Electrochemical Mechanism and Model of H₂S Corrosion of Carbon Steel

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Abstract

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Electrochemical Mechanism and Model of H₂S Corrosion of Carbon Steel

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The mechanism of carbon steel corrosion in H_2S environment (sour corrosion) has been investigated since 1950s and still poorly understood now. This obstacle hinders the development of an effective protocol for corrosion control and protection in sour environment. The goal of this thesis project is to understand H_2S corrosion mechanism through systematic experimental studies and to build a mechanistic corrosion model to simulate the corrosion process at different conditions, including H_2S partial pressure, pH, flow rate, and temperature.

The first part of the project investigated electrochemical behavior of carbon steel corrosion in pure H_2S environments. Initially, the uniform H_2S corrosion mechanisms were experimentally studied in short term corrosion experiments (lasting 1-2 hr) before any significant interference from iron sulfide corrosion product layers occurred. Corrosion rates were obtained by linear polarization resistance (LPR). Mechanisms related to H_2S/CO_2 corrosion were investigated using potentiodynamic sweeps and by comparison with electrochemical modeling. LPR results showed that corrosion rates increased with increasing temperature, partial pressure of H_2S , flow rate and decreasing pH. Results of potentiodynamic sweeps show the presence of H_2S could affect both cathodic reactions and the anodic reaction. An electrochemical model was developed and can be used to predict the effect of temperature, pH, pH₂S and flow on corrosion

mechanisms of mild steel in aqueous solutions containing H_2S in the absence of protective iron sulfide layers.

In the second part of the project, the combined action of H_2S and CO_2 corrosion was investigated. Experiments were conducted at the different H_2S concentrations ranging from 0 to 10% in the gas phase at 1 bar total pressure at pH 4.0 and pH 5.0. Results showed that the presence of H_2S slowed the charge transfer kinetics related to H_2CO_3 and H_2O reduction reactions at the steel surface. An electrochemical corrosion model was developed for a mixed H_2S/CO_2 system which was calibrated with new experimental results and compared to data in the open literature.

The third part of the project investigated the effect of the iron sulfide corrosion product layer on H_2S corrosion and kinetics of iron sulfide formation. The existence of the thin "inner" iron sulfide layer and its effect on H_2S corrosion were clarified based on literature research. The effect of the "outer" iron sulfide layer was investigated using a new experimental set-up which permitted continuous replenishment of fluid to control the surface water chemistry, especially the pH. The effect of pH, flow rate, and temperature on iron sulfide corrosion product layer growth and corrosion rate was examined. High pH, low flow rate and increased temperature lead to a higher precipitation rate of iron sulfide on the steel surface and to the formation of a protective iron sulfide layer.

Finally, a comprehensive mechanistic transient model of uniform CO_2/H_2S corrosion of carbon steel has been developed, covering three main processes underpinning corrosion: aqueous chemical reaction in the bulk solution, electrochemical reactions including the mass transport between the bulk solution and the steel surface, and a corrosion product growth model for iron carbonate and iron sulfide layers.

Dedication

To My parents, Jinyuan Zheng and Yaque Zhu My wife, Jing Ning And all other family members

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Figure 138. XRD analysis of surface corrosion products after 6 days corrosion, showing mackinawite. Conditions: pH 5.0, 60rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2

Chapter 1. Introduction

In oil and gas production and transportation, a key challenge is ensuring process safety, integrity of infrastructure, environmental protection and, most importantly, the safety of personnel. Hydrogen sulfide (H_2S) gas is toxic, highly corrosive, and explosive, so the internal corrosion of carbon steel in the presence of H_2S represents a significant problem [1]–[4]. Although some high cost corrosion resistant alloys (CRAs) have been developed to resist H_2S corrosion, carbon steel is still the principal construction material for oil and gas pipelines due to its advantages in economy, availability and strength [1]. Corrosion of carbon steel in H_2S containing media has been investigated since the 1940s [4], and this has recently received increased attention due to the harsher environmental and chemical factors relating to newly exploitable sources of oil and gas, which usually contain H_2S gas. However, until now, H_2S corrosion research remains confusing and sometimes even contradictory. Consequently, it is very important to improve the understanding, prediction, and mitigation of H_2S corrosion for oil and gas production.

Corrosion of carbon steel in aqueous solutions can be divided into three mechanistic elements: the homogenous water chemistry in the aqueous solution, the electrochemical reactions that occur on the bare steel surface, and the formation and growth of a protective corrosion product layer. These three mechanistic components have been intensely investigated for CO_2 corrosion over the past 30 years; therefore, they are now well understood [5]–[9]. Several CO_2 corrosion models have been developed to predict uniform CO_2 corrosion [10]. Good agreement was typically obtained between these models in iron carbonate layer-free conditions, but deviation is observed when an iron carbonate corrosion product layer is present.

Compared to CO_2 corrosion, corrosion in H_2S environments is considered to be more difficult to predict and combat because of inadequate understanding of the mechanisms involved. Experimental investigations have been performed in various studies on H_2S corrosion [4], [11]. Most research was focused on specific aspects such as the effect of H_2S on water chemistry and the effect of H_2S on the formation of various crystalline polymorphs of iron sulfide corrosion product, such as mackinawite, greigite, troilite, pyrrhotite and pyrite.[12]. Only a handful of the research focused on the effect of H_2S on the electrochemical anodic and cathodic processes [13], [14].

The research described in this dissertation was undertaken to rectify this by conducting a systematic investigation of the influence of H_2S on anodic and cathodic reactions in both pure H_2S and mixed CO_2/H_2S environments. The effect of other parameters in H_2S environments such as pH, temperature and flow rate is also examined. Based on the experimental results, an electrochemical model of H_2S corrosion without corrosion product layer growth has been developed and calibrated with reliable data.

However, long-term H₂S corrosion is more related to iron sulfide (FeS) corrosion product layer formation and its effect on corrosion of mild steel. The corrosion product layer can provide protection for a long time, but equally so, deep attack may develop rapidly due to failure of the layer or formation of different iron sulfides. The magnitude of the corrosion attack is very dependent upon the nature of the iron sulfide corrosion product layer [15]–[19]. A protective layer is usually dense and has good adherence to the steel surface. A less protective layer is usually porous, flaky, and non-adherent to the steel surface. This may also lead to localized corrosion and failures. In order to study the effect of iron sulfide layer on corrosion in a controlled way, a new experimental set-up with continuous replenishment of fluid has been developed. A number of existing hypotheses related to the nature and role of iron sulfide corrosion product layer formation on H_2S corrosion were tested. For example, in order to deconvolute the effect of iron sulfide precipitation on corrosion, one of the most fundamental problems is to determine the surface water chemistry at the steel surface. This is needed to calculate the surface precipitation rate. As it is almost impossible to measure directly, a mechanistic two-node model of uniform CO_2/H_2S corrosion of carbon steel was developed to calculate this, based upon mass transfer equations, chemical equilibria and charge neutrality equations. Eventually the full effect of corrosion product layer (both iron carbonate and iron sulfide) on corrosion was built in and properly accounted for in the model.

The current project has not only provided a better understanding of the mechanism of H_2S corrosion but also developed a mechanistic model for predicting the corrosion rate of carbon steel in CO_2/H_2S aqueous environments in the oil and gas industry, which was not available before.

