A Study of Prediction of the Behavior of Hydrogen Sulfide Corrosion in Mild Steel Used for Petroleum Pipelines

M.B.A. Deemantha and G.I.P. De Silva

Abstract: Hydrogen sulfide (H₂S) corrosion is a common problem in oil, gas and Petrochemical/Chemical industries. This becomes a particularly dangerous form of corrosion in the industry as it occurs without any warning. Petroleum refining industry can be identified as one of the industries which faces the disastrous consequences of H₂S corrosion. Most of the petroleum pipelines are made out of mild steel that is easily attacked by H₂S corrosion. H₂S corrosion begins with the synergistic effect of tensile force and H₂S rich environment imposed on mild steel. This corrosion can only be detected using complicated inspection methods such as electro-chemical techniques, non-destructive test methods and optical testing methods etc. But, these techniques have become more complicated to inspect the corrosion due to different environments where the pipelines are set up. The main drawback of these techniques is that any damage that is detected has already occurred. Therefore, necessity of a model to predict the rate and behavior of H₂S corrosion has been arising and being discussed for years. This article summarizes major factors affecting H₂S corrosion, existing corrosion prediction models and their pros and cons. Furthermore, this paper reviews how corrosion kinetics involve in H₂S corrosion and proposed corrosion mechanisms by researchers.

Keywords: H₂S Corrosion, Corrosion rate, Mechanism, Kinetics, Iron Sulphide

1. Introduction

Sulphur compounds, including hydrogen sulfide (H₂S), can be identified as one of the main reasons for corrosion failures in oil, gas and petrochemical industry. Hydrogen sulfide can be identified as the most dangerous compound which exists in oil and gas reservoirs. Thus, it can significantly reduce service life of transportation pipelines and processing facilities in oil and gas industries [1]. JRC (Joint research center of European commission) scientific and policy reports published in 2013 for corrosion related accidents in petroleum refineries [2] illustrate that the contribution of hydrogen sulfide, sulphur and sulphur compounds is significantly higher for corrosion failures compared to the contribution of other chemical substances (Figure 1). Wet sulphur in metal causes different types of corrosion such as hydrogen blistering, hydrogen induced cracking, stress oriented hydrogen induced cracking, hydrogen sulfide corrosion cracking and sulfide stress corrosion cracking etc. [3]. Several researchers have carried out investigations for the development of models which could predict the corrosive behavior of mild steel occurring due to hydrogen sulfide corrosion that is also known as sour corrosion in some of the literature. Because of the abundance of hydrogen sulfide emissions at petroleum refining processes and mild steels are susceptible for H₂S corrosion, pipelines are prone to corrode by hydrogen sulfide corrosion. Therefore, the industry is seeking for a proper model to predict the corrosion behavior.

Basically, it has been identified that hydrogen sulfide corrosion of mild steel is affected by six main factors. They are gas composition, iron sulfide scale, temperature, time period, flow effects and solution composition [4] [5]. Moreover, it is necessary to focus on the thermodynamic aspects of corrosion at developing a model.

This review paper expects to deliver an abstract of factors that causes to initiate and propagate H₂S corrosion, a basic comparison of existing H₂S corrosion prediction models and the proposed mechanisms of H₂S corrosion used for developing models.

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A – Sulphur/Sulphur compounds; B – Water; C – Hydrogen Sulphide; D – Other, E – Ammonia/Ammonia Compounds; F – Crude Oil; G – Hydrogen; H – Chlorine/Chlorine ions; I – Hydrocarbon/Hydrocarbon mixture; J – Hydrogen Chloride; K – Hydrogen Fluorides

Figure 1 - Process Related Substances cited as Contributed to Corrosion Failures [2]

Even though several mechanistic models have been developed to predict the rate of hydrogen sulfide corrosion, they have failed to predict the corrosion rate more accurately. Most of the models are valid only under certain conditions.

2. Overview of Reviewed Prediction Models and Lab Data

Corrosion testing results obtained by Smith [3], Zheng et al. [5], Sun et al. [6], Asmara et al. [7], Srdjan et al. [8] and in house data were directly used for this study.

This study is carried out based on the previous research works on general corrosion of mild steel, sulphide stress corrosion, hydrogen sulphide corrosion, sulphide stress cracking and corrosion that is possible to occur in sour environment. The data collection includes testing parameters in sour systems, partial pressure of gases such as H₂S and CO₂, gas composition, corrosion scale formation, reaction time, temperature, flow rates and pH values, etc.

