

A MECHANISTIC MODEL OF H₂S CORROSION OF MILD STEEL

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ABSTRACT

Glass cell experiments were conducted to investigate the mechanism and kinetics of mild steel corrosion in H₂S environments which is accompanied by iron sulfide scale formation. By using the weight change method, the rates of corrosion and scale formation were found. It was also concluded that mackinawite is the predominant type of iron sulfide that formed on the steel surface under the test conditions studied, probably by a direct reaction of H₂S with the underlying steel. Based on the experimental results, a mechanistic model of uniform H₂S corrosion of mild steel is presented that is able to predict the rate of corrosion with time. In the model, the corrosion rate of mild steel in H₂S corrosion is a function of H₂S gas concentration, temperature, velocity, and the protectiveness of the mackinawite scale. The amount of scale retained on the steel surface depends on the scale formation rate as well as the scale damage rate. The scale formation may occur by corrosion and/or precipitation, while the scale damage can be by mechanical or chemical means.

Keywords: mechanism, kinetics, mackinawite, mechanistic model, solid state reaction, H₂S corrosion

INTRODUCTION

Internal CO₂ corrosion of mild steel in the presence of hydrogen sulfide (H₂S) represents a significant problem for the oil and gas industry¹⁻⁶. Surface scale formation is one of the important factors governing the corrosion rate. The scale growth depends primarily on the kinetics of the scale formation. As a part of a larger project focusing on the formation of both iron carbonate and iron sulfides in CO₂/H₂S corrosion, the kinetics of iron carbonate has been quantified and reported in a recent publication⁷. In contrast to relatively straightforward iron carbonate precipitation in pure CO₂ corrosion, in an H₂S environment, many types of iron sulfides^{1-5, 8, 9} may form such as amorphous ferrous sulfide, mackinawite, cubic ferrous sulfide, smythite, greigite, pyrrhotite, troilite, and pyrite, among which mackinawite is considered to form first on the steel surface by a direct surface reaction¹⁻⁴. The unknown mechanisms of H₂S corrosion makes it difficult to quantify the kinetics of iron sulfide scale formation. Therefore, in this study, the mechanism of H₂S corrosion as well as iron sulfide formation is investigated and a model of the overall process is proposed in this paper.

EXPERIMENTAL PROCEDURE

The experiments which served as a basis for the development of the model were already described in the previous publication.¹⁰ Here, only the most important features of the experimental program will be mentioned to facilitate following of the text below. The experiments were performed at atmospheric pressure in glass cells filled with a 1 wt.% NaCl aqueous solution continuously purged with a mixture N₂ (>99.9 vol%) and H₂S gases (H₂S concentrations in the gas inlet: 0.0075 vol% to 10 vol%). The H₂S concentrations in both the gas phase (in ppm_w and Pa) and the liquid phase (in mol/l) under different test conditions are shown in Table 2. Rectangular and cylindrical specimens made from X65 pipeline steel were exposed for 1-24h at 25-80°C. The chemical composition of the X65 steel used for all the experiments is shown in Table 1. Weight change measurement was used to obtain both the corrosion rate of mild steel and the retention rate of iron sulfide scale.

SUMMARY OF THE EXPERIMENTAL RESULTS

It was observed and previously reported¹⁰ that in pure H₂S corrosion of mild steel there was no significant effect of dissolved Fe²⁺ concentration on neither the corrosion rate nor the iron sulfide scale retention rate. This was in sharp contrast with pure CO₂ corrosion where the iron carbonate scale formation rate is a strong function of dissolved Fe²⁺ concentration i.e. it depends heavily on iron carbonate supersaturation, which is a major driving force for iron carbonate scale formation by precipitation.⁷ Actually it was long known that iron sulfide films form even in solutions which are well undersaturated,¹ i.e. at pH much lower than pH5.0-5.5 which was used in this study. In addition, the structure and morphology of the iron sulfide films formed in H₂S corrosion (which was

identified primarily as mackinawite) is very different from the iron carbonate films formed in CO₂ corrosion. One observes layered crystalline iron sulfide films, with cracks and delaminations, often with the imprint of the underlying metal surface clearly visible even after long exposures.¹⁰ Therefore it is hypothesized here that iron sulfide films observed in the experiments form primarily by a direct heterogeneous chemical reaction between H₂S and iron at the steel surface (often referred to as a “solid state reaction”).* This hypothesis does not exclude the possibility of iron sulfide films forming by precipitation in supersaturated solutions 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 H₂S and the steel surface. Even more importantly it is thought that the thin and tight iron sulfide films formed in this way are one of the most important controlling factors in H₂S corrosion.

Effect of H₂S concentration

A number of experiments were conducted to investigate the effect of H₂S gas concentration on the mackinawite scale formation in the solutions with H₂S/N₂ at the temperature of 80°C. Figure 1 shows the comparison of corrosion rate and scale retention rates expressed in the same molar units vs. H₂S gas concentration after a 1 hour exposure. The value for the scaling tendency which is the ratio of the two rates is also shown. The comparison indicates that both the corrosion rate and scale retention rate increase with the increase of H₂S gas concentration, however, the corrosion rate is always higher than the scale retention rate. The scaling 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. As a very small increase in the dissolved Fe²⁺ was measured in the solution it was concluded that some of the iron sulfide that formed on the steel spalled off in a spontaneous process probably due to intrinsic growth stresses (since no flow was present in these experiments that would impose extrinsic hydrodynamic stresses). In Figure 2 the same kind of data is presented for a 24 hour exposure where a broader range of H₂S gas concentrations was used: 0.0075 vol% – 10 vol%. The same conclusions apply as for the 1 hour exposure with the exception that the magnitude of both the corrosion rate and scale retention rate is almost an order of magnitude lower after 24 hours. Interestingly, the scaling tendency remains in approximately the same range 33-70% 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 reaction rate with time is accentuated by the direct comparison of the 1-hour and 24-hour corrosion rates (Figure 3) and scale retention rates (Figure 4) at different H₂S gas concentration. Clearly the iron sulfide scale that is retained on the surface over time becomes gradually more protective.

Effect of temperature

The effect of temperature on both the corrosion rate and the scale retention rate is shown in Figure 5 for a 1 hour exposure and in Figure 6 for a 24 hour exposure at 1 vol% H₂S gas concentration. Very weak temperature dependence is observed even for the

* This hypothesis is not entirely new, it has been mentioned a number of times in various publications on H₂S corrosion of steel.¹⁻⁴

shorter term exposure which all but disappears for the longer exposure times. The same is obtained in experiments at H₂S gas concentrations of 10 vol%, as shown in Figure 7 and Figure 8. This seems to suggest that the corrosion rate is predominantly controlled by the presence of the iron sulfide scale, 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 8000 rpm which corresponds to a peripheral velocity of approximately 4 m/s and a wall-shear stress of 57 Pa, in experiments done with 0.04 vol% of H₂S in the gas phase. The corrosion rate as a function of reaction time at different velocities is shown in Figure 9. The corrosion rate clearly increases with velocity and the effect is much more pronounced for shorter exposure times. For longer exposures in flowing conditions, the corrosion rates decrease significantly just as they did in experiments conducted under stagnant conditions, due to a buildup of a protective iron sulfide scale. However, as shown in Figure 10, the scaling tendency which is on average 50%, in stagnant conditions decreases to below 20% under flowing conditions. This suggests that a much larger fraction of the iron sulfide scale formed in the corrosion process is lost to the solution due to the hydrodynamic stresses induced by the flow. Iron sulfide film dissolution could be excluded due to a slight supersaturation of the solution with respect to mackinawite.

It has been reported^{6,11} that the presence of chloride ions may have an effect on the H₂S corrosion rate of the mild steel; however, this effect was not studied and will not be discussed in the present paper.

MODEL OF H₂S CORROSION

Physico-chemical model

There seems to be a consensus that mackinawite scale forms on the steel surface as a product of H₂S corrosion^{1-4, 8, 9}. In this study mackinawite was also found to be the dominant iron sulfide species, as previously described¹⁰. Clearly, other types of iron sulfide film were observed in the past on steel surfaces attacked by H₂S, particularly in long exposures; however it is still unclear what effect the variation in film composition may have on the corrosion rate.

Based on an analogy with iron carbonate formation in CO₂ solutions and due to its rather low solubility, mackinawite was also thought to form by a precipitation mechanism¹⁰. While this is clearly a theoretical possibility, as argued above, mackinawite formation via a direct heterogeneous chemical reaction with iron on the steel surface seems to be the more relevant mechanism. Many pieces of evidence seem to support this conclusion:

- very high reactivity of H₂S with iron, mackinawite scale has been shown to form in extremely fast (less than seconds)^{1, 2, 12}, which is much faster than what one would expect from typical kinetics of a precipitation process¹;
- formation of mackinawite scale in highly undersaturated solutions (pH2-3) where it is thermodynamically unstable (soluble^{*})¹;
- no effect of solution supersaturation level on the rate of mackinawite formation¹⁰;
- layered structure of mackinawite scale often containing cracks and delaminations, with steel surface imprint visible even after rather long exposures¹⁰ (also see Figure 11);
- amount of mackinawite scale always being smaller than the amount of iron lost to corrosion of mild steel (expressed in molar units, see for example Figure 1 - Figure 8) and a lack of substantial mackinawite scale formation on stainless steel and other corrosion resistant alloys (see Figure 12), both suggesting that the iron “source” in mackinawite is the metal itself, rather than the bulk solution;
- very similar structure and morphology of the mackinawite scale seen in high temperature sulfidation of mild steel exposed to gaseous and hydrocarbon environments^{13, 14, 15}, where the precipitation mechanism is impossible.