Chapter 2. Literature Review

Corrosion can be defined as the deterioration of materials because of chemical reactions with the environments. Of these, the most important one is electrochemical reactions of metals, which requires four essential components: the anode, the cathode, the electrolyte and the conductive material (an electrical path to connect the anode and the cathode). Moreover, a corrosion system in an aqueous solution could be considered as a short-circuited electrochemical cell in which the anode and the cathode are connected by the metal itself. In corrosion science studies, there are mainly three topics that have been studied: water chemistry, electrochemical reactions on the bare steel surface, and formation and growth of protective corrosion product layers. Water chemistry defines the equilibrium concentration of different species at different conditions such as temperature and pressure. An electrochemical reaction usually contains three steps: the reactant transported from the bulk solution to the steel surface; charge transfer reaction at the steel surface and the reaction product transported away from the steel surface to the bulk solution. The formation and growth of protective corrosion product layers play a very important role in governing the corrosion process and can even make the corrosion rate reduce from 10-100 mm/year to 0.01-1 mm/year [20]. If these three elements of the corrosion process can be investigated and fully understood, a reliable mechanistic corrosion model can be developed to predict the corrosion process. How CO₂ and H₂S affect these three elements is discussed and reviewed in the text below. An overview of the current CO₂/H₂S corrosion model is also given.

2.1 CO₂ Corrosion

Corrosion by carbon dioxide represents a major problem for the oil and gas industry. Pipelines are exposed to mixtures of hydrocarbons and aqueous solutions that contain high levels of CO_2 . How CO_2 affects the corrosion process via the influence on water chemistry, electrochemical reactions on the bare steel surface, and the initiation and growth of protective corrosion product layer are reviewed below.

2.1.1 Water Chemistry

There are always various quantities of gaseous CO_2 and water in oil and gas transmission pipelines. Dry CO_2 gas is not corrosive, but when it dissolves in water, a series of chemical reactions occur, and that may make the resultant solution corrosive to carbon steel. These reactions have been listed in Table 1 and are taken into consideration in order to calculate accurate species concentrations at different conditions [6], [21], [22]. The equations for calculating the equilibrium constants are given in Table 2 below.

conceptionang equinoritant expressions						
Name	Homogenous chemical reaction		Equilibrium expression			
CO ₂ dissolution	$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$	(1)	$K_{sol} = \frac{c_{CO_2}}{pCO_2}$	(2)		
CO ₂ hydration	$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$	(3)	$K_{hyd} = \frac{C_{H_2CO_3}}{C_{CO_2}}$	(4)		
Carbonic acid dissociation	$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^{(aq)}$	(5)	$K_{ca} = \frac{c_{HCO_3^-} c_{H^+}}{c_{H_2 CO_3}}$	(6)		
Bicarbonate ion dissociation	$\mathrm{HCO}_{3^{-}(\mathrm{aq})} \rightleftharpoons \mathrm{H^{+}}_{(\mathrm{aq})} + \mathrm{CO}_{3^{2^{-}}(\mathrm{aq})}$	(7)	$K_{bi} = \frac{c_{CO_3^2} - c_{H^+}}{c_{HCO_3^-}}$	(8)		
Water dissociation	$\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})} \rightleftharpoons \mathrm{H}^{+}_{(\mathrm{aq})} + \mathrm{OH}^{-}_{(\mathrm{aq})}$	(9)	$K_{wa} = c_{H^+} c_{OH^-}$	(10)		

 Table 1. Main chemical reactions occurring in an aqueous CO2 solution and corresponding equilibrium expressions

* "g" stands for gas phase. "aq" stands for aqueous. "l" stands for liquid. In the following text, if not particularly indicated, CO_2 and H_2S are always referring to the aqueous CO_2 and H_2S phase

Table 2. The empirical equations for the equilibrium constants

Equilibrium constant		Source
$K_{sol} = \frac{14.5}{1.00258} \times 10^{-(2.27+5.65\times10^{-3}T_f - 8.06\times10^{-6}T_f^2 + 0.075I} molar/bar$	(11)	[23]
$K_{hyd} = 2.58 \times 10^{-3}$	(12)	[24]
$ \begin{aligned} K_{ca} &= \\ 387.6 \times \\ 10^{-\left(6.41 - 1.594 \times 10^{-3} T_{f} + 3.52 \times 10^{-6} T_{f}^{2} - 3.07 \times 10^{-5} p - 0.4772 I^{\frac{1}{2}} + 0.11807 I\right)} molar \end{aligned} $	(13)	[23]
$K_{bi} = 10^{-(10.61 - 4.97 \times 10^{-3}T_f + 1.331 \times 10^{-5}T_f^2 - 2.624 \times 10^{-5}p - 1.66I^{\frac{1}{2}} + 0.34661I)} molar$	(14)	[23]
$K_{wa} = 10^{-(29.3868 - 0.0737549T_k + 7.47881 \times 10^{-5}T_k^2)} molar^2$	(15)	[25]

* T_f is temperature in degrees Fahrenheit, T_k is absolute temperature in Kelvin, $I=\frac{1}{2}\sum_i c_i z_i^2$ is ionic strength in molar, and p is the pressure in bar.

To calculate the bulk concentrations of all these species, and the solution pH, in an aqueous CO_2 solution, a water chemistry model is established. In an open system, the amount of gaseous CO_2 is much larger relative to that of water. An example is a glasscell system with continuous purging of gaseous CO_2 , at a constant pressure. There are 6 unknown aqueous concentrations of species in solution (CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-} , OH^- , H^+). Five equations relating to the equilibrium expressions are listed in Table 2. One more equation is needed to determine the species concentration in the aqueous CO2 solution (6 unknowns need 6 equations to resolve). Since the aqueous solution is always charge neutral, the electro-neutrality equation must be followed, as equation (16) shows:

$$c_{H^+} = c_{HCO_3^-} + 2c_{CO_3^{2-}} + c_{OH^-}$$
(16)

Equation (16) is valid only for a pure, CO_2 -saturated aqueous solution in the absence of other species. If other ions, such as Fe^{2+} (usually produced by corrosion of steel) or CI^- or Na^+ , etc., are added in the aqueous solution, then Equation (16) must be adjusted to include these species, as Equation (17) shows.

$$c_{H^+} + 2c_{Fe^{2+}} + c_{Na^+} = c_{HCO_3^-} + 2c_{CO_3^{2-}} + c_{OH^-} + c_{Cl^-}$$
(17)

The solution pH is usually observed to increase in corrosion tests, particularly for a small volume autoclave or glass cell, due to the release of Fe²⁺ from the dissolution of carbon steel, thereby perturbing the distribution of the ionic species given in Equation (17). Dilute hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions are often used to adjust the pH of the solution as the addition of Na⁺ or Cl⁻ can change the species concentrations in relations to Equation (17). Moreover, if other homogeneous reactions occur when other species are introduced, the appropriate reaction equilibrium expressions need to be included, as would be the case for H₂S addition.

However, in a closed system (the amount of gaseous CO_2 is limited, such as in an autoclave), the pressure of gaseous CO_2 is no longer constant. Based on the simple water chemistry model developed above, this additional unknown (p CO_2) required an additional equation account for. For a closed system for CO_2 corrosion, it is the conserved equation of the total amount of carbonic species (in moles), shown in (18):

$$N_{CO_{2}(g)} + N_{CO_{2}(aq)} + N_{H_{2}CO_{3}} + N_{HCO_{3}^{-}} + N_{CO_{3}^{2-}} = constant$$
(18)

The concentrations of different species in both the gas phase and the aqueous solution can then be calculated based on Equations (2) to (18) for a closed system.

From the water chemistry model described above, the pH is a function of the CO_2 partial pressure. The pH decreases with increasing CO_2 partial pressure. CO_2 is not only providing additional cathodic reaction species (H₂CO₃), but also acidifying the solution by carbonic acid dissociation. The pH of the solution is very important as hydrogen ion is a species involved in the cathodic reaction at the steel surface; the lower the pH, the more corrosive the solution is, and *vice versa*. Another significance of pH and CO_2 pressure is that they can impact the formation of the corrosion product layers, iron carbonate, by affecting the saturation of iron carbonate (S_{FeCO₃}) [26] defined as follows:

$$S_{FeCO_3} = \frac{c_{Fe^{2+}}c_{CO_3^{2-}}}{K_{spFeCO_3}}$$
 (19)

where K_{spFeCO_3} is the solubility product of iron carbonate (siderite).