Figures taken by each experiment for this review paper are listed below:
Figure 1 – Reference [2]
Figure 2 – Reference [1]
Figures 3, 4 and 6, 7, 8 - Reference [6]
Figure 5 – Reference 3

3. Discussion

Parameters which are known to involve in the initiation and propagation of hydrogen sulphide corrosion, the mechanisms and the kinetics of corrosion are required to be clearly clarified at the development of a prediction model. The accuracy of developed models depends upon the aforementioned considerations. A detailed discussion of these considerations, and pros and cons of selected models are illustrated below.

3.1 Parameters which Effect the Sulphide Stress Corrosion

Mild steel is subjected to corrosion in the presence of hydrogen sulphide, forming cracks through the metal. The initiation and propagation of this corrosion are governed by hydrogen sulphide composition, iron sulphide scale, temperature, exposure time, and flow effect and solution composition. It has been found that hydrocarbons and oilfield chemicals, sulfide species and elemental sulfur affect the rate and behavior of hydrogen sulfide corrosion based on the environmental conditions [3]. In the research work, experiments have been carried out in two different sour environments. They are N₂/H₂S environment and CO₂/H₂S environment.

3.1.1 Effect of H₂S Concentration

The experiments carried out by Sun et al. [6] showed that the increment of H₂S concentration increases the corrosion rate as well as scale retention rate in N₂/H₂S environment under the conditions of total pressure of 1 bar, temperature of 80°C, initial Fe²⁺ aqueous concentration of 0 ppm, pH value of 5.0-5.5 and reaction time of 1hr (Figure 2). In the same study, it was shown that the effect of H₂S concentration is reduced with the exposure time. Furthermore, it showed that the corrosion rate and scale retention rate increase monotonically under the aforementioned conditions. However, the investigation carried out by Zheng et al. [5] in H₂S/CO₂ environment showed a reduction of corrosion rate when the H₂S concentration is slightly increased from zero concentration. Nevertheless, beyond a certain H₂S concentration, a continuous increment of corrosion rate was observed. (Figure 3). The same behaviour can be seen in the investigation carried out by Smith and Pacheco [9].

References for each equation in this review paper are listed as [6] to [8].
3.1.2 Effect of Time Duration

The effect of iron sulphide scale has been implied by Sun et al. [6] using two plots of corrosion rate vs H₂S concentration at two different time durations (Figure 4). They describe that the iron sulphide layer becomes gradually more protective with time when lower corrosion rates are recorded. They conducted experiments for 24 h and 1 h for this comparison. This protectiveness of the iron sulphide layer has been described by Omar et al. [11] in their experiments such that the type of iron sulphide formed on the steel determines the corrosion rate. The formation of different types of iron sulfide scales depends on the thermodynamic and kinetics of scale formation [3].

However, Smith [3] mentioned in his study of the sour corrosion of carbon steel that the scales formed during extended exposures are complex and layered structures formed by one or more types of iron sulfides (Figure 5).

3.1.3 Effect of Flow Rate

Sun et al. [6] revealed that the effect of flow speed of the solution on H₂S corrosion rate strongly depends upon the time duration that the steel exposes to the sour environment. Furthermore, the results of this experiment elaborated that the corrosion rate is significantly increased with higher flow rates for shorter exposure times while the corrosion rate decreased with the same higher flow rates but for longer exposure times (Figure 6). Smith [3] mentioned in his study that the autoclave experiments carried out at an in-house facility show that the flow rate significantly accelerates the corrosion rate. However, Omar et al. [11] mention in their investigation, which was conducted to study the effect of velocity on sour corrosion using a floor loop, that there is no significant effect of flow rate on sour corrosion.
3.1.4 Effect of Temperature

Sun et al. [6] mentioned in their research that the effect of temperature on corrosion rate is not significant. The test conditions of the experiment were kept such that temperature is varied within the range of 25-80°C for 1h and 24h exposures. Results of the experiment revealed a weak temperature dependence for corrosion rate at shorter term exposures while the temperature dependence is negligible for long term exposures. This behaviour was observed in both high and low H₂S concentration conditions. But Smith [3] in his study mentions that in-house high temperature experiments indicate that the corrosion rate initially decreased and gradually became constant with increasing temperature under low H₂S concentrations, and the corrosion rate initially increased and then decreased with increasing temperature under high H₂S concentrations. These observations imply that there is a peak value for the corrosion rate when the temperature is increased under fixed H₂S concentration. However, the experiments conducted by Pugh et al. [12], under the conditions of temperature of 25-55°C for six weeks exposure, mentioned that the corrosion rate decreases with increasing temperature. This study further revealed that the corrosion rate is dominated by the iron sulphide scale which forms with time.

