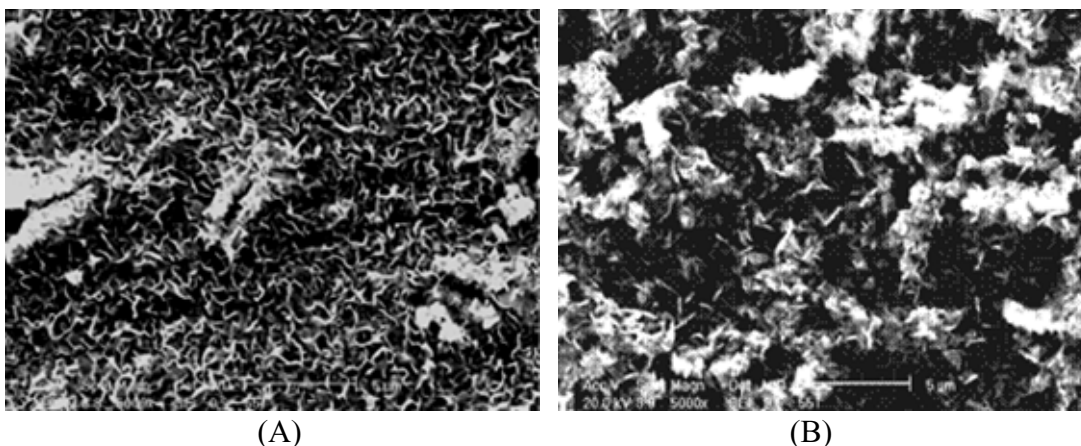


Figure 31. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 10% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 0ppm, the total reaction time is (A) 0.83 hour, (B) 24 hours.

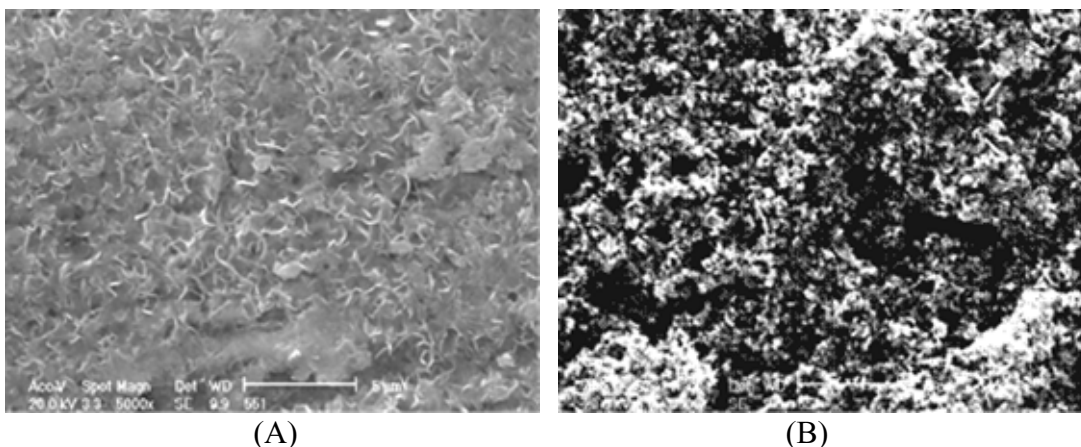


Figure 32. The morphology (5000X) of iron sulfide films formed on the X65 carbon steel surface under the conditions of 10% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 50ppm, the total reaction time is (A) 0.83 hour, (B) 24 hours.