When pH and CO₂ pressure are increased, making $c_{CO_3^2}$ higher by reaction (20), iron carbonate is readily formed and protects the steel surface when $S_{FeCO_3} > 1$.

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons 2H_{(aq)}^+ + CO_{3(aq)}^{2-}$$
 (20)

In summary, the water chemistry, especially the pH, can be changed due to the presence of CO_2 in the system. Therefore, the other two parts of the corrosion process, electrochemical reactions and corrosion product formation are affected.

2.1.2 Electrochemical Reactions

As the CO₂ corrosion process is an electrochemical process occurring at the steel surface. The kinetics of different electrochemical reactions is one of the most important factors affecting corrosion processes. The overall reaction is given by equation (21) or equation (22). The appropriate form depends on whether saturation of iron carbonate is exceeded (S_{FeCO_3} >1) and solid iron carbonate forms or not.

$$Fe_{(s)} + CO_{2(g)} + H_2O_{(l)} \Longrightarrow Fe^{2+}_{(aq)} + CO_{3}^{2-}_{(aq)} + H_{2(g)}$$
 (21)

$$Fe_{(s)} + CO_{2(g)} + H_2O_{(l)} \Longrightarrow FeCO_{3(s)} + H_{2(g)}$$

$$(22)$$

The above reaction consists of two simultaneous electrochemical half-reactions: anodic reaction (oxidation) and cathodic reaction (reduction), which have been extensively investigated in the literature. [5], [6], [9], [21], [26]. The rates of the electrochemical reactions can be dependent on the mass transport rates of reactants to the steel surface and products away from the steel surface.

2.1.2.1 Anodic Reaction

The main anodic reaction is the oxidative dissolution of iron to give ferrous ions:

$$\operatorname{Fe}_{(s)} \to \operatorname{Fe}^{2+}_{(aq)} + 2e$$
 (23)

The mechanism and kinetics of anodic iron dissolution reaction in strong acid solution was proposed by Bockris, *et al.* (1961) [27], shown in Equations (24), (25) and (26).

$$Fe_{(s)} + OH_{(aq)}^- \rightleftharpoons FeOH_{(ad)} + e^-$$
 (24)

$$\operatorname{FeOH}_{(\mathrm{ad})} \xrightarrow{\operatorname{RDS}} \operatorname{FeOH}_{(\mathrm{ad})}^+ + e^-$$
 (25)

$$FeOH^+_{(ad)} \rightarrow Fe^{2+}_{(aq)} + e^-$$
(26)

here, "ad" stands for the adsorbed complex at the metal surface.

The rate determining step (RDS) is reaction (25), which is dependent on the surface coverage of $FeOH_{(ad)}$, an active complex formed by adsorption of OH⁻ on the iron surface. It has been widely agreed that the anodic reaction rate has a first order dependence with respect to OH⁻ at pH < 4. The pH dependence then disappears gradually at pH > 4 as the surface becomes saturated with OH⁻ ions.

In a CO₂ environment, the mechanism of the anodic iron dissolution has been debated. In the middle of the 1970s, the mechanism of iron dissolution in a strong acid solution described above was adopted by de Waard and Milliams [22] in their studies of CO₂ corrosion. Experimental results by Schmitt and Rothmann [28] in CO₂ containing Na₂SO₄ solution in the temperature range of 25°C to 75°C also confirmed an anodic Tafel-slope of $b_a = 40 \pm 1$ mV, following the uncatalyzed mechanism for iron dissolution proposed by Bockris, *et al.* Independence of the anodic reaction rate on flow was also found in their works. Hurlen and Gunvaldsen [29] found CO₂ has little effect on the

anodic reaction of iron in the active state. In the 1990s, Linter and Burstein[30] also reported that the kinetics of the iron dissolution is unaffected by CO_2 . Videm, *et al.* [31], [32] determined that the rate of iron dissolution is proportional to the OH⁻ concentration and is flow independent at pH < 4.5. Potentiodynamic sweep and galvanostatic techniques were used by Nešić, *et al.* [6], [33]. An expression for the anodic reaction rate calculation was given as follows:

$$i_a = k(c_{0H^-})^{a_1} (pCO_2)^{a_2} 10^{\frac{E}{b_a}}$$
(27)

Here $a_1=2$, when pH < 4; $a_1=0$ when pH > 5 and there is a transition zone between pH 4 and 5. The effect of pCO₂ becomes noticeable for pCO₂ < 0.1 bar ($a_2 = 1$) and seems to vanish after pCO₂ > 0.1 bar ($a_2 = 0$).

Finally, Nešić [34] suggested that the reaction rate for the active iron dissolution is independent of flow and not a strong function of pCO_2 and pH, but increases with temperature in a CO_2 environment. Moreover, there may be some variations in the kinetics of anodic reaction from one type of carbon steel to another; however, the corresponding corrosion process does not appreciably vary, as it is typically controlled by the cathodic reactions, especially the mass transport process of species from the bulk solution to the steel surface.

2.1.2.2 Cathodic Reaction

The three cathodic reactions commonly proposed and adopted for de-aerated CO₂ saturated solution are:

$$2H_{(aq)}^{+} + 2e^{-} \rightarrow H_{2(g)}$$
 (28)

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$$2H_2CO_{3_{(ag)}} + 2e^- \rightarrow H_{2_{(g)}} + HCO_{3_{(ag)}}^-$$
 (29)

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + OH_{(aq)}^-$$
 (30)

Reaction (28) is well known as hydrogen evolution or hydrogen ion (H⁺) reduction, which has been intensely investigated in strong acid solutions with different substrates [35] in the absence of CO_2 . The reaction rate of H⁺ reduction depends on the concentration of H⁺, temperature, and mass transport processes. The H⁺ ions need to be transported from the bulk solution to the metal surface before the reaction takes place on the metal surface. The diffusion limiting rate of H⁺ reduction was found to be ten times lower with one pH unit decrease in strong acid solution.

de Waard and Milliams [22] investigated CO_2 corrosion of steel in 1975 and found that the corrosion rate in CO_2 gas purged solution is significantly different from what is expected for fully dissociated strong acid solutions at the same pH. They explained the fact by introducing an additional reaction (29), the so called "direct reduction" of H₂CO₃. According to the authors, the release of hydrogen from the adsorbed H₂CO₃ is a rate controlling step for aqueous CO₂ corrosion, which meant that the corrosion process is under charge transfer control of direct H₂CO₃ reduction. Schmittt and Rothmann[36] adopted the mechanism of direct reduction of H₂CO₃, but proposed that the rate determining step is the slow heterogeneous hydration of adsorbed aqueous CO₂, as (31) follows:

$$CO_{2(ad)} + H_2O_{(l)} \to H_2CO_{3(ad)}$$
 (31)

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Gray, *et al.* [21], [37] suggested a similar cathodic reactions mechanism to Schmitt and Rothman. However, they concluded that the rate controlling step is the homogeneous CO_2 hydration, reaction (4), rather than the heterogeneous reaction, reaction (31). Similarly, Nešić also proposed the homogeneous hydration of aqueous CO_2 into H₂CO₃ as the rate determining step and suggested CO_2 corrosion cathodic limiting current is contributed to one or more of the following processes: the diffusion of H⁺ ions, the diffusion of H₂CO₃ and the homogeneous hydration of CO₂.