If this is accepted as sufficient evidence, it can be concluded that the corrosion of mild steel in H₂S aqueous environments proceeds by a very fast direct heterogeneous chemical reaction at the steel surface to form a solid adherent mackinawite scale. The overall reaction scheme can be written as:



As both the initial and final state of Fe is solid, this reaction is often referred to as the “solid state corrosion reaction”. The formed mackinawite scale may dissolve depending on the solution saturation level. For the typical pH range seen in oilfield brines (pH 4-7) the solution is almost always supersaturated with respect to iron sulfide and the mackinawite scale does not dissolve, actually in long exposures it may grow slowly by precipitation from the bulk¹⁶. If the pH is decreased below pH4 the dissolution rate will increase to a point where in the range pH2-pH3 no mackinawite can be detected on the steel surface.¹

Even if aqueous H₂S is a weak acid just like carbonic acid, the corrosion mechanism proposed above differs in sequence from what is believed to happen to steel

* A case can be made that the reasoning about solubility of iron sulfide based on conditions *in the bulk* is invalid since *at a steel surface*, due to corrosion of iron, there always exists a somewhat higher pH and a possibility to exceed the solubility limit, even in acidic solutions. In an extreme this would apply to any pH (however low) as well as to other precipitating salts such as iron carbonate. In reality, iron carbonate films *are never* observed at pH significantly below the solubility limit (based on bulk conditions) while iron sulfide films *are*. This fact undermines the theoretically plausible argument about the importance of surface conditions. In addition, basing arguments on a surface pH, which is virtually immeasurable, is not very practical and is incompatible with the bulk of the chemical and electrochemical literature.

exposed to pure CO₂ solutions in the same pH range (pH4-7). In CO₂ corrosion of steel, iron first dissolves to form aqueous Fe²⁺ which then may or may not precipitate at the metal surface to form iron carbonate (e.g. below pH5 iron carbonate typically does not form and above pH6 it is almost always there). In H₂S solutions, steel corrosion proceeds to first form a mackinawite scale which then may or may not dissolve.

This first layer of mackinawite that forms very fast is extremely thin (<< 1 μm) and is invisible to the naked eye and even by a typical SEM¹². However it is rather protective and for example reduces a CO₂ driven corrosion rate typically by an order of magnitude¹².

With increased exposure times, at high H₂S concentrations and temperature, the thin mackinawite film grows rapidly. It is still unclear whether this growth is supported by H₂S penetration through the crystalline layer (by solid state diffusion) or is it by ionic conduction of S²⁻, HS⁻, Fe²⁺, etc. through the semiconductive mackinawite matrix. Outward diffusion of ferrous species is consistent with an electrochemical iron dissolution mechanism and a mackinawite continued growth at the outer film/solution interface. The inward diffusion of sulfide species is consistent with the here proposed direct chemical reaction mechanism (1) and leads to mackinawite formation at the inner film interface with the steel. In both cases the mechanical integrity of the growing layer is weakened. Outward migration of Fe²⁺ leaves “voids” at the metal/mackinawite interface i.e. it “undermines” the film what manifests itself as poor “adhesion” of the film to the steel. Inward diffusion of the sulfide species leads to internal stresses in the film as described below.

In the latter scenario, the solid state corrosion reaction (1) keeps generating mackinawite at the inner interface of the mackinawite film with the steel. This leads to epitaxial stresses arising from the different crystalline structures of the source iron and the iron sulfide that formed in its place¹³. What is more important, the solid FeS is calculated to be 2.56 times more voluminous than the iron it replaced, at the mackinawite/steel interface. This, so called Pilling-Bedworth ratio (PBR)¹³, leads to an increase of internal compressive stresses in the mackinawite film. When the mechanical limit of the mackinawite is exceeded micro-cracking of the film occurs, thereby relieving the internal stresses and the process starts all over again. These micro-cracks, which most likely occur at mackinawite grain boundaries, serve as preferred pathways for more rapid penetration of sulfide species which fuel the solid state reaction (1) to go faster¹⁷. It is expected that in some instances, at stress concentration points, large cracks in the film may appear as shown in Figure 11. The sulfide species penetrate even more easily at these locations to feed the corrosion reaction (1), which makes even more sulfide film at those locations and causes even more internal stressing and film failure. It is not difficult to see how this feed-forward scenario could lead to an exponential growth of the reaction rate and localized corrosion. This scenario also offers an explanation for an apparently odd occurrence in H₂S corrosion: experimental observations indicate that pits are usually full of iron sulfide and even have a cap of sulfide which is thicker than elsewhere on the steel surface, as shown in Figure 13 provided by Brown¹⁸. This appearance is very different from localized attack in CO₂ corrosion where pits are bare while the

surrounding steel is covered with a protective film. Finally, in this scenario the hydrogen gas evolved by the corrosion reaction (1) builds up at the steel/film interface as it diffuses out through the mackinawite film with difficulty. This may lead to the retardation of the atomic hydrogen recombination reaction and hydrogen penetration into the steel. Indeed, the hydrogen built-up at the steel/film interface may even bubble out and cause further damage to the mackinawite film. The last few points are purely hypothetical and were discussed here only because they are consistent with proposed mechanism of H₂S corrosion of steel and the resulting iron sulfide film growth. As there is no direct evidence for them in the short term experiments presented here, these hypotheses need to be directly confirmed in the future.

As the mackinawite film goes through the growth/micro-cracking cycle, it thickens. As larger cracks appear, whole layers of the film may partially delaminate from the steel surface starting another cycle of rapid film growth underneath, as shown in Figure 14. Over longer exposures, this cyclic growth/delamination process leads to a layered outer sulfide scale which is very porous. As this outer scale grows it will spontaneously spall a process assisted by flow. Notwithstanding, if the bulk solution is undersaturated (typically at 3 < pH < 4) the outer porous mackinawite scale will dissolve away as fast as it forms, what may happen even to tight inner mackinawite film at pH < 3.¹

In summary, in H₂S corrosion of mild steel two types of mackinawite layers form on the steel surface:

- a very thin (<<1 μm) and tight inner film and
- a much thicker (1-10 μm) layered outer scale which is loose and very porous.

The outer scale may be intermixed with any iron sulfide or iron carbonate that may have precipitated out given the right water chemistry and long exposure time, what would change its properties and appearance. Both the inner mackinawite film and the outer scale act as barriers for the diffusion of the sulfide species* fueling the solid state corrosion reaction (1). This is in addition to the diffusion resistance through the aqueous mass transfer boundary layer.

Mathematical model

Based on the experimental results and the description of the H₂S corrosion process presented above a mathematical model can be constructed. The key assumptions are:

- the corrosion process happens via a direct heterogeneous solid state reaction (1) at the steel surface;
- there is always a very thin (<<1 μm) but dense film of mackinawite at the steel surface which acts as a solid state diffusion barrier for the sulfide species involved in the corrosion reaction;
- this film continuously goes through a cyclic process of growth, cracking and delamination, what generates the outer mackinawite scale;

* In the authors' opinion, the outward diffusion by the Fe²⁺ can be neglected as it is inconsistent with the proposed solid state corrosion reaction (1) and would lead to a formation of a very different looking and behaving sulfide film which is more akin to iron carbonate.

- this outer scale grows in thickness (typically $>1\mu\text{m}$) over time and also presents a diffusion barrier;
- the outer scale is layered, very porous and rather loosely attached, over time it peels and spalls, a process aggravated by the flow.

Due to the presence of the inner mackinawite film and possibly the outer scale it is assumed that the corrosion rate of steel in H_2S solutions is always under mass transfer control. Based on the discussions above, a schematic of the H_2S corrosion process is shown in Figure 15.