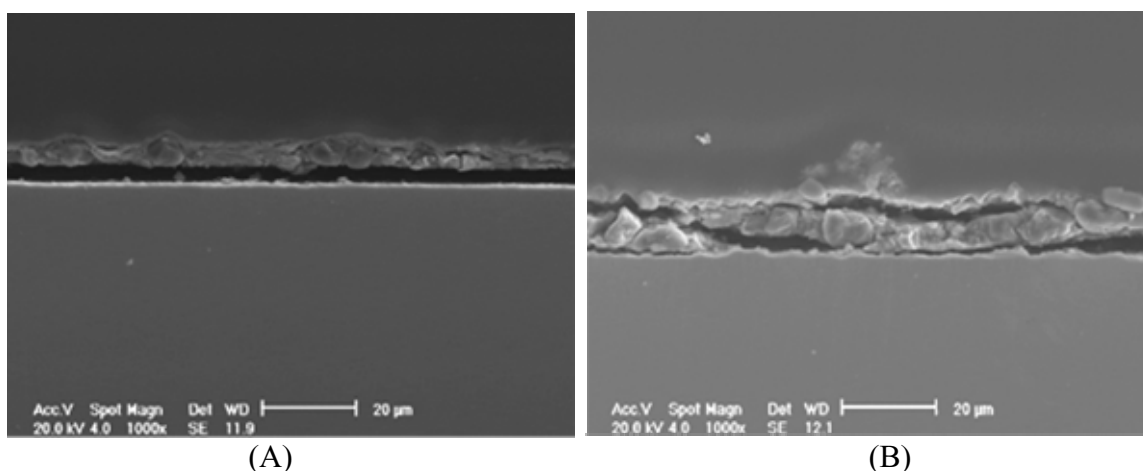


Figure 33. Cross section of the films formed on the X65 carbon steel surface (at 1000X) under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, (A)  $\text{Fe}^{2+}=0\text{ppm}$ , (B)  $\text{Fe}^{2+}=50\text{ppm}$ , the total reaction time is 24 hours.

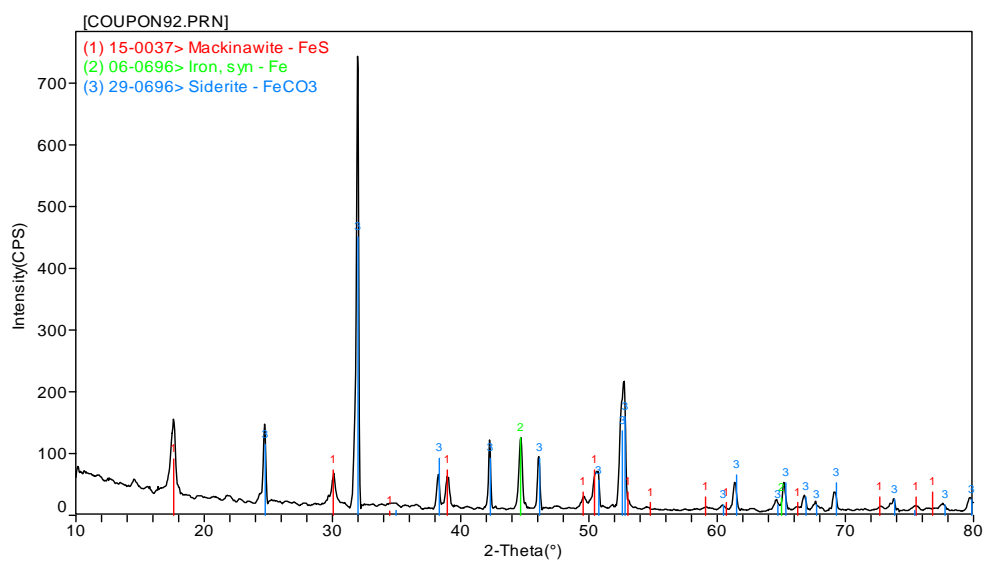


Figure 34. XRD results of the films formed on the X65 carbon steel surface under the conditions of 0.1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6,  $\text{Fe}^{2+}=50\text{ppm}$ , the total reaction time is 24 hours.