3.2 Existing Corrosion Prediction Models

Most of the existing models for the prediction of H₂S corrosion has been developed assuming the corrosion rate is under the theory of mass transfer control [7, 8, 9]. Hence, models have been developed considering fundamental physico-chemical theories. Therefore, three types of diffusion fluxes have been considered at the development of the model. They are H₂S fluxes of convective diffusion throughout the mass transfer boundary layer Eq. (1), molecular diffusion through the liquid in the porous outer scale Eq. (2) and solid state diffusion through the inner Mackinawite film Eq. (4), where Mackinawite is the most common type of iron sulphide that forms on the liquid –metal surface in sour environments. The propagation of corrosion due to these three fluxes has been graphically represented in Figure 7.

\[
Flux_{H_2S} = k_{m,H_2S} (c_{b,H_2S} - c_{o,H_2S}) \quad \ldots (1)
\]

where,
\[
K_{m,H_2S} \quad - \quad \text{Mass transfer coefficient for H}_2\text{S in the hydrodynamic boundary layer.}
\]
\[
c_{b,H_2S} \quad - \quad \text{Bulk concentration of H}_2\text{S in the liquid phase in mol/m}^3.
\]
\[
c_{o,H_2S} \quad - \quad \text{Interfacial concentration of H}_2\text{S at the outer scale/solution interface in mol/m}^3.
\]

\[
Flux_{H_2S} = D_{H_2S} \frac{\psi}{\delta_{os}} (c_{o,H_2S} - c_{l,H_2S}) \quad \ldots (2)
\]

where,
\[
D_{H_2S} \quad - \quad \text{Diffusion coefficient for dissolved H}_2\text{S in water.}
\]
\[
\psi \quad - \quad \text{Outer Mackinawite scale porosity.}
\]
\[
\psi \quad - \quad \text{Outer Mackinawite scale tortuosity factor.}
\]
\[
c_{o,H_2S} \quad - \quad \text{Interfacial concentration of H}_2\text{S at the outer scale/solution interface in mol/m}^3.
\]
\[
c_{l,H_2S} \quad - \quad \text{Interfacial concentration of H}_2\text{S at the inner scale/film interface in mol/m}^3.
\]
\[
\delta_{os} \quad - \quad \text{Thickness of the Mackinawite scale in m.}
\]
\[
\delta_{os} \text{ can be calculated using the Eq. (3).}
\]

\[
\delta_{os} = \frac{m_{os}}{\rho_{FeS} \ \ A} \quad \ldots (3)
\]

where,
\[
m_{os} \quad - \quad \text{Mass of the Mackinawite scale in kg.}
\]
\[
A \quad - \quad \text{Surface area of the steel in m}^2.
\]
\[
\rho_{FeS} \quad - \quad \text{Density of FeS scale.}
\]

\[
Flux_{H_2S} = A_{H_2S} e^{\frac{B_{H_2S}}{RT}} \ln \frac{c_{l,H_2A}}{c_{s,H_2S}} \quad \ldots (4)
\]

where,
\[
A_{H_2S} \quad - \quad \text{Surface area of the steel in m}^2
\]
\[
B_{H_2S} \quad - \quad \text{Arrhenius constants where B_{H_2S} = 15500 j/mol.}
\]
In steady state, it is assumed that three fluxes are equal to each other. Therefore a formula Eq. (5) for the corrosion rate can be derived by equating the three fluxes and eliminating unknown terms $C_{o,H_2S}$ and $C_{i,H_2S}$.

\[
CR_{R2S} = A_{R2S}e^{RT_{E}} \ln \frac{C_{i,H_2S} - CR_{R2S}}{CR_{R2S}} = A_{R2S}e^{RT_{E}} \ln \frac{C_{i,H_2S} - CR_{R2S}}{C_{S,H_2S}}
\]

... (5)

Figure 7 - Schematic of H_2S Corrosion Process

Sun et al. [6] showed in their experiments that, when the H_2S concentration is very low, the corrosion process is largely driven by the reduction of H^+. Therefore, they suggest that the model becomes more accurate when the corrosion rate is calculated as the sum of the corrosion caused by both H_2S and H^+. They suggest that the corrosion rate caused by H^+ can be calculated following the Equations written for the fluxes of H_2S (Equs. 1, 2 and 3). All the terms associated with H_2S should be replaced with H^+ for the calculation of fluxes of H^+ and corrosion rate caused by H^+. The corrosion rates of the developed model [5] agreed with the corrosion rates in experimental results at the high concentration of H_2S (10%), but at low concentrations (0.1% and 1%) of H_2S, the model agreed with the experimental results only for long term exposures (Figure 8).