However, Remita, *et al.* [38] rejected the direct reduction hypothesis and concluded that the higher corrosion rates in a CO_2 purged solution is mainly due to the "buffering" effect of CO_2 . This is described as lowering or stabilizing the pH at the steel surface by providing additional sources of H⁺ ions via dissociation of carbonic acid. By comparison of modeling results with their experimental polarization results, direct reduction of carbonic acid did not need to be taken into consideration. Linter and Burstein[30] also rejected the direct reduction of H₂CO₃ or HCO₃⁻ because they are thermodynamically unfavorable in comparison with reduction of the other components.

It is important to know whether direct reduction of H_2CO_3 plays any role in the usual corrosion conditions, because it can help to better predict CO_2 corrosion at a high pressure of CO_2 . However, until now, an agreement on this subject has not been reached by the current research efforts, which is the focus of ongoing project in Institute for Corrosion and Multiphase Technology (ICMT) at Ohio University.

As the availability of hydrogen ions decreases, at pH > 5 and lower partial pressure of CO₂ ($p_{CO_2} \ll 1bar$), H₂O reduction, reaction (30), can become important. This reaction is under charge transfer control and insensitive to flow since water molecules are omnipresent at the steel surface.

2.1.2.3 Mass Transport

Mass transport plays a very important role in the corrosion process, since it has significant interplay with electrochemical reactions at the steel surface. Mass transfer in an electrochemical system typically involves transport of ions from the bulk of solution to the steel surface and *vice versa*. During the electrochemical reaction process, certain species are consumed or produced at the steel surface. Their surface concentration is changing, dependent how fast the mass transfer process can replenish or sweep away solution species. This directly affects the electrochemical reaction rate and changes the corrosion rate.

Mass transport of species is governed by three mechanisms: diffusion due to the concentration gradient, electro-migration of ions in the electric field, and convection due to the bulk flow of solution. Mass transport due to electro-migration is usually negligible. Electro-migration of ions is due to the potential gradient. In a solution with large amounts of supporting electrolyte, such as a NaCl solution, any electric field established due to variation of diffusion can easily be reduced [8]. Convective mass transport arises due to the bulk velocity. However, the component of the mean velocity perpendicular to the steel surface is zero close to the surface and the convection in the diffusion boundary layer is eliminated. Thus, the mass transport process is dominated by diffusion near the steel surface. Both molecular and eddy diffusion contribute to the total (effective)
diffusion. Molecular diffusion occurs within a liquid boundary layer under the influence of the concentration gradient. Eddy diffusion is the diffusion of mass by eddies in turbulent flow. Their contributions to mass transport are both included when calculating mass transfer coefficients.

Thus far it has been believed that in the potential region with higher current densities, where Tafel behavior is no longer observed, H⁺ reduction is controlled by the mass transfer process [6], [39] and direct H_2CO_3 reduction is observed to be controlled by the interaction between mass transfer process and chemical reaction (slow CO_2 hydration) [6], [36].

2.1.3 Iron Carbonate Protective Corrosion Product Layer Formation

In CO₂ corrosion, several corrosion products can be observed, such as cementite (Fe₃C), iron carbonate (siderite, FeCO₃) and magnetite (Fe₃O₄), which depend on the corrosion conditions. Of these, iron carbonate is the most common corrosion product layer for CO₂ corrosion. It forms on the steel surface by reaction (32). The iron carbonate layer can be protective by acting as a diffusion barrier for corrosive species and covering the steel surface.

$$Fe^{2^{+}}(aq) + CO_{3}^{2^{-}}(aq) \rightleftharpoons FeCO_{3}(s)$$

$$(32)$$

The formation of the iron carbonate layer is largely dependent on solution water chemistry and temperature [19], [26]. Saturation of iron carbonate (S_{FeCO_3}) as defined in Equation (19) is used to describe whether the iron carbonate layer can form or not. If the saturation value is less than one (undersaturation), the precipitation of iron carbonate is

impossible. When saturation is greater than one (supersaturation), an appreciable amount of iron carbonate precipitates on the steel surface. Moreover, another important concept, scaling tendency (ST) as shown in Equation (33), is introduced by van Hunnik *et al.* [40] and used to describe the protectiveness of the iron carbonate layer.

$$ST = \frac{PR}{CR}$$
(33)

Here PR represents the precipitation rate and CR represents the corrosion rate, in the same units. When PR is specified for precipitation rate on the steel surface, ST will be referred to SST (surface scaling tendency). When ST value is greater than a critical value, which indicates the precipitation of iron carbonate proceeds faster than the corrosion of steel, the conditions are favorable for the formation of dense and protective iron carbonate layer. When ST value is less than the critical value, porous and unprotective iron carbonate layer are likely to form. Apparently, the protectiveness of iron carbonate layer is determined by the competition between corrosion and precipitation.

2.1.4 Key Influential Factors

Many factors can affect corrosion by influencing the individual component processes described above: the water chemistry of the solution, the electrochemical reactions, and the formation and growth of the corrosion product layer. Actually, these three components are interdependent and affect each other. The water chemistry can affect the electrochemical reactions and the corrosion product formation by changing the concentrations of different species. The electrochemical reactions can also change the water chemistry by releasing the Fe^{2+} to solution and make it favorable for corrosion product formation. Corrosion product formation can reduce the electrochemical reaction rates by covering the steel surface or acting as a diffusion barrier and also change the water chemistry by consuming Fe^{2+} . Several important factors in uniform CO₂ corrosion will be discussed in the following text.

2.1.4.1 Effect of pH

The solution pH represents the concentration of the free H⁺ ions available for H⁺ reduction as reflected by reaction (28). The lower pH causes high corrosion rate and *vice versa*. Moreover, another significance of pH is that it indirectly relates to the formation of iron carbonate corrosion product layer by changing the saturation of iron carbonate (S_{FeCO_3}) . Higher pH of the solution leads to an increase in carbonate concentration, as Equation (20) shows, and helps the formation of iron carbonate, which would change the corrosion rate.

From the water chemistry component introduced in the last section, it can be seen that pH is not only determined by CO_2 partial pressure, but also depends on other species in the aqueous solution. Formation water often contains various ions such as Fe^{2+} , Na^+ , Ca^{2+} , CI^- , SO_4^{2-} , CO_3^{2-} and HCO_3^{-} [41]; the presence of HCO_3^{-} will help increase the pH. Condensed water usually does not contain extraneous ions [41]. The solution pH will usually be lower, making condensed water more corrosive.

2.1.4.2 Effect of CO₂ pressure

According to the water chemistry model described in the previous section, the higher the partial pressure of CO_2 (p CO_2), the higher the concentration of H_2CO_3 will be in the solution. Therefore, more H⁺ ions from H_2CO_3 dissociation can be produced, and

higher corrosion rates are expected due to higher H⁺ reduction rates. Nevertheless, the corrosion rate is observed to increase with pCO_2 increase even at a constant pH. That is because the increase of H₂CO₃ concentration enhances H₂CO₃ reduction rate according to reaction (29). Moreover, under some conditions favorable for iron carbonate layer formation, the increase in pCO₂ could lead to the increase of $CO_3^{2^-}$ ion concentrations and the saturation for iron carbonate, which accelerated the formation of iron carbonate and reduce the corrosion rate. This is particularly true when the pCO₂ reaches a very high value, such as at supercritical levels [20].

2.1.4.3 *Effect of temperature*

The corrosion rate is expected to increase with temperature due to the acceleration of all the processes including electrochemical reactions, chemical reactions, and the mass transport process in solution. However, this is only the case when no protective corrosion product layer, such as iron carbonate, is present on the steel surface. An increase of temperature can also promote the kinetics of iron carbonate layer formation, which slows down the corrosion rate. Therefore a peak corrosion rate is usually observed at an elevated temperature [21].