One can write the flux of sulfide species due to:

- convective diffusion through the mass transfer boundary layer

$$Flux_{H_2S} = k_{m,H_2S} (c_{b,H_2S} - c_{o,H_2S}) \quad (2)$$

- molecular diffusion through the liquid in the porous outer scale

$$Flux_{H_2S} = \frac{D_{H_2S} \varepsilon \Psi}{\delta_{os}} (c_{o,H_2S} - c_{i,H_2S}) \quad (3)$$

- solid state diffusion through the inner mackinawite film

$$Flux_{H_2S} = A_{H_2S} e^{-\frac{B_{H_2S}}{RT_k}} \ln \left(\frac{c_{i,H_2S}}{c_{s,H_2S}} \right) \quad (4)$$

where:

$Flux_{H_2S}$	is expressed in $\text{mol}/(\text{m}^2\text{s})$,
k_{m,H_2S}	is the mass transfer coefficient for H_2S in the hydrodynamic boundary layer, $k_{m,H_2S} = 1.00 \times 10^{-4}$ in nearly stagnant condition, in m/s ,
c_{b,H_2S}	is the bulk concentration of H_2S in the liquid phase in mol/m^3 ,
c_{o,H_2S}	is the interfacial concentration of H_2S at the outer scale/solution interface in mol/m^3 ,
D_{H_2S}	is the diffusion coefficient for dissolved H_2S in water, $D_{H_2S} = 2.00 \times 10^{-9}$, in m^2/s ,
ε	is the outer mackinawite scale porosity,
Ψ	is the outer mackinawite scale tortuosity factor,
c_{i,H_2S}	is the interfacial concentration of H_2S at the inner scale/film interface in mol/m^3 .
δ_{os}	is the thickness of the mackinawite scale $\delta_{os} = m_{os} / (\rho_{FeS} A)$ in m ,

m_{os} is the mass of the mackinawite scale in kg,
 A is the surface area of the steel in m^2 ,
 A_{H_2S}, B_{H_2S} are the Arrhenius constants, $A_{H_2S} = 1.30 \times 10^{-4} \text{ mol}/(m^2s)$ and $B_{H_2S} = 15500 \text{ J/mol}$,
 T_k is the temperature in Kelvin,
 c_{s,H_2S} is the concentration of H_2S on the steel surface and is set to 1.00×10^{-7} in mol/m^3 .

In a steady state the three fluxes are equal to each other and are equal to the corrosion rate CR_{H_2S} . By eliminating the unknown interfacial concentrations c_{o,H_2S} and c_{i,H_2S} from equations (2) to (4), the following equation is obtained for the corrosion rate of steel due to H_2S :

$$CR_{H_2S} = A_{H_2S} e^{-\frac{B_{H_2S}}{RT_k}} \ln \frac{c_{b,H_2S} - CR_{H_2S} \left(\frac{\delta_{0.5}}{D_{H_2S} \epsilon \Psi} + \frac{1}{k_{m,H_2S}} \right)}{c_{s,H_2S}} \quad (5)$$

This is a nonlinear equation with respect to CR_{H_2S} which does not have an explicit solution but can be solved by using a simple numerical algorithm such as the interval halving method or similar. These are available as ready-made routines in spreadsheet applications or in any common computer programming language. The prediction for CR_{H_2S} depends on a number of constants used in the model which can be either found in handbooks (such as D_{H_2S}), calculated from the established theory (e.g. k_{m,H_2S}) or are determined from the experiments (e.g. $A_{H_2S}, B_{H_2S}, c_{s,H_2S}$). The unknown properties of the outer sulfide scale change with time and need to be calculated as described below.

It is assumed that the amount of scale retained on the metal surface at any point in time depends on the balance of:

- scale formation (generated by spalling of the thin mackinawite film underneath it and by precipitation from the solution), and
- scale damage (by hydrodynamic stresses and/or by chemical dissolution)

$$\underbrace{SRR}_{\substack{\text{scale} \\ \text{retention} \\ \text{rate}}} = \underbrace{SFR}_{\substack{\text{scale} \\ \text{formation} \\ \text{rate}}} - \underbrace{SDR}_{\substack{\text{scale} \\ \text{damage} \\ \text{rate}}} \quad (6)$$

where all the terms are expressed in $\text{mol}/(m^2s)$. As in this study it was found that precipitation of iron sulfide did not play a significant role, neither did chemical dissolution of the scale it can be written:

$$\underbrace{SRR}_{\substack{\text{scale} \\ \text{retention} \\ \text{rate}}} = \underbrace{CR}_{\substack{\text{corrosion} \\ \text{rate}}} - \underbrace{SDR_m}_{\substack{\text{mechanical} \\ \text{scale damage} \\ \text{rate}}} \quad (7)$$

Experiments have shown that even in stagnant conditions about half of the sulfide scale that formed was lost from the steel surface by spalling, i.e. $SDR_m \approx 0.5 CR$. Furthermore, the rate of scale removal in flowing conditions increased with velocity and one can write:

$$SDR_m = 0.5(1 + c v^a) CR \quad (8)$$

where c (≈ 0.55) and a (≈ 0.2) are experimentally determined constants for a rotating cylinder flow geometry. Clearly more experimentation is required to determine how and if they apply in pipe flow.

Once the scale retention rate SRR is known, the change in mass of the outer scale can be easily calculated as:

$$\Delta m_{os} = SRR M_{FeS} A \Delta t \quad (9)$$

where M_{FeS} is the molar mass of iron sulfide in kg/mol, Δt is the time interval in seconds. The porosity of the outer mackinawite scale was determined to be very high ($\varepsilon \approx 0.9$), however due to its layered structure the tortuosity factor was found to be very low $\Psi = 0.003$.

A time-marching solution procedure could now be established where:

1. the corrosion rate CR_{H_2S} in the absence of sulfide scale can be calculated by using equation (5), and assuming $\delta_{os} = 0$,
2. the amount of sulfide scale Δm_{os} formed over a time interval Δt is calculated by using equation (9),
3. the new corrosion rate CR_{H_2S} in the presence of sulfide scale can be calculated by using equation (5),
4. a new time interval Δt is set and steps 2 and 3 repeated.

A small complication arises from the fact that at very low H_2S gas concentrations (ppm_w range) iron sulfide still forms and controls the corrosion rate; however the corrosion process is largely driven by the reduction of protons.* In an analogy with the approach laid out above, the convective diffusion flux of protons through the mass transfer boundary layer is:

* Similar is true in combined CO_2/H_2S corrosion of steel which is driven by CO_2 but largely controlled by the presence of iron sulfide films. Mixed CO_2/H_2S corrosion is not considered in this paper.

$$Flux_{H^+} = k_{m,H^+} (c_{b,H^+} - c_{o,H^+}) \quad (10)$$

which in a steady state is equal to the diffusion flux through the pores of the iron sulfide scale:

$$Flux_{H^+} = \frac{D_{H^+} \varepsilon \Psi}{\delta_{oc}} (c_{o,H^+} - c_{i,H^+}) \quad (11)$$

which is equal to the solid state diffusion flux through the thin mackinawite film:

$$Flux_{H^+} = A_{H^+} e^{-\frac{B_{H^+}}{RT_k}} \ln \left(\frac{c_{i,H^+}}{c_{s,H^+}} \right) \quad (12)$$

which is equal to the corrosion rate by protons CR_{H^+} . By eliminating the unknown interfacial concentrations c_{o,H^+} and c_{i,H^+} from equations (10) to (12), the following expression is obtained for the corrosion rate driven by protons and controlled by the presence of the iron sulfide scale:

$$CR_{H^+} = A_{H^+} e^{-\frac{B_{H^+}}{RT_k}} \ln \frac{c_{b,H^+} - CR_{H^+} \left(\frac{\delta_{0.5}}{D_{H^+} \varepsilon \Psi} + \frac{1}{k_{m,H^+}} \right)}{c_{s,H^+}} \quad (13)$$

where

- $Flux_{H^+}$ is expressed in mol/(m²s),
- k_{m,H^+} is the mass transfer coefficient for protons in the hydrodynamic boundary layer, $k_{m,H^+} = 3.00 \times 10^{-4}$ in nearly stagnant condition, in m/s,
- c_{b,H^+} is the bulk concentration of H⁺ in the liquid phase in mol/m³,
- c_{o,H^+} is the interfacial concentration of H⁺ at the outer scale/solution interface in mol/m³,
- D_{H^+} is the diffusion coefficient for dissolved H⁺ in water, $D_{H^+} = 2.80 \times 10^{-8}$, in m²/s,
- c_{i,H^+} is the interfacial concentration of H⁺ at the inner scale/film interface in mol/m³.
- A_{H^+}, B_{H^+} are the Arrhenius constants, $A_{H^+} = 3.9 \times 10^{-4}$ mol/(m²s) and $B_{H^+} = 15500$ J/mol.

c_{s,H^+} is the concentration of H^+ on the steel surface and is set to 1.00×10^{-7} in mol/m^3 .

The total rate of corrosion is equal to the sum of the corrosion caused by H_2S and the corrosion caused by H^+ .

$$CR = CR_{H_2S} + CR_{H^+} \quad (14)$$

This completes the description of a basic mechanistic model of pure H_2S corrosion of mild steel. A number of important effects are not covered by the model as presented above:

- corrosion due to CO_2 , organic acids, etc.;
- formation of scale due to precipitation of iron sulfide, iron carbonate, etc.;
- dissolution of the outer scale and inner film due to a very low pH;
- localized attack.

The first three effects have been already accounted for in a more comprehensive CO_2/H_2S model (MULTICORP V4.0); however the presentation of this model exceeds the scope of the present paper.

VERIFICATION AND TESTING OF THE MODEL

The model predictions are compared with the experimental results at different test conditions. Figure 16 shows the comparison of the corrosion rate vs. the reaction time for a series of experiments done at 80°C . One should keep in mind that the experimental results are time-averages over 1 h and 1-24 h periods while the predictions represent “instantaneous” corrosion rates. Clearly the model successfully captures the downward trend of the corrosion rate with time as well as the undesirable effect of high H_2S concentrations on the general corrosion rate. Figure 17 shows the comparison of the measured and predicted scale retention at different reaction times. The predicted scale growth is rapid in the first few hours and then gradually levels off, leading to what is often referred to as a “parabolic film growth regime”. After all the cases available in this experimental study were simulated with the model, the comparison of the predicted H_2S corrosion rates and the measured values is shown in Figure 18. Overall one can claim reasonable agreement keeping in mind the scatter in the experimental results.