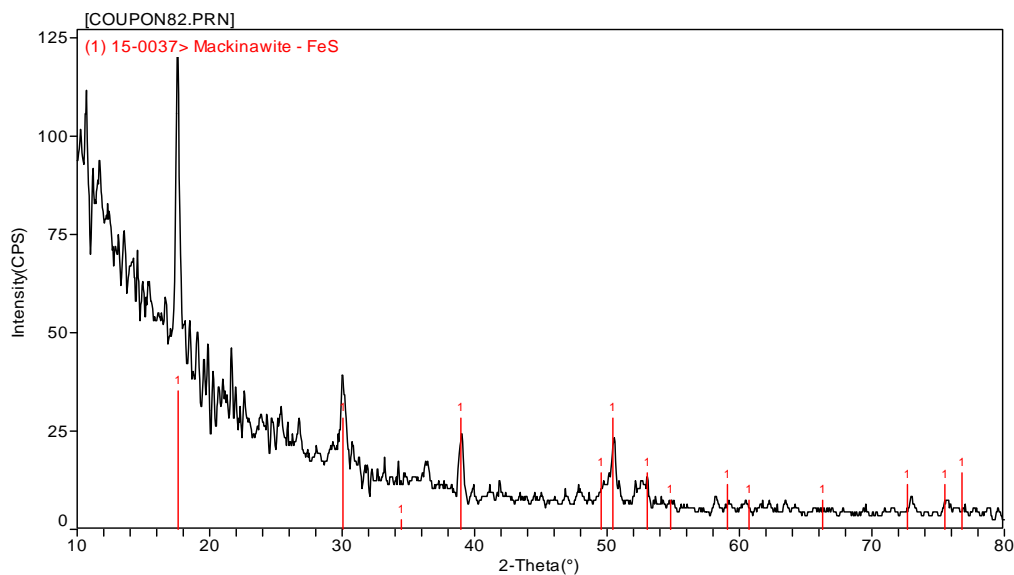


Figure 35. XRD results of the films formed on the X65 carbon steel surface under the conditions of 1% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 50ppm, the total reaction time is 24 hours.

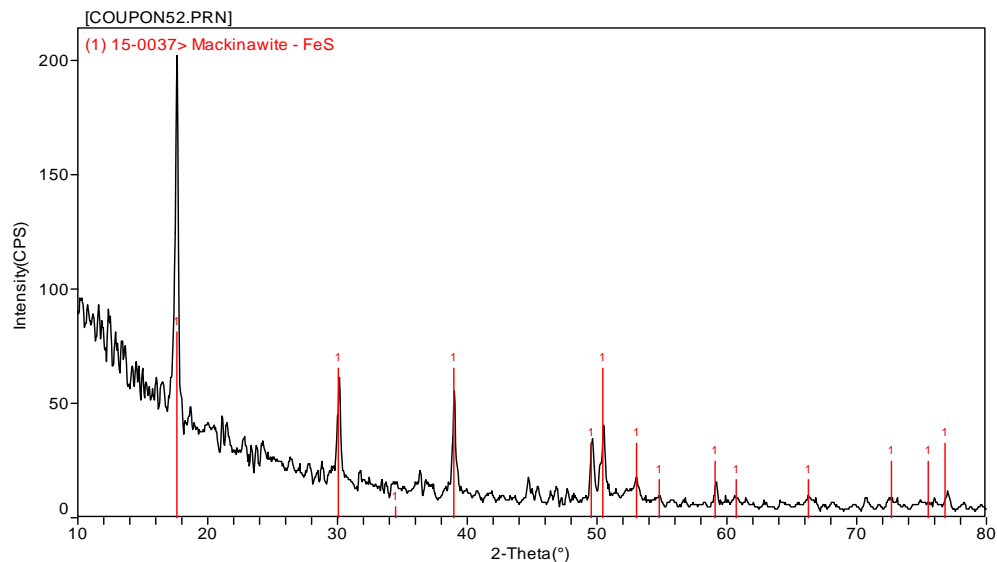


Figure 36. XRD results of the films formed on the X65 carbon steel surface under the conditions of 10% H<sub>2</sub>S (H<sub>2</sub>S/CO<sub>2</sub> gas), T 80°C, pH 6.5~6.6, Fe<sup>2+</sup> = 50ppm, the total reaction time is 24 hours.