2.1.4.4 Effect of flow

As mentioned earlier, flow can enhance transport of reactant towards the steel surface and corrosion product away from the steel surface. The higher corrosion rate is expected with higher flow. This point has been confirmed in the case of corrosion without the formation of corrosion product layer [9], [26]. However, when a protective corrosion product layer formed on the steel surface, the corrosion rate was observed to be insensitive to flow rate [7], which is indicative of the mass transfer resistance contributed

mainly by the protective layer. Another important aspect of the flow effect on corrosion is that wall shear stress at high flow has been hypothesized to be able to mechanically remove the protective corrosion product layers and initiate localized corrosion. A large quantity of research work has been conducted to study this effect [42], [43] but no significant effect of flow was observed.

2.2 H₂S Corrosion

Hydrogen sulfide (H_2S) is a notorious hazardous pollutant, commonly associated with the oil and gas industry. According to safety standards, exposure to a concentration of as low as 10 ppm can cause personal stress, and it is deleterious to human health and may eventually lead to death at a concentration higher than 250 ppm. The H_2S corrosion of carbon steel has become a major issue encountered in the oil and gas industry. The mechanism of general H_2S corrosion has been debated by researchers over the past several decades [15], [16], [18], [19], [44], and still remains unclear. This even extends to the basic question as to whether H_2S corrosion of steel is a purely chemical reaction or electrochemical reaction.

2.2.1 Water Chemistry

Similar to the CO_2 case, H_2S is a weak acid and can partially dissociate to produce H⁺ ions. At low pressure, the solubility of H_2S gas can be calculated by Henry's law. The chemical reactions occurring in the bulk solution and corresponding equilibrium expressions are listed in Table 3. Many studies have been conducted to study the thermodynamics of H_2S water chemistry [12]. The equations for calculating equilibrium constants selected in the current study are given in Table 4.

Name	Homogenous chemical reaction		Equilibrium expres	sion
H ₂ S gas dissolution	$H_2S_{(g)} \rightleftharpoons H_2S_{(aq)}$	(34)	$K_{sol_{(H_2S)}} = \frac{c_{H_2S}}{p_{H_2S}}$	(35)
H ₂ S dissociation	$H_2S_{(aq)} \rightleftharpoons H^+_{(aq)} + HS^{(aq)}$	(36)	$K_{hs} = \frac{c_{HS} - c_{H^+}}{c_{H_2S}}$	(37)
HS ⁻ ion dissociation	$HS^{(aq)} \rightleftharpoons H^+_{(aq)} + S^{2-}_{(aq)}$	(38)	$K_{bs} = \frac{c_{S^2} - c_{H^+}}{c_{HS^-}}$	(39)

Table 3. Key chemical reactions in aqueous H₂S solution and corresponding equilibrium expressions

Table 4. The empirical equations for the equilibrium constants

Equilibrium constant		Source
$K_{sol_{(H_2S)}} = 10^{-(634.27 + 0.2709 T_k - 0.00011132 T_k^2 - 16719/T_k - 261.9Log_{10}T_k)}$ molar/bar	(40)	[45]
$K_{hs} = 10^{782.43945 + 0.36126 T_k - 0.00016722 T_k^2 - 20565.7315 T_k - 142.7417222 Log(T_k)}$ molar	(41)	[45]
$K_{bs} = 10^{(-23.93 + 0.030446 * T_k - 2.4831 * 10^{-5} * T_k^2)} $ molar	(42)	[25]

The concentration of different sulfide species can be predicted by a water chemistry model similar to that for a CO_2 environment. In an open system, there are 5 variable of the concentration of species in aqueous H_2S solutions (H⁺, OH⁻, H_2S , HS⁻, S²⁻), which is corresponding to 4 pairs of equilibrium expressions in Table 3 and Table 4. The new electroneutrality equation is:

$$c_{H^+} = c_{HS^-} + 2c_{S^{2-}} + c_{OH^-} \tag{43}$$

In a closed system, an additional unknown variable, pH_2S , is required to account for. The total amount of sulfide species (in moles) is conserved, given in Equation (53) below:

$$N_{H_{2S_{(a)}}} + N_{H_{2S_{(aa)}}} + N_{HS^{-}} + N_{S^{2-}} = constant$$
(44)

Figure 1 shows a distribution of equilibrium sulfide species changing with pH at 1bar, 25 °C by employing the open system model. If the closed system model is applied, the distribution of equilibrium sulfide species changing with pH is shown in Figure 2.



Figure 1. Equilibrium concentration of sulfide species as a function of pH for an open system at $pH_2S = 0.1$ bar and 25 °C.



Figure 2. Equilibrium concentration of sulfide species as a function of pH for an closed system at gas volume / liquid volume =1:1 and initial $pH_2S = 0.1$ bar and 25 °C.

From Table 1 and Table 3, it can be seen that the fundamental difference between the CO₂ and the H₂S water chemistry is that the gaseous CO₂ must undergo two steps: a dissolution step and a slow hydration step to form H₂CO₃ before dissociation while gaseous H₂S can directly dissolve to form acidic aqueous H₂S. H₂CO₃ concentration can be calculated by $c_{H_2CO_3} = K_{sol}K_{hyd} * pCO_2$ based on Equations (2) and (4). Aqueous H₂S concentration can be calculated using $c_{H_2S} = K_{sol}(_{H_2S}) * pH_2S$. Over the range of 20°C to 80°C, the ratio between $K_{sol}K_{hyd}$ for the CO₂ system and $K_{sol}(_{H_2S})$ at the different temperatures is shown in Table 5, which is around 1000. This indicates that the concentration of aqueous H₂S will be about 1100 times higher than aqueous H₂CO₃ at the same partial pressures of CO₂ or H₂S gas. In other words, in a 1 bar pCO₂ system the concentration of aqueous H₂CO₃ is equivalent to the concentration of aqueous H₂S when the pH₂S is about 1 mbar (1000ppm at 1 bar total pressure).

T _c (°C)	20	40	60	80
K_{sol} * K_{hyd} (molar/bar)	9.0×10 ⁻⁵	6.3×10 ⁻⁵	4.7×10 ⁻⁵	3.6×10 ⁻⁵
$K_{sol(H_2S)}$ (molar/bar)	1.1×10^{-1}	6.9×10 ⁻²	5.0×10 ⁻²	4.0×10 ⁻²
Ratios of $K_{sol(H_2S)}$ with $K_{sol} * K_{hyd}$	1.2×10^{3}	1.1×10 ³	1.1×10 ³	1.1×10^{3}

Table 5. The ratio between $K_{sol} * K_{hyd}$ and $K_{sol(H_2S)}$

Figure 3 shows equilibrium concentrations as a function of pH for a mixed CO_2/H_2S open system in this condition. The concentration of aqueous H_2S is almost the same as the concentration of H_2CO_3 . However, the concentration of HS^- is much smaller than the HCO_3^- concentration when the concentrations of H_2CO_3 and H_2S are the same because the dissociation constant for H_2S is 500 to 2000 times smaller than that for H_2CO_3 , which also means that the H^+ release from aqueous H_2S is also much smaller. Therefore, at the same pressure of H_2S and CO_2 (for example, 1 bar), the concentration of aqueous H_2S concentration is much higher (almost 1000 times higher) than aqueous H_2CO_3 concentration, but the resulting pH is almost the same in both conditions due to the lower dissociation constant for H_2S .



Figure 3. Equilibrium concentrations of different species as a function of pH for a mixed CO_2/H_2S open system.