The model was tested by making simulations outside the range of parameters used in the experimental study described above, i.e. the model was used to extrapolate the corrosion rates to higher partial pressures of H_2S as well as much longer exposure times (both are very complicated and expensive to achieve in a laboratory setting). In Figure 19 one can see the predictions ranging from partial pressure of H_2S as low as 0.16 Pa in the gas phase (what corresponds to 1.6 ppm_w at 1 bar total pressure) all the way up to 2.7 bar H_2S partial pressure. The simulations were extended to 10 years and shown on a log-scale. Clearly, the corrosion rate decreases to a very low value in all cases, while at the lowest

H₂S concentration it may take less than a day at the highest it may take as long as few years. The film thickness prediction is shown in Figure 20, indicating a scale thickness which is only a few mm thick even at the highest H₂S partial pressures and in very long exposures.

CONCLUSIONS

The primary findings of this project are:

- Mackinawite is the predominant iron sulfide formed on the steel surface, most likely by solid state reaction.
- The corrosion rate of mild steel in H₂S corrosion is affected by H₂S gas concentration, temperature, velocity, and the protectiveness of the scale.
- The scale retained on the steel surface depends on both the scale formation rate and the scale damage rate. The scale formation rate includes both the corrosion rate and precipitation rate. The scale damage rate includes the damages by both mechanical removal and chemical removal.
- A mechanistic model of H₂S corrosion is developed to accurately predict the H₂S corrosion process.

ACKNOWLEDGEMENTS

During this work, W. Sun was supported by Ohio University Donald Clippinger Fellowship. A part of the experiments in this paper were conducted in CANMET Materials Technology Laboratory, Natural Resources Canada and the authors acknowledge Dr. Sankara Papavinasam for his support. The authors would also like to acknowledge the companies who provided the financial support and technical guidance for this project. They are BP, Champion Technologies, Chevron, Clariant, ConocoPhillips, ENI, ExxonMobil, MI SWACO, Nalco, Saudi Aramco, Shell, Total, Tenaris, Baker Petrolite, Columbia Gas Transmission, and PPT.

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TABLE

Table 1. Chemical Composition of X65 (wt.%) (Fe is the 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

Table 2. The concentrations of sulfide species at different concentrations of H₂S in the gas inlet stream and the H₂S solution at pH 5 and P_{tot} 1 bar.

Temperature / °C	H ₂ S concentration in the gas / vol%	$c_{H_2S(g)}$ ppm _w	$c_{H_2S(g)}$ Pa	$c_{H_2S(aq)}$ mol/l
25	0.01	119	9.8	9.4E-6
	0.1	1189	98	9.4E-5
	1	11871	981	9.4E-4
	10	116512	9808	9.4E-3
60	0.1	1049	81	4E-5
	1	10471	813	4E-4
	10	102998	8132	4E-3
80	0.0075	58	4	1.58E-6
	0.015	116	8	3.16E-6
	0.024	186	13	5.06E-6
	0.04	310	22	8.44E-6
	0.1	776	54	2.11E-5
	1	7752	539	2.11E-4
	10	76573	5392	2.11E-3

FIGURES

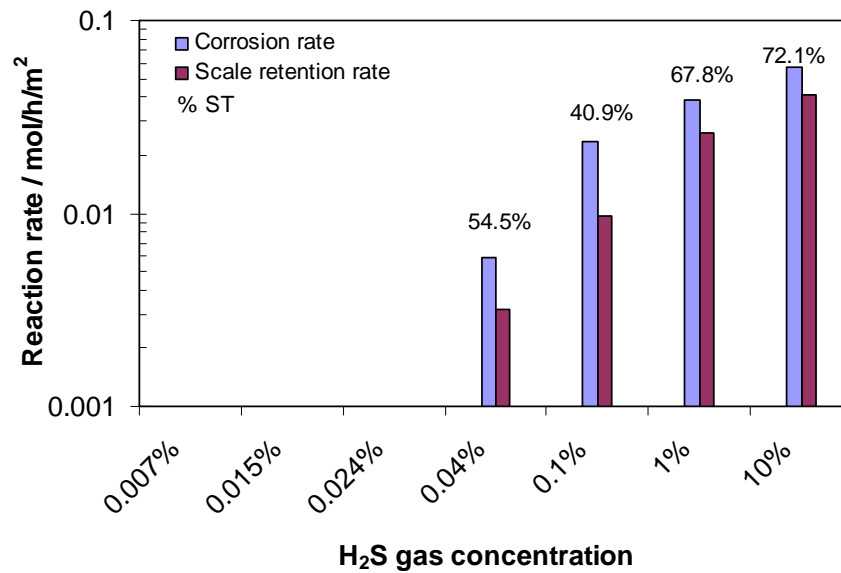


Figure 1. The comparison of corrosion rate (CR) and scale retention rate (SRR) in the same molar units as a function of H₂S gas concentration; ST=SRR/CR stands for Scaling Tendency; total pressure p=1 bar, T=80°C, initial Fe²⁺ aqueous concentration: 0 ppm, pH 5.0-5.5, reaction time 1 hr.

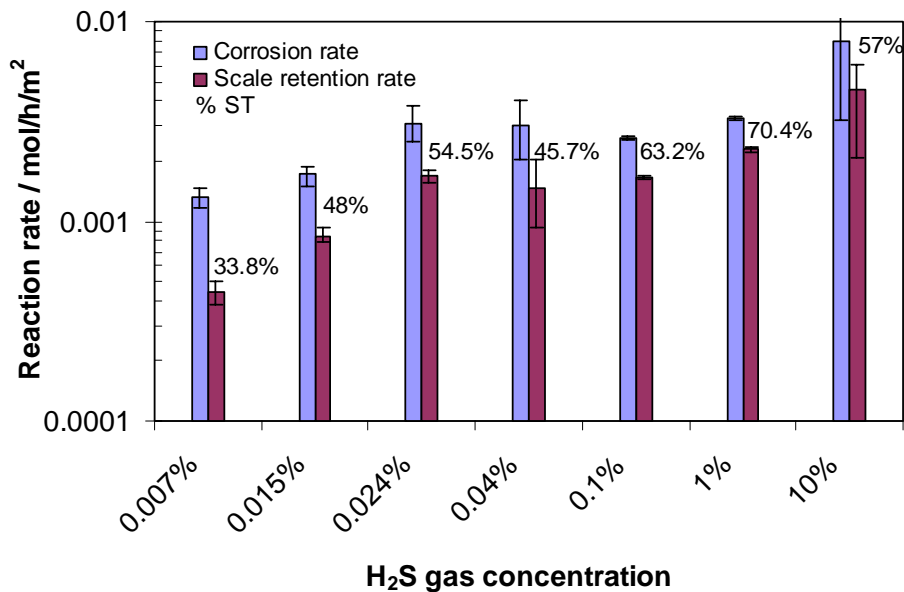


Figure 2. The comparison of corrosion rate (CR) and scale retention rate (SRR) in the same molar units as a function of H₂S gas concentration; ST=SRR/CR stands for Scaling Tendency; total pressure p=1 bar, T=80°C, initial Fe²⁺ aqueous concentration: 0 ppm, pH 5.0-5.5, reaction time: 24 hr.

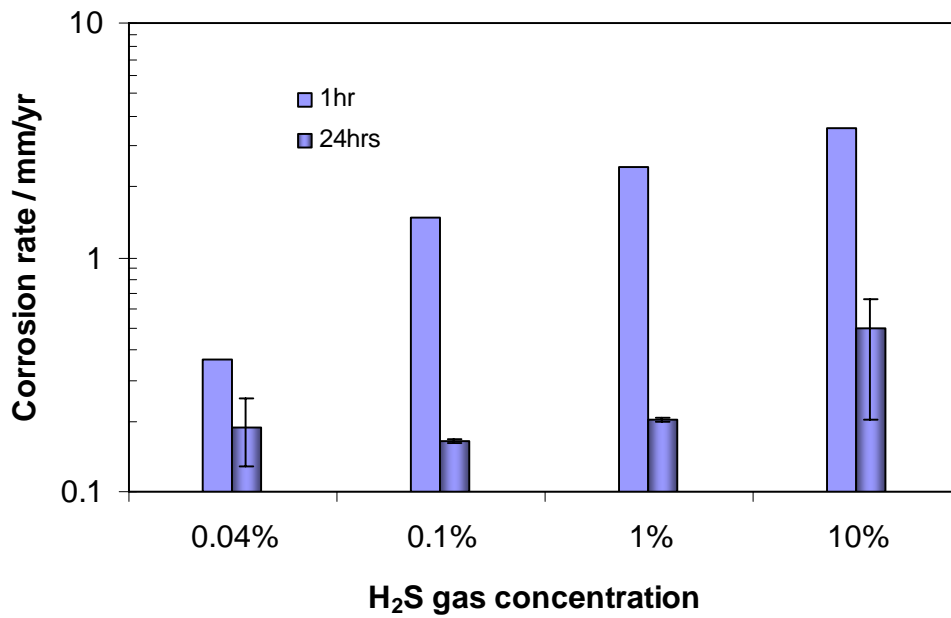


Figure 3. The corrosion rate vs. H₂S gas concentration after 1 hr and 24 hr exposure at total pressure p=1 bar, T=80°C, initial Fe²⁺ aqueous concentration: 0 ppm, pH 5.0-5.5.