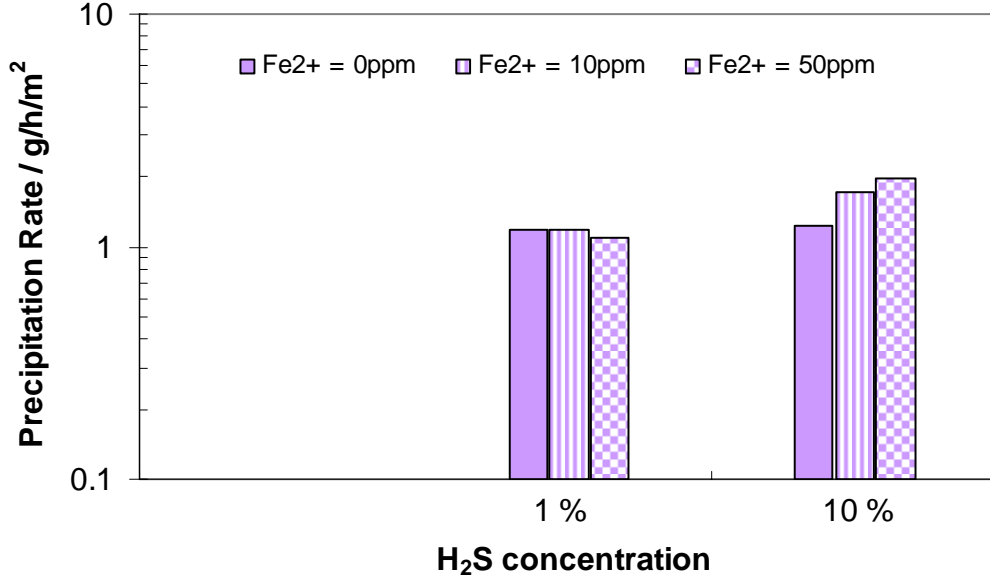


Figure 37. The precipitation rate of films formed on the X65 carbon steel surface at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/CO<sub>2</sub> under the conditions of T 60°C, pH 6.5~6.6, the total reaction time is 1 hour.

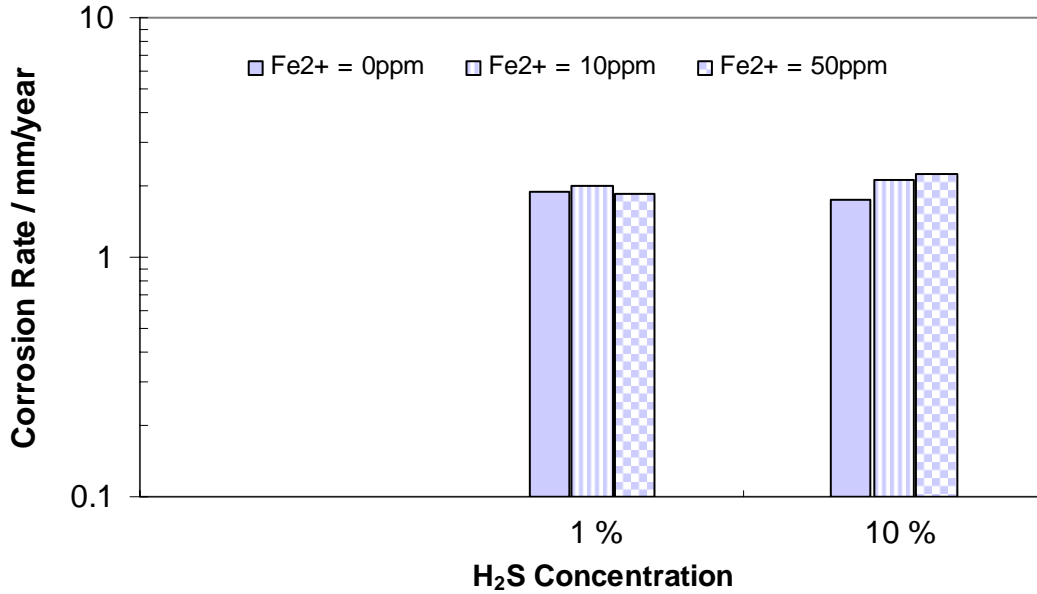


Figure 38. The corrosion rate of X65 carbon steel at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/CO<sub>2</sub> under the conditions of T 60°C, pH 6.5~6.6, the total reaction time is 1 hour.