2.2.2 Corrosion Mechanism

The overall reaction for general H₂S corrosion is given by reaction (45) or (46) depending on the saturation level of iron sulfide S_{FeS} , with form (45) being more appropriate when $S_{FeS} < 1$ and form (46) when $S_{FeS} > 1$.

$$Fe_{(s)} + H_2S_{(aq)} \rightarrow Fe_{(aq)}^{2+} + H_{2(g)} + S_{(aq)}^{2-}$$
 (45)

$$Fe_{(s)} + H_2S_{(aq)} \rightarrow FeS_{(s)} + H_{2(g)}$$

$$\tag{46}$$

The mechanism of general H_2S corrosion has been debated over the past several decades [15], [16], [19], [44], and still remains unclear. Two corrosion mechanisms have been proposed: an electrochemical reaction mechanism and a non-electrochemical reaction mechanism. These are reviewed below.

In this mechanism, the anodic reaction in H_2S system is iron dissolution, as shown in reaction (23).

$$Fe_{(s)} \to Fe_{(aq)}^{2+} + 2e^{-}$$
 (23)

Morris, *et al.* [46] used a mild steel rotating disc electrode (RDE) to study corrosion in aqueous solutions of acid pH (pH 3.0 to pH 4.0) with H₂S. They found that the presence of H₂S shifted the anodic polarization curves of steel toward more negative potentials in weak acid solutions, with Tafel slopes of the anodic processes at ~ 0.041 V/decade. They found the corrosion reaction order with H₂S to be $n_{H_2S} = (\partial \log i_{corr}/\partial \log c_{H_2S}) = 0.2$. Iofa, *et al.* [47], also found acceleration effects of H₂S on the anodic reaction and attributed this effect to the chemisorption and catalysis of HS⁻ ion, in the similar way as the acceleration of the anodic reaction process by OH⁻ ion adsorption. Cheng *et al.* [14] found the anodic dissolution current (*i*_a) increased with pH and H₂S concentration with reaction orders of about $n_{pH}=n_{H_2S}=0.25$ and i_{corr} increased with c_{H_2S} by a reaction order $n_{H_2S}=[\partial \log i_{corr}/\partial \log c_{H_2S})_{pH,E} = 0.20$ when $c_{H_2S}/c_{H_1} < 10^{1.5}$.

Shoesmith, *et al.* [16] proposed an iron dissolution mechanism in the presence of H_2S as follows:

$$Fe_{(s)} + HS_{(aq)}^- \rightleftharpoons FeSH_{(ad)}^-$$
 (47)

$$\operatorname{FeSH}^{-}_{(ad)} \to \operatorname{FeSH}^{+}_{(ad)} + 2e^{-}$$
 (48)

In this mechanism, bisulfide is adsorbed at the surface then two electrons are released in one step, which is unlikely to occur. However, the iron dissolution mechanism can be rewritten to appear similar to the one proposed by Bockris, *et al.* [27], this time for a solution containing H_2S , as proposed by Ma *et al.* [48]:

$$Fe_{(s)} + H_2S_{(aq)} \rightleftharpoons FeSH_{(ad)}^- + H_{(aq)}^+$$
(49)

$$\operatorname{FeSH}_{(ad)}^{-} \rightleftharpoons \operatorname{FeSH}_{(ad)}^{-} + e^{-}$$
 (50)

$$\operatorname{FeSH}_{(\operatorname{ad})} \xrightarrow{RDS} \operatorname{FeSH}_{(\operatorname{ad})}^{+} + e^{-}$$
 (51)

$$FeSH_{(ad)}^{+} + H_{(aq)}^{+} \rightleftharpoons Fe_{(aq)}^{2+} + H_2S_{(aq)}$$
(52)

Reaction (51) is the rate determining step. Combining reactions (49) to (52), the total anodic reaction will be the Reaction (23). It should be noted that the species $FeSH^+_{(ad)}$ may evolve into solid iron sulfide directly in the following way depending on the H⁺ concentration (pH) and the solubility of iron sulfide:

$$\operatorname{FeSH}^+_{(\mathrm{ad})} \rightleftharpoons \operatorname{FeS}_{(\mathrm{s})} + \operatorname{H}^+_{(\mathrm{aq})} \tag{53}$$

Combining reactions (49) - (51) and reaction (53), the total anodic reaction becomes:

$$Fe_{(s)} + H_2S_{(aq)} \rightarrow FeS_{(s)} + 2H_{(aq)}^+ + 2e^-$$
 (54)

This reaction could be considered as the direct formation of iron sulfide on the steel surface.

Similar to the CO_2 case, aqueous H_2S can also act as an additional reservoir of hydrogen ions and promote H^+ reduction.

 H_2S is an excellent electron acceptor [49], and easier to receive electrons and reduced at the steel surface. Moreover, there is a strong chemisorption of H_2S on iron via the sulfur atom [50], [51]. This places the hydrogen close to the metal surface enabling it to convert H⁺ to an adsorbed H atom without prior dissociation. Therefore, there is also a possibility of direct reduction of H_2S :

$$2H_2S_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2HS_{(aq)}^-$$
 (55)

Regarding this reaction, Morris, *et al.* [46] found that a cathodic limiting current density in an acidic solution gradually disappears as the concentration of H_2S increased. They concluded the cathodic reaction process was under activation control and the Tafel slope didn't change with H_2S , staying consistently in the range of $b_c = 0.110 - 0.116$ V/decade.

Analogous to what is observed for carbonic acid, the corrosion rate should increase with increased concentration of H_2S . However, for dominant conditions in oil and gas fields (pH > 3), an iron sulfide layer seems to always exist on the steel surface when H_2S is present. This layer's protective properties act to control H_2S corrosion, usually reducing the general corrosion rate.

As concentrations of Fe²⁺ and S²⁻reach the solubility limit, an iron sulfide layer is increasingly likely to form on the steel surface (usually a particular polymorph called mackinawite due to its fast precipitation kinetics[52]–[55]). The formation reactions for iron sulfide (S_{FeS}) can be written in different ways, depending on the pathway and the corresponding expressions for saturation can be written as shown in Table 6.

Table 6. Various iron sulfide formation reactions and expressions of saturation S_{FeS}			
Iron sulfide(mackinawite) precipitation reactions		Expressions of saturation of	
		FeS	
$Fe_{(aq)}^{2+} + H_2S_{(aq)} \stackrel{K_{sp,H_2S}}{\longleftrightarrow} FeS(s) + 2H_{(aq)}^+$	(56)	$S_{Fes} = \frac{c_{Fe^2} + c_{H_2S}}{K_{sp,H_2S} \times c_{H^+}^2}$	(57)
$Fe^{2+}_{(aq)} + HS^{-}_{(aq)} \stackrel{K_{sp,HS}^{-}}{\longleftrightarrow} FeS(s) + H^{+}_{(aq)}$	(58)	$S_{Fes} = \frac{c_{Fe^{2}} + c_{HS^{-}}}{K_{sp,HS^{-}} \times c_{H^{+}}}$	(59)
$\operatorname{Fe}_{(\operatorname{aq})}^{2+} + \operatorname{S}_{(\operatorname{aq})}^{2-} \xleftarrow{K_{\operatorname{sp},S^{2-}}} \operatorname{FeS}(s)$	(60)	$S_{Fes} = \frac{c_{Fe^{2}} + c_{S^{2-}}}{K_{sp,S^{2-}}}$	(61)

Apparently, the precipitation of iron sulfide (mackinawite) has fast reaction kinetics in comparison to iron carbonate precipitation [52] [54].