Zheng et al. [5] considered the electrochemical theories for the development of their model. The model was successful only for short term exposures. Asmara et al. [7] mentioned in their study that the empirical models are preferable; nevertheless, they do not account for the influence of crack geometry, direct slip dislocation, film properties, and atomic dissolution for the model. Therefore, the research group developed another model Eq. (6) using the mechano-chemical theory for crack propagation.

\[
\frac{dn}{dt} = A_0 \varepsilon_{ct}^n \sigma_m
\]

where, 
- $\frac{dn}{dt}$ - Crack propagation rate 
- $\varepsilon_{ct}$ - crack tip strain rate at the tip 
- $A_0$ - Rate coefficient 
- $\sigma_m$ - Material factor constant 
- $n$ - Numerical constant - depends on water conductivity and corrosion potential

3.3 Kinetics and Proposed Mechanisms of H_2S Corrosion

As discussed in section 3.2, there are some contradictory outcomes of the different models proposed to predict the corrosion rate under same conditions. Therefore, in case of developing a more accurate model, it is required to focus on in-depth analysis of corrosion mechanisms.

Mechanism of sour corrosion is not clearly defined so far. Therefore, the researches have proposed different forms of mechanism depending on their research experience. The
mechanism of H₂S corrosion has been defined based on the kinetics of iron sulfide formation, precipitation and dissolution. Generally, it is assumed that the formation of iron sulfide occur by direct heterogeneous reactions with iron and sulfide. The general equations for the formation of iron sulfide are shown below.

### Cathode Reactions

**H₂S Dissolution**

\[ \text{H}_2\text{S(g)} \leftrightarrow \text{H}_2\text{S(aq)} \quad \text{...(7)} \]

**H₂S Dissociation**

\[ \text{H}_2\text{S(aq)} \leftrightarrow \text{HS}^-\text{(aq)} + \text{H}^+(\text{aq}) \quad \text{...(8)} \]

**HS⁻ Dissociation**

\[ \text{HS}^-\text{(aq)} \leftrightarrow \text{H}^+(\text{aq}) + \text{S}^{2-}\text{(aq)} \quad \text{...(9)} \]

### Anode Reactions

**Dissolution of Steel**

\[ \text{Fe} \leftrightarrow \text{Fe}^{2+}\text{(aq)} + 2\text{e}^- \quad \text{...(10)} \]

**FeS Formation**

\[ \text{Fe}^{2+}\text{(aq)} + \text{S}^{2-}\text{(aq)} \leftrightarrow \text{FeS(s)} \quad \text{...(11)} \]

In addition to these reactions, different researches have introduced different reactions that may occur in the same environment.

Loff et al. [14] introduced four steps that may occur in the sour environment which is leading Hydrogen atoms to enter into the metal.

\[ \text{H}_2\text{S} \rightarrow \text{H}^+ + \text{HS}^- \quad \text{...(12)} \]

\[ \text{HS}^- \rightarrow \text{HS}^-\text{ads} \quad \text{...(13)} \]

\[ \text{HS}^- + \text{H}_2\text{O}^- \rightarrow (\text{H-S-H})\text{ads} + \text{H}_2\text{O} \quad \text{...(14)} \]

\[ (\text{H-S-H})\text{ads} + \text{e}^- \rightarrow \text{HS}^-\text{ads} + \text{Hads} \quad \text{...(15)} \]

Kawashima et al. [16] proposed another reaction model that leads to introduce hydrogen atoms to the metal.

\[ \text{H}_2\text{Sads} + \text{e}^- \rightarrow \text{H}_2\text{Sads}- \quad \text{...(16)} \]

\[ \text{H}^+ \rightarrow \text{Hads}^+ \quad \text{...(17)} \]

\[ \text{H}_2\text{Sads}- + \text{Hads}^+ \rightarrow \text{H}_2\text{S-Hads} \quad \text{...(18)} \]

\[ \text{H}_2\text{S-Hads} \rightarrow \text{H}_2\text{Sads} + \text{Hads} \quad \text{...(19)} \]

where H₂S-Hads is an unstable combination which results to form atomic hydrogen due to the quick dissociation.