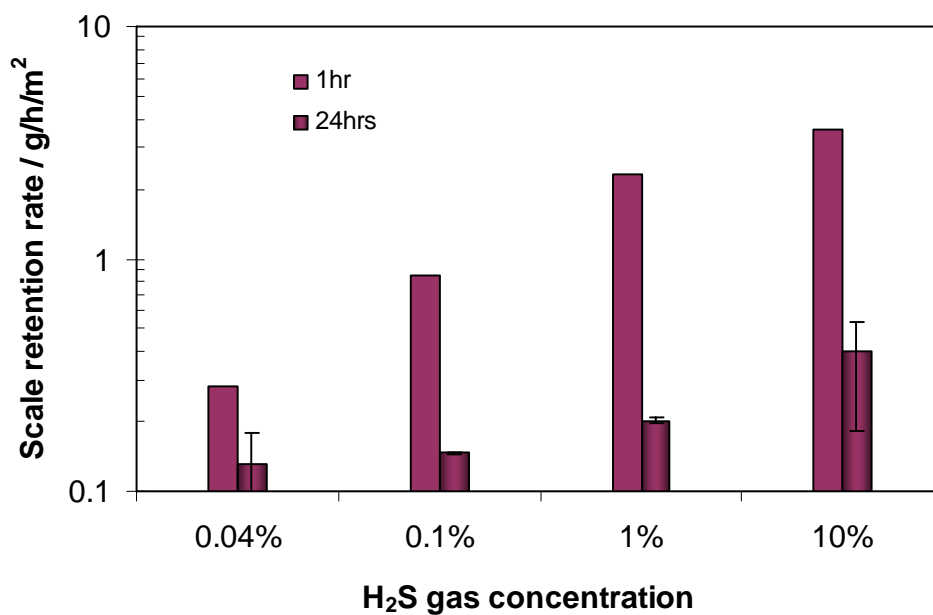


Figure 4. The scale retention rate vs. H₂S gas concentration after 1 hr and 24 hr exposure at total pressure p=1 bar, T=80°C, initial Fe²⁺ aqueous concentration: 0 ppm, pH 5.0-5.5.

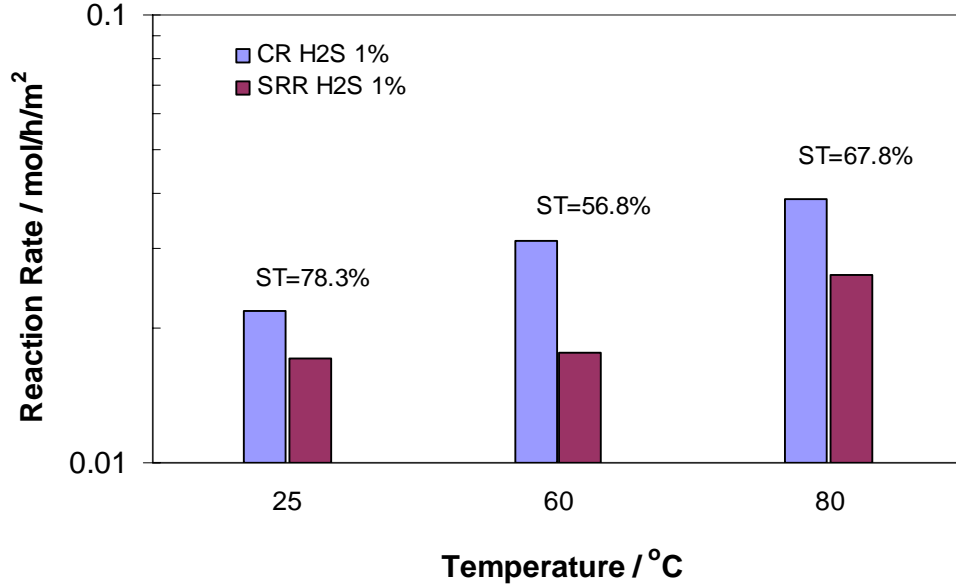


Figure 5. The corrosion rate (CR) and scale retention rate (SRR) vs. temperature, ST=SRR/CR stands for Scaling Tendency; conditions: total pressure p=1 bar, H₂S gas concentration is 1%, initial Fe²⁺ aqueous concentration: 0 ppm, pH 5.0-5.5, reaction time: 1 hr.

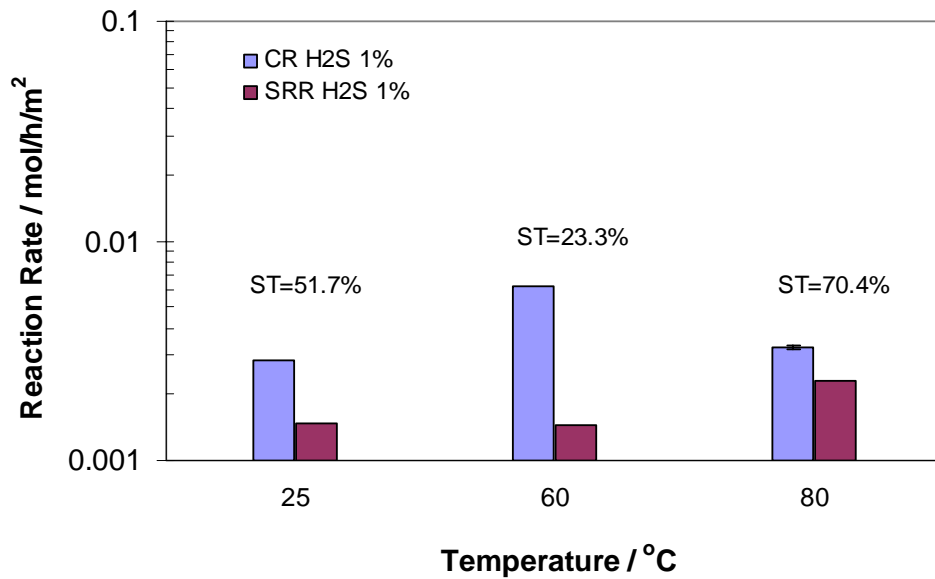


Figure 6. The corrosion rate (CR) and scale retention rate (SRR) vs. temperature, ST=SRR/CR stands for Scaling Tendency; conditions: total pressure p=1 bar, H₂S gas concentration: 1%, initial Fe²⁺ aqueous concentration: 0 ppm, pH 5.0-5.5, reaction time: 24 hr.

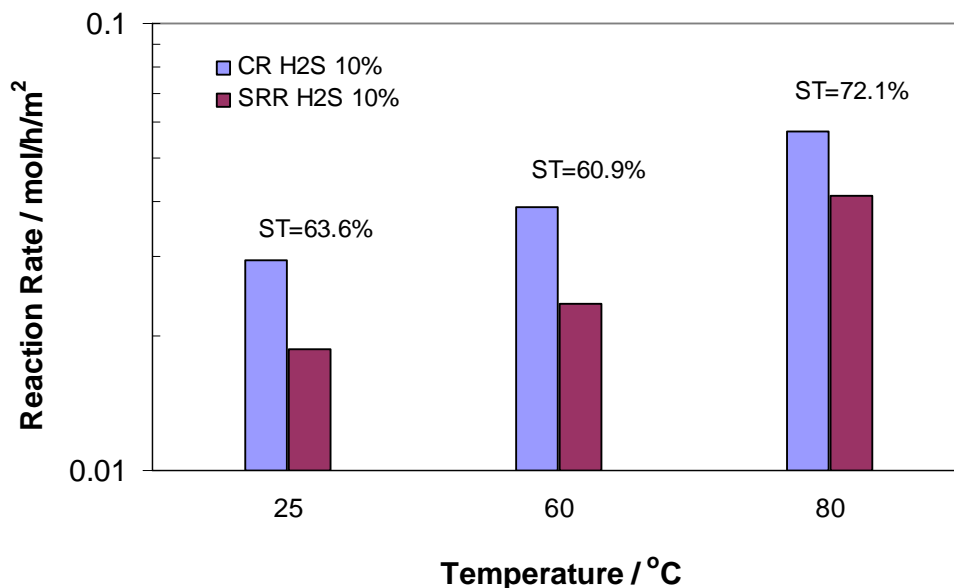


Figure 7. The corrosion rate (CR) and scale retention rate (SRR) vs. temperature, ST=SRR/CR stands for Scaling Tendency; conditions: total pressure p=1 bar, H₂S gas concentration: 10%, initial Fe²⁺ aqueous concentration: 0 ppm, pH 5.0-5.5, and reaction time 1 hr.