2.2.2.2 Non-electrochemical reaction mechanism

There is another mechanism of H_2S corrosion, the "direct reaction" mechanism, which is also called a "solid state reaction", proposed by Shoesmith, *et al.* [16] and used in Sun and Nešić's mechanistic model [56]. In an aqueous H_2S solution, H_2S is directly adsorbed on the steel surface to form an iron sulfide (mackinawite) film by "direct reaction", which can be represented by:

$$\operatorname{Fe}_{(s)} + \operatorname{H}_2 S_{(aq)} \to \operatorname{FeS}_{(s)} + \operatorname{H}_{2(g)}$$

$$\tag{62}$$

This initial thin iron sulfide film goes through a cyclic process of growth, internal stress cracking and delamination, and generates an outer sulfide layer from the steel surface.

According to Sun and Nešić [56], the evidence for the "direct reaction mechanism" can be listed as follows:

- Aqueous H₂S has a very high reactivity with iron. The mackinawite layer has been shown to form rapidly (order of seconds); this is much faster than the typical kinetics of a precipitation process.
- 2. Formation of mackinawite layers is observed in highly under-saturated solutions (e.g., pH 3) where it would be considered soluble.
- 3. There is an insignificant effect of the bulk solution saturation level on the rate of mackinawite formation.
- 4. Steel surface features, such as polishing marks, are visible even after long term exposure.
- 5. In contrast to an iron or mild steel, no substantial mackinawite layer formation on stainless steel or other corrosion resistant alloys was observed. This suggests that the iron "source" in mackinawite is from the steel itself, rather than the bulk solution.
- 6. The structures and morphologies for the mackinawite layer at low temperature (20 80 °C) is similar to the corrosion product layer observed in high-temperature sulfidation of mild steel exposed to gaseous or hydrocarbon environments [57]–[59], where the precipitation mechanism is impossible.

However, these pieces of evidence can also be explained by the electrochemical reaction mechanism. The first point regarding the high reactivity of aqueous H_2S with iron can be explained by the fast kinetics of mackinawite precipitation. Rickard, *et al.*, reported that the precipitation kinetics of mackinawite at neutral pH (6-8) is of the order of milliseconds, and an apparatus for the study of the fast precipitation reactions was built for this reason [53]–[55].

The second piece of evidence that the iron sulfide can form in highly undersaturated solutions can be explained by two points: the surface pH and chemisorption of H_2S . First, there always exists a higher surface pH [60] and elevated Fe^{2+} ion concentration at a steel surface due to the corrosion of iron, especially at low flow conditions. Therefore, local conditions at the surface can readily exceed the mackinawite solubility limit and thus favor mackinawite formation, even when the bulk solution is still considered to be undersaturated. This situation can also occur for iron carbonate formation, which has been proven to be governed by a precipitation mechanism. Iron carbonate can form in under-saturated bulk solutions [61], especially in stagnant conditions with a high pCO₂. Building on an analogy between iron carbonate and iron sulfide precipitation processes, the H_2CO_3 concentration (80°C, 3.61×10⁻⁴ mol/L) at the 10 bar pCO_2 condition is almost the same as the aqueous H₂S concentration (80°C, 3. $\times 10^{-4}$ mol/L) at the 0.01 bar pH₂S condition. Moreover, the iron sulfide precipitation rate is faster than iron carbonate precipitation [54]. Thus, iron sulfide precipitation on the steel surface is possible in undersaturated bulk conditions even at low pH₂S conditions (0.01 bar). Secondly, at the extremely low pH and low H₂S concentration (for example, pH3, 0.01 mbar), iron sulfide is also observed, but it is detected only by XPS and not

XRD. Many researchers argued that amorphous iron sulfide formed on the steel surface so it was not detect by XRD. However, Rickard, *et al.* [62] and Wolthers, *et al.* [63] have proven that amorphous iron sulfide is nanoparticle mackinawite, which can be detected by XRD with a broad peak at 18 degrees 20. On the other hand, the XPS results which were used to claim iron sulfide formation can be explained by the chemisorption of H_2S on the iron surface. Careful comparison of the XPS results shows almost exactly the same peaks location for reported analyses in different sulfur-Fe systems. Chemical binding energy between Fe and S atoms for iron sulfide in both aqueous H_2S [61] and thiols environment [64] is the same, around 162 eV [65], [66]. This indicates that chemisorption of H_2S onto the steel surface in aqueous H_2S solution may occur, analogous to the situation for thiols onto iron.

The third piece of evidence presented by Sun and Nešić [56] in support of their proposed mechanism is that there is an insignificant effect of bulk solution saturation level on the rate of mackinawite formation. This can be alternatively explained with three arguments. First, the bulk solution saturation level was changed by Sun and Nešić [56], by adding Fe^{2+} ions into solution at the beginning of the corrosion experiments. As iron sulfide precipitation is very fast, the saturation level would rapidly approach close to 1, even if the initial saturation value is much higher. Second, the rate of mackinawite formation mostly depends on the surface water chemistry, which may be significantly different from bulk water chemistry. Third, it was reported by Rickard, *et al.* [54] that the rate of iron sulfide precipitation in the Fe^{2+} -H₂S-H₂O system is absent of any significant dependence on the dissolved Fe^{2+} concentration. They explained that dissolved Fe^{2+} is involved in an earlier, faster process which does not involve precipitation. All these three points explain why the rate of mackinawite formation is not strongly dependent on bulk solution saturation level.

The fourth piece of evidence presented by Sun and Nešić [56] is that steel surface features, such as polishing marks, are visible even after long term exposures. There are two reasons for this experimental phenomenon. First, the precipitation of mackinawite is usually occurring on the steel surface. The Fe^{2+} ions never get very "far" away from the steel surface due to high local pH and rapid mackinawite precipitation kinetics. This makes the mackinawite layer forming at the steel surface take on the steel surface morphological features. Secondly, the particle size of mackinawite is usually small due to fast precipitation kinetics, much faster than iron carbonate precipitation. Iron carbonate crystal will nucleate and undergo relatively slow intergrowth on the steel surface, with iron carbonate crystal morphologies clearly distinct from the underlying steel surface features. The disappearance of steel surface features has also been observed in H_2S environments when other iron sulfide polymorphs are present, such as pyrrhotite or troilite, which is more analogous to iron carbonate precipitation [67].

The fifth piece of evidence presented by Sun and Nešić [56] is that: "no substantial mackinawite (FeS) layer formation on a stainless steel or other corrosion resistant alloys was observed". Actually this point has been proven wrong. Mackinawite layers can easily be formed even on a platinum surface when -0.70 V potential (*vs.* saturated Ag/AgCl, close to corrosion potential of carbon steel) was applied [68]. This can be explained by the change of surface water chemistry with potential. When -0.70 V was not applied, the cathodic reaction of H⁺ reduction is so small (H⁺ is not consumed) that the platinum surface water chemistry is exactly the same as the bulk water chemistry,

and the precipitation will be almost the same for the platinum surface and the bulk solution. When -0.70 V was applied, the H⁺ ion reduction rate increased, and H⁺ ions were consumed on the platinum surface making the local surface pH higher. The precipitation of the mackinawite layer will then occur more readily on the platinum surface, which is similar to the carbon steel surface at the corrosion potential. Moreover, the texture of precipitated iron sulfide on the platinum substrate (Figure 4 (a)) is exactly the same as the iron sulfide formed by carbon steel corrosion (Figure 4(b)), which indicates a precipitation mechanism can be applied to iron sulfide formation in the carbon steel corrosion. Moreover, it was reported by Rickard [69] that the precipitated iron sulfide has the same texture with iron sulfide formed by iron corrosion, shown in Figure 4 (d)) does not have the same texture of precipitated mackinawite as reported in the other, higher pH₂S and higher pH, experiments. This may indicate that no mackinawite formed on the steel surface, or it is present as a thin chemisorbed iron sulfide layer.