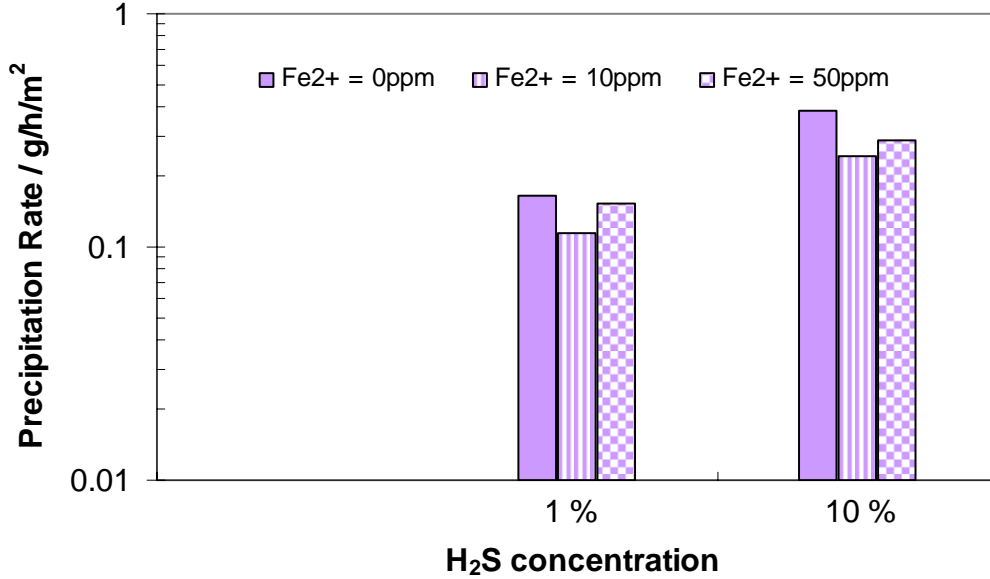


Figure 39. The precipitation rate of films formed on the X65 carbon steel surface at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/CO<sub>2</sub> under the conditions of T 60°C, pH 6.5~6.6, the total reaction time is approximately 20 hours.

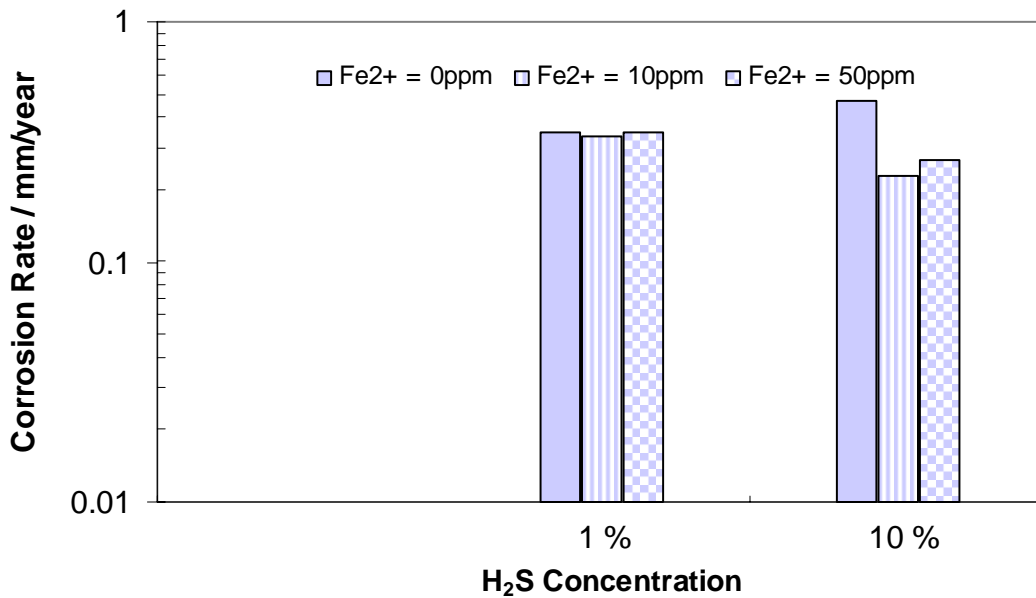


Figure 40. The corrosion rate of X65 carbon steel at different H<sub>2</sub>S concentration and initial Fe<sup>2+</sup> concentration in the solutions with H<sub>2</sub>S/CO<sub>2</sub> under the conditions of T 60°C, pH 6.5~6.6, the total reaction time is approximately 20 hours.