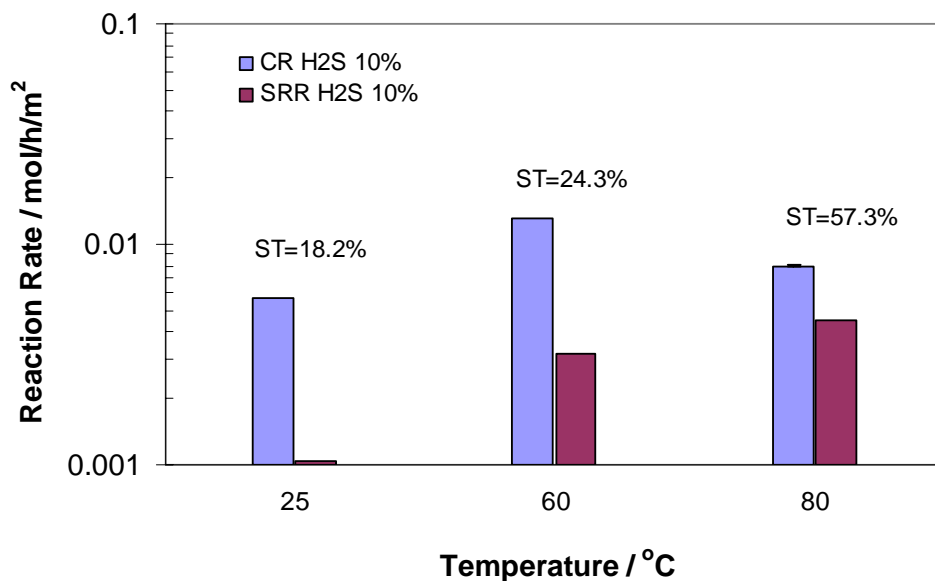


Figure 8. The corrosion rate (CR) and scale retention rate (SRR) vs. temperature, ST=SRR/CR stands for Scaling Tendency; conditions: total pressure p=1 bar, H₂S gas concentration: 10%, initial Fe²⁺ aqueous concentration: 0 ppm, pH 5.0-5.5, and reaction time: 24 hr.

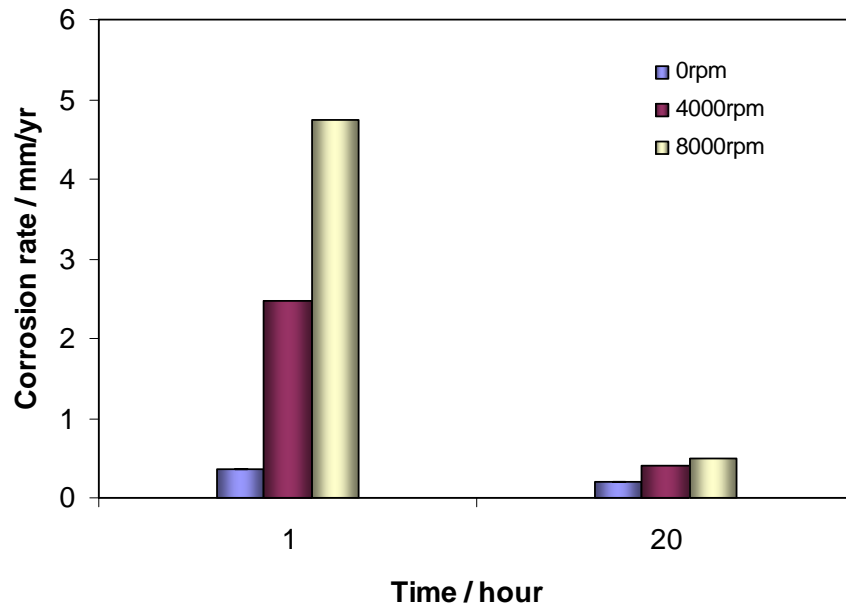


Figure 9. The corrosion rate vs. time for different rotational speeds; conditions: total pressure $p=1$ bar, $T=25^{\circ}\text{C}$, H_2S gas concentration: 0.04%, initial Fe^{2+} aqueous concentration: 0 ppm, pH 5.0-5.5.

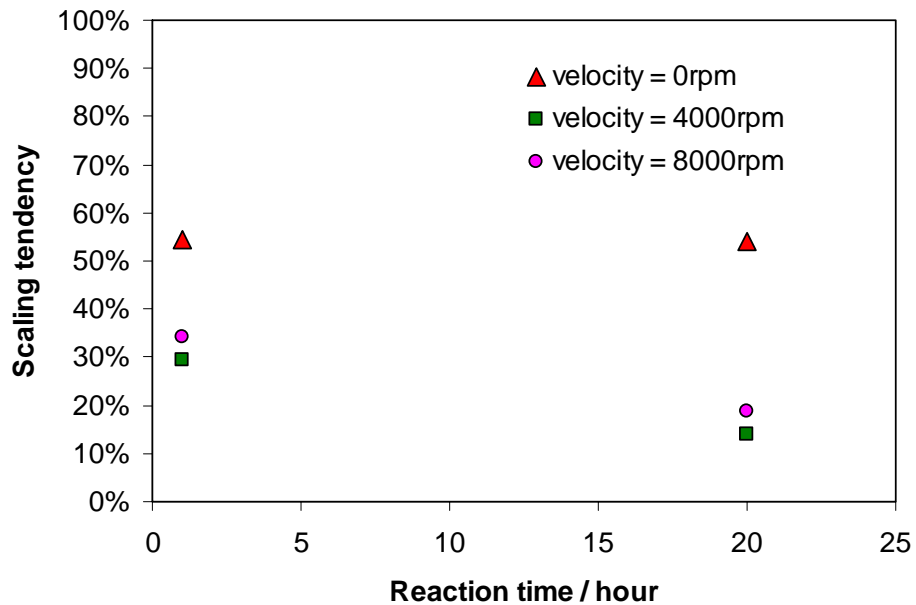
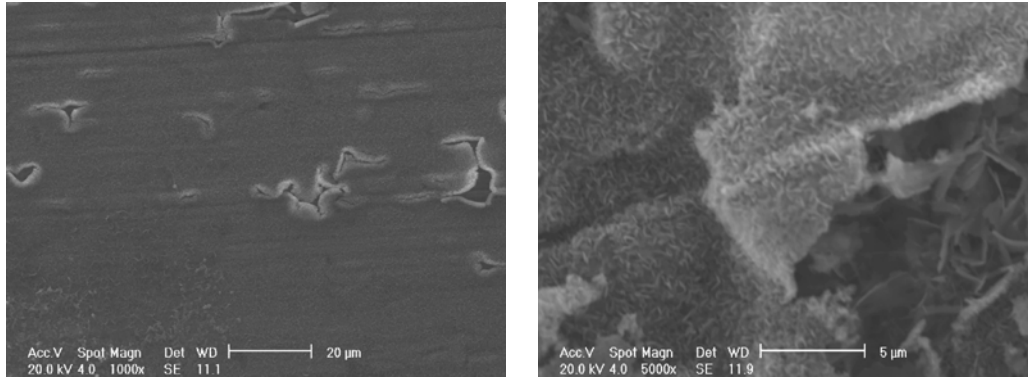


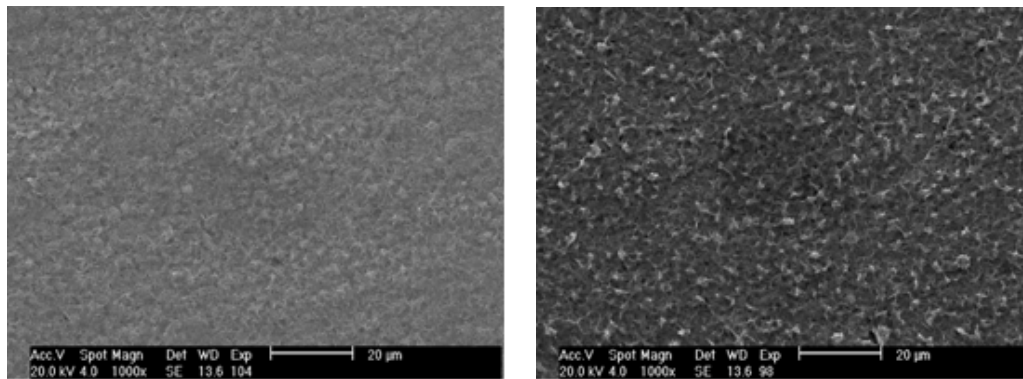
Figure 10. The comparison of scaling tendency vs. reaction time under the conditions of total pressure $p=1$ bar, $T=25^{\circ}\text{C}$, H_2S gas concentration 0.04%, initial Fe^{2+} aqueous concentration 0 ppm, and velocity 0, 4000, and 8000rpm.