### 3.3.1 Propagation of the Corrosion

Following the formation of initial iron sulfide layer, the thickness of the layer begins to grow if the dissolution rate of FeS does not equal or exceed the formation rate. The growth of iron sulfide scale and the propagation of corrosion occur simultaneously. The study of sour corrosion mechanism under controlled pH by Omal et al. [10] proposes that the propagation of corrosion or propagation of iron sulfide scale is governed by galvanic corrosion reactions. The authors suggest that the corrosion product (Iron sulfide scale) is coupled with the steel surface to propagate the corrosion reactions. It means that the iron sulfide scale acts as a cathode while the steel is producing Fe²⁺ ions creating a galvanic cell arrangement (Figure 9). The experiment revealed that the aggressiveness of the corrosion changes depends on the corrosion product. Corrosion becomes more aggressive if the corrosion product is pyrrhotite (polymorph of iron sulfide) and it becomes less aggressive with the corrosion product of pyrite. The results obtained in that research indicate the following trend of corrosiveness towards steel: Pyrite (FeS₂) > Smythite (Fe₃S₄) > Greigite (Fe₃S₄) > Mackinawite (FeS₀₋₁) > Pyrrhotite (FeS₀₋₁). But the research has failed to mention how Fe²⁺ combine with S²⁻ to produce iron sulfides.

![Figure 9 - Galvanic Cell Arrangement between Base Metal (Mild steel) and Corrosion Product](image-url)

Smith et al. [3] have presented an acceptable mechanism for the combination of Fe²⁺ with S²⁻. They suggest that the Fe²⁺ ions diffuse outward from the metal surface through the porous iron sulfide scale. Subsequently sulfide ions combine with Fe²⁺ to form iron sulfide.

The research work carried out by Sun et al. [6] to study the propagation of sour corrosion reports that the multiple ruptures on iron sulfide layers allow hydrogen sulfides to enter into the steel surface. Sun et al.’s model says that these ruptures are pathways to meet solution and the surface to occur corrosion reactions. But Shoesmith et al. [16] mentioned that there is a possibility of nucleating different
types of iron sulfide layers in locations out of these paths. Therefore, it can be concluded that the ruptures are not the only path of the propagation of the corrosion. An answer for this dilemma is suggested by Paper and Smith [17] using the structure of Mackinawite (which is a polymorph of iron sulfide) as well as the main polymorph that could be formed during the sour corrosion reactions.

Mackinawite forms a sheet-like structure and it has been shown that divalent ions can be held within the intra-planar structure of Mackinawite. Therefore, Fe\textsuperscript{2+} ions should also be able to migrate away from the metal surface and towards the film-electrolyte boundary by moving along this path. Hence, there is a possibility for the formation of iron sulfide out of the aforementioned ruptured pathways. Therefore, it could be concluded that there are three basic ways that sulfide and ferrous iron species can move for the propagation of corrosion through the formation of iron sulfide.

1. Fe\textsuperscript{2+} ions diffuse outward through cracks/porous film to the film-bulk solution interface to form precipitates of iron sulfides as shown by reaction paths “e” in Figure 10.
2. Sulfide ions move along the ruptured pathways “d” because of the diffusion of sulfide species to the base metal through ruptured paths.
3. Fe\textsuperscript{2+} ions move between the planes of the Mackinawite until they reach a sulfide source at the film-electrolyte boundary to form one of the Fe-S species.

Ferrous ions or FeHS\textsuperscript{+} ions that diffuse out of the cracks to the film/bulk solution interface are also available to either enhance the local film growth or nucleate new FeS crystals.

5. Conclusions

A significant level of research work has been carried out in the past fifteen years for the investigation of sour environment corrosion including hydrogen sulphide corrosion and sulphide stress corrosion. However, none of the research work could clarify the behaviour of corrosion comprehensively and accurately to develop a proper prediction model. Even though a number of corrosion prediction models have been developed for years, they are valid only under certain conditions.

Figure 10 - Different Reaction Pathways for Mackinawite

It can be concluded that the following findings of this study are significant in developing a proper model to predict the rate of hydrogen sulphide corrosion.

1. The main factors which determine the behaviour of hydrogen sulphide corrosion are hydrogen sulphide concentration, iron sulphide scale, temperature, exposure time, flow effect and solution composition.
2. Physio-chemical, electro-chemical and mechano-chemical aspects should be considered at the development of a prediction model.
3. Hydrogen sulphide concentration is the key factor of determining the rate of corrosion as diffusivity of H\textsubscript{2}S as well as H\textsuperscript{+} atoms play a major role in the propagation of corrosion.
4. Temperature does not predominantly affect the corrosion rate compared to the other parameters.
5. The type of iron sulphide scale determines the behaviour of the propagation of corrosion.
6. The effect of flow rate on the rate of corrosion has not been identified yet.

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