(a)

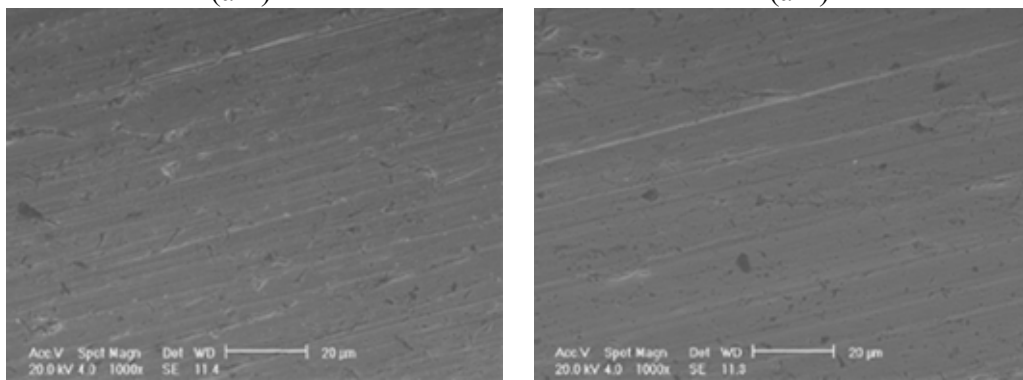
(b)

Figure 11. The film morphology showing polishing marks on the X65 mild steel (a) 1000X and (b) 5000X, under the conditions of total pressure $p=1$ bar, initial Fe^{2+} aqueous concentration 0 ppm, H_2S gas concentration 10%, T 60°C , reaction time 1 hour, pH 5.0-5.5, and velocity 0rpm.



(a-1)

(a-2)



(b-1)

(b-2)

Figure 12. The film morphology on the different steel surface (a-1) X65 mild steel Fe^{2+} 0 ppm, (a-2) X65 mild steel Fe^{2+} 50 ppm, (b-1) 316 stainless steel Fe^{2+} 0 ppm, (b-2) 316 stainless steel Fe^{2+} 50 ppm, under the conditions of total pressure $p=1$ bar, H_2S gas concentration 0.1%, T 80°C , reaction time 24 hours, pH 5.0-5.5, and velocity 0rpm.

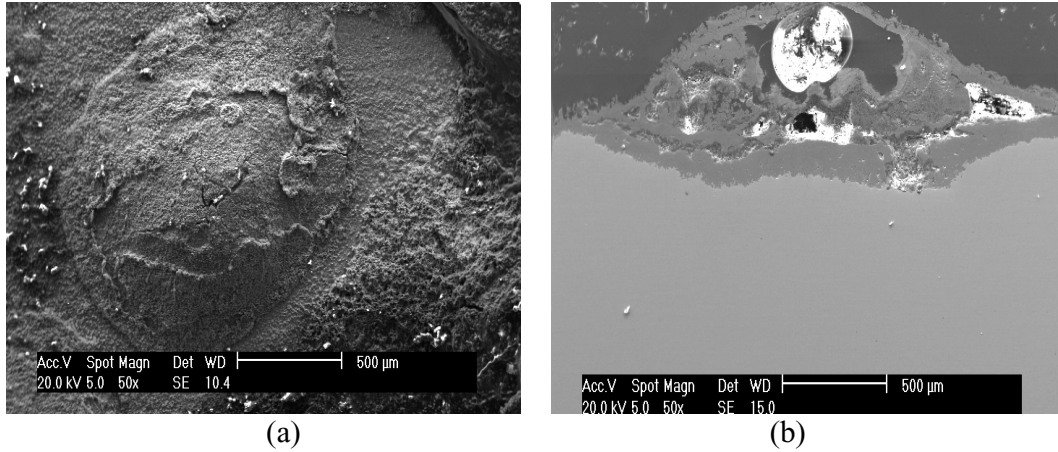


Figure 13. The morphology (a) and cross section (b) of the localized attack on the X65 mild steel surface in $\text{CO}_2/\text{H}_2\text{S}$ environment under the conditions of P_{tot} 8bar, $P_{\text{H}_2\text{S}}$ 8mbar, P_{CO_2} 7.5bar, T 60°C, and the total reaction time is 10 days¹⁸.

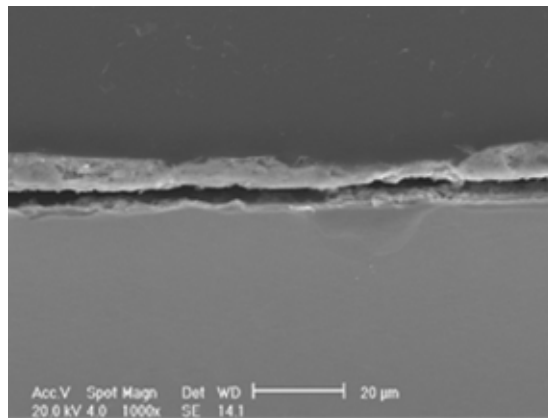


Figure 14. Cross section of the scale formed on the X65 mild steel surface (at 1000X) under the conditions of total pressure $p=1$ bar, initial Fe^{2+} aqueous concentration 0 ppm, H_2S gas concentration 1% ($\text{H}_2\text{S}/\text{N}_2$ gas), T 80°C, pH 5, the total reaction time is 24 hours.

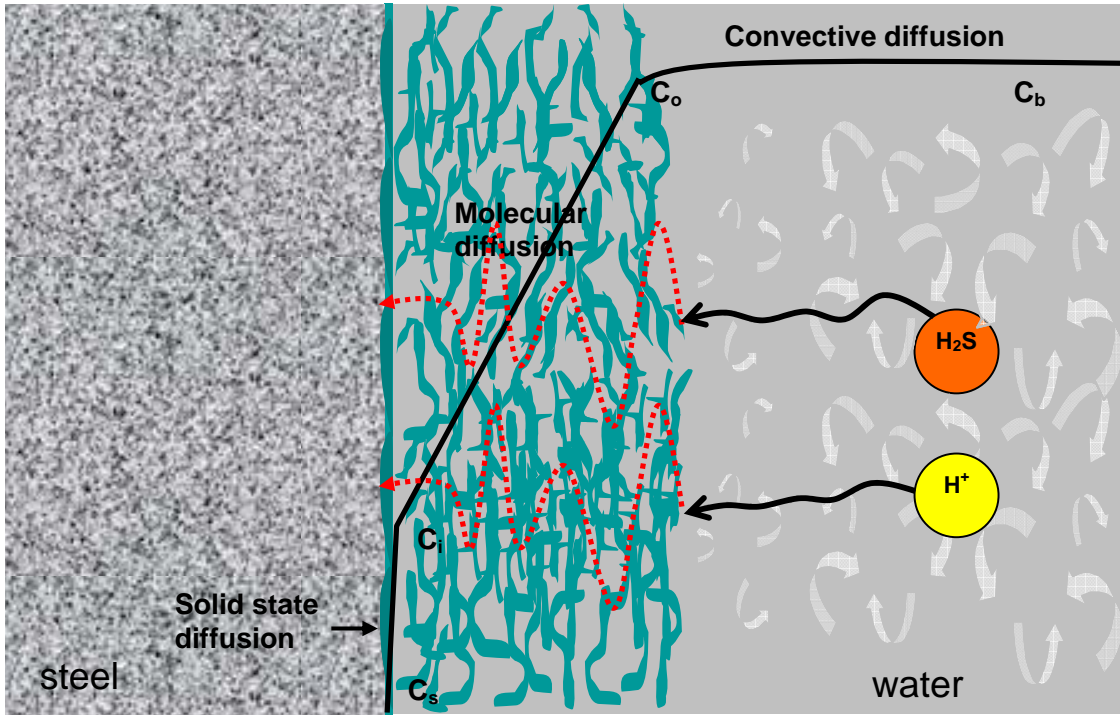


Figure 15. A schematic of the H_2S corrosion process.

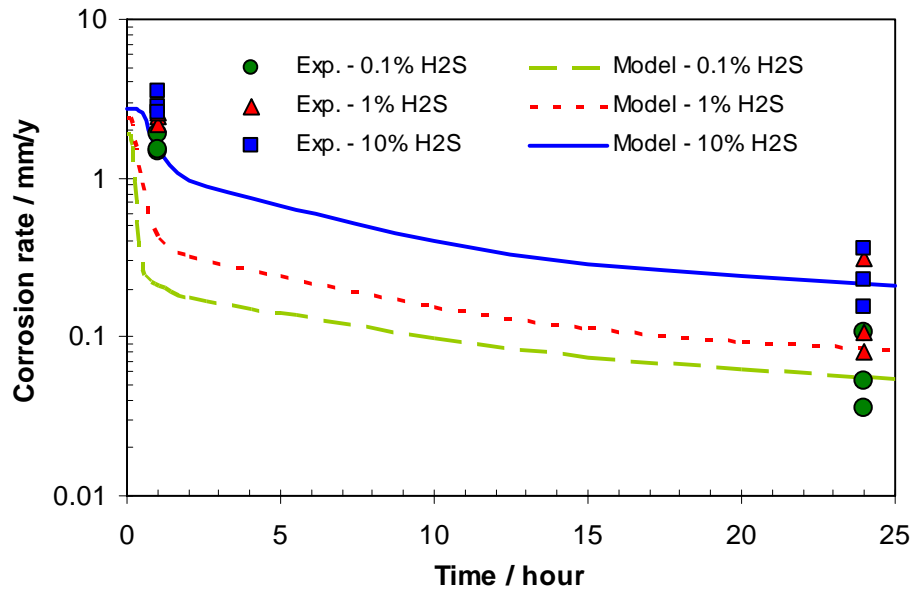


Figure 16. The experimental and prediction corrosion rate vs. time under the conditions of total pressure $p=1$ bar, H_2S gas concentration from 0.1% to 10%, T 80°C, reaction time of 1 hour and 24 hours, pH 5.0-5.5, and velocity 0rpm.

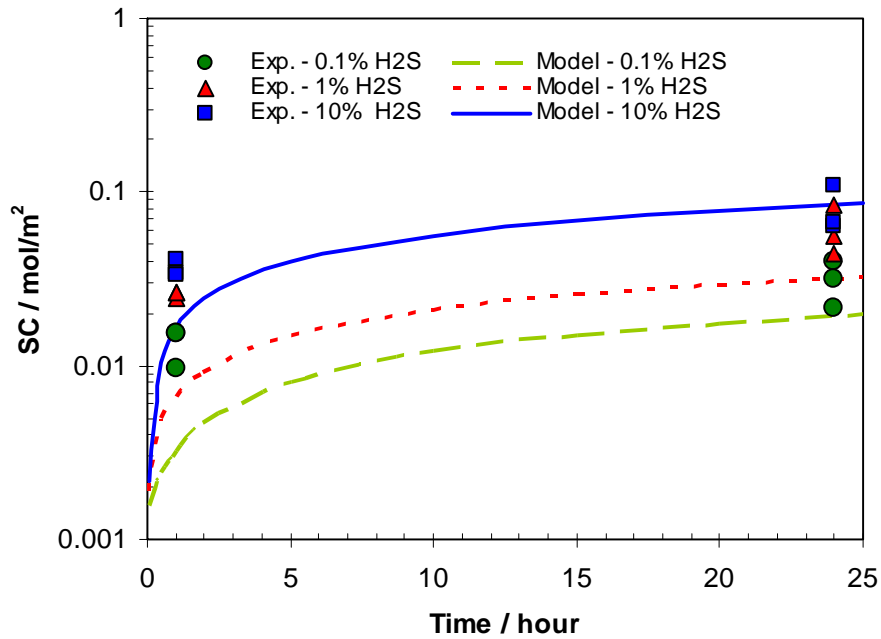


Figure 17. The experimental results and predictions of the scale retention vs. time under the conditions of total pressure $p=1$ bar, H_2S gas concentration from 0.1% to 10%, T $80^\circ C$, reaction time of 1 hour and 24 hours, pH 5.0-5.5, and velocity 0rpm.

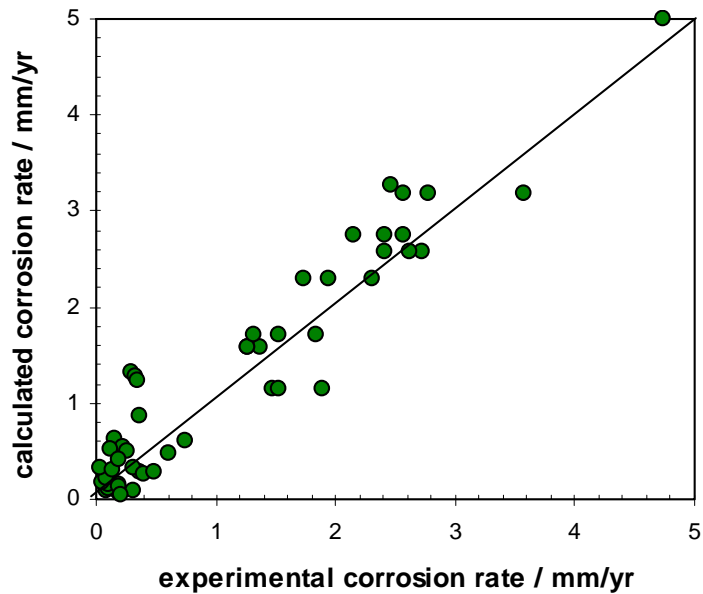


Figure 18. The comparison of the experimental corrosion rate and the calculated corrosion rate under the conditions of total pressure $p=1$ bar, H_2S gas concentration from 0.0075% to 10%, T $25^\circ C$, $60^\circ C$, and $80^\circ C$, reaction time of 1 hour and 24 hours, pH 5.0-5.5, and velocity from 0rpm to 8000rpm.

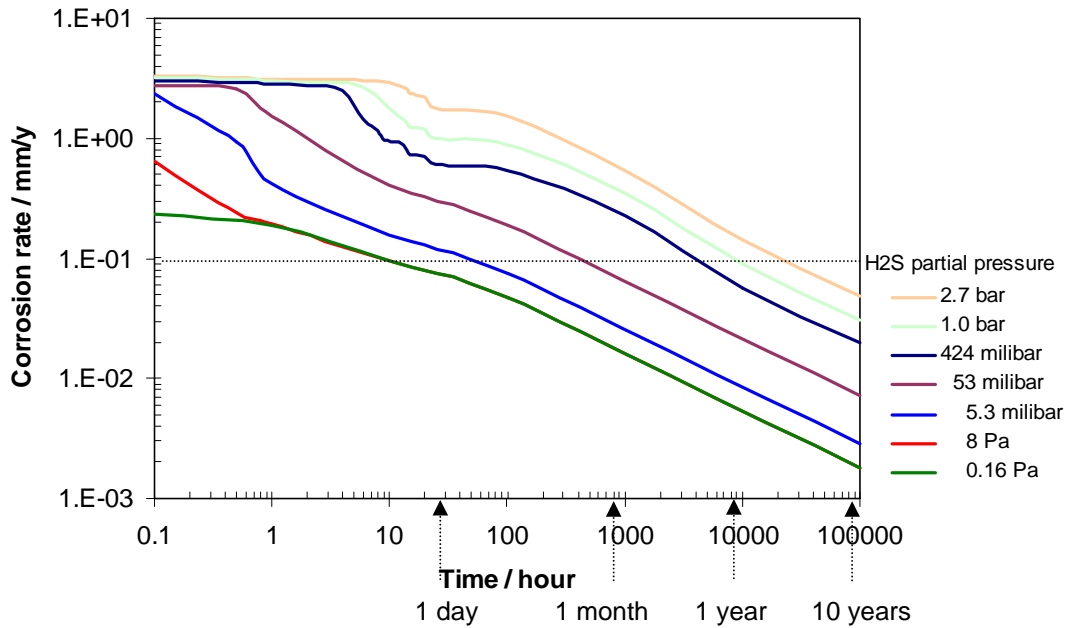


Figure 19. Simulated corrosion rate as a function of time for a range of H₂S partial pressures; conditions T 80°C, pH 5, and stagnant.

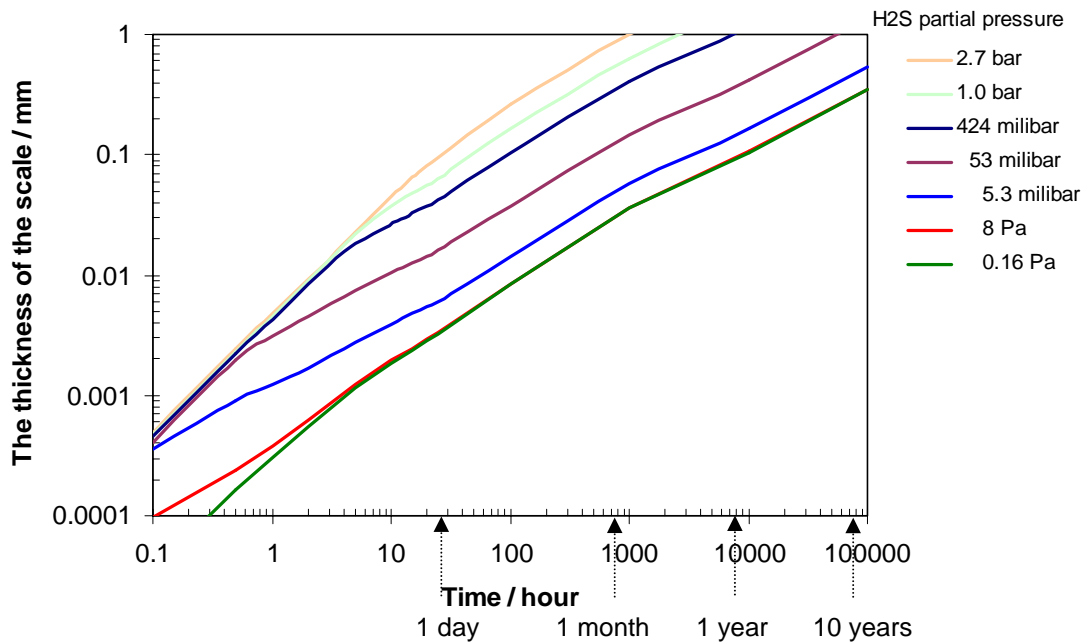


Figure 20. Simulated sulfide scale thickness as a function of time for a range of H₂S partial pressures; conditions: T 80°C, pH 5, and stagnant.