(a) Precipitated iron sulfide on Pt at 1% H_2S/N_2 , T=30°C, pH 5.3-5.5 initial Fe²⁺ = 100ppm, potential: -0.7 V Vs. saturated Ag/AgCl[68].



(c) The morphology of iron sulfide produced by iron corrosion[69]



(b) Formed iron sulfide on carbon steel surface under the conditions of 10% H_2S (H_2S/N_2 gas), T 80 °C , pH 5.2, initial Fe²⁺ = 0ppm, the total reaction time is 1hr [19].



(d) The morphology of X65 carbon steel surface under the conditions of 100ppm $\rm H_2S,\,T\,25\ ^\circ C$, pH 4.0[61]



The sixth point is that "similar structures and morphologies for the corrosion product layer have been observed in high-temperature sulfidation of mild steel exposed to gaseous or hydrocarbon environments". Sulfidation is a similar process to oxidation and an analogy between sulfidation and oxidation can be made. A three-dimensional metal oxide film is usually transformed from a two-dimensional adsorbed oxygen layer. The process appears to be very difficult at room temperature, because the growth of an oxide film requires that ions pass an energy barrier to move into or through the oxide, which is not easily to occur at room temperature. At low temperature, only an electrochemical mechanism or a tunneling electrons transfer mechanism can be used to explain the formation of oxide film, as described by Cabrera and Mott [70]. Some researchers have even argued that high temperature oxidation in gas or hydrocarbon environments should be considered in terms of an electrochemical mechanism. If dissimilar metals are galvanic coupled, the corrosion rate should be affected according to the electrochemical nature of oxidation. In fact, such effects were observed by Ilschner-Gensch [71]. The reaction of silver with gaseous iodine at 174 °C is accelerated by contact of the silver with tantalum, platinum, or graphite. If this analogy can be made for sulfidation, a similar electrochemical mechanism for both low temperature and high temperature sulfidation can explain why the similar structures and morphologies for the corrosion product layer are observed.

Therefore experimental evidence increasingly points to the electrochemical nature of H_2S corrosion, which is shown in Appendix A. The primary goal of the current dissertation is to investigate the H_2S corrosion mechanism systematically using electrochemical techniques.

2.2.3 Physicochemical Properties of Iron Sulfides and Their Effect on Corrosion

In the previous section, only the iron sulfide, mackinawite was discussed. Iron sulfides can, however, possess a wide range of different structure types in corrosion systems, as shown in Table 7. In addition, corrosion product layers can have a wide variety of morphologies. These can be further characterized in terms of crystal size, crystallographic orientation, and lattice defects, as well as phase composition. Surface morphology can be further characterized in terms of cracking, blistering, and layering.

Name	Formula	Structure
amorphous	FeS	non-crystalline, nano particle of mackinawite
mackinawite	FeS	tetragonal, two dimensional layer structure
		consisting of stacked FeS sheets
cubic FeS	FeS	cubic
troilite	FeS	hexagonal
pyrrhotite	$Fe_{1-x}S$	Monoclinic, hexagonal or orthorhombic
greigite	Fe_3S_4	cubic
pyrite	FeS ₂	cubic

Layer thickness, porosity, and tortuosity are parameters relating to the film structure. These three parameters can profoundly affect the transport kinetics of corrosion species to the metal surface, thereby influencing corrosion processes. The mass transfer rate will be low if the thickness is high, porosity is low and tortuosity is high.

In addition, there are two types of electrical conductivity: electronic and ionic conductivity; each is summarized in Table 8 [72]. These two different modes of conductivity have important mechanistic implications on corrosion mechanisms, as shown in Figure 5. If the film is electrically conductive, the hydrogen ion reduction can take place at the outer iron sulfide surface. If the film is ion conductive, corrosion reactions can take place (hydrogen evolution and iron dissolution) at the metal surface. It can be difficult to differentiate between the two mechanisms. However, the fact that

blistering and stress cracking of corrosion product films occur indicates that hydrogen evolution takes place on the metal surface.



Figure 5. Mass and electron transfer through the compact iron sulfide [73].

Conduction type	Material	σ(S/cm)	
	Ionic crystals	<10 ⁻¹⁸ -10 ⁻⁴	
Ionic	Solid electrolytes	10^{-3} -10 ¹	
	Strong (liquid) electrolytes	$10^{-3}-10^{1}$	
	Metals	10^{1} - 10^{5}	
Electronic	Semiconductors	10^{-5} - 10^{2}	
	Insulators	<10 ⁻¹²	

Table 8. Typical values of conductivity for different materials

Regarding iron sulfide conductivity, some references [74], [75] list it as a conductor but without specifying phase type, which is inherently inaccurate. An analogy can be made with iron oxides, for example, Fe_3O_4 , magnetite, is an electrical conductor with conductivity significantly higher (×10⁶) than insulating Fe_2O_3 (10-100 µS/cm,

hematite) [76]–[79]. The relative conductivities of mackinawite, pyrrhotite and pyrite are briefly discussed below as they are usually found in sour corrosion.

The conductivity of mackinawite is a controversial subject. Some references have proposed that mackinawite is electronically conductive, hypothesizing that single mackinawite sheets are metallic. Devey, *et al.*, [80] used density functional theory to propose that Fe valence electrons within mackinawite are delocalized, hence mackinawite exhibits a metallic character parallel to its layers. Perpendicular to the layers it is claimed to act as an insulator. Due to its highly reactive nature towards oxidation, there is still no direct evidence to prove mackinawite sheets are conductive and that it exhibits electronic anisotropy.

For pyrrhotite, Wranglén [81] and Hihara [82] reported that the conductivity (σ) of Fe_{0.98}S (metal deficient) is 1600 S/cm parallel to the c-axis and 2630 S/cm perpendicular to the c-axis (cf. graphite, σ =1000 S/cm); they further described this phase as a p-type semiconductor with its conduction dependent on the c/a ratio. This anisotropic conductivity behavior has been confirmed by Pomoni [83], Vaughan and Craig [84].

Pyrite has been reported as a n-type semiconductor [84], and even has been used as a conductor for solar cell applications [49].

The conductivity of different phases of iron sulfide will likely play an important role in corrosion processes and requires further investigation.

2.2.4 Key Influential Factors

There is a large quantity of literature relating to H_2S corrosion studies. Smith and Joosten [4] reviewed research relating to CO_2/H_2S corrosion in oilfield environments and pointed out that much of the literature was somewhat confusing and often contradictory.

Recently, based on theories from published literature and their own experimental results, Sun and Nešić [56] proposed a mechanistic model to predict the corrosion rate of carbon steel, referred to in the section above. This mechanistic model does account for the effect of several factors, such as H_2S and CO_2 partial pressures, temperature, pH, etc. Sun, *et al.*, [11] conducted a parametric study of sour corrosion to provide a better understanding of corrosion in H_2S gas environments. Various factors such as gas composition (CO_2 partial pressure and H_2S partial pressure), corrosion product layer formation, temperature, reaction time, flow, and water composition were evaluated and their impacts on corrosion rate discussed. In spite of the prior sour corrosion studies, there is still a lack of a consensus as to how the various parameters affect H_2S corrosion, therefore, key factors influencing H_2S corrosion are reviewed here to clarify the effects of these parameters on H_2S corrosion.

2.2.4.1 Effect of partial pressure of H_2S

When H_2S is introduced to a pure CO_2 corrosion system and/or strong acid corrosion, the corrosion rate is retarded when even a very small concentration of H_2S was introduced. Choi, *et al.*, [61] found the corrosion rate decreased from 2 mm/y to 0.4 mm/y after the introduction of 100 ppm H_2S . Singer, *et al.*, [85] reported that the pure CO_2 corrosion rate was 8 mm/year at 2 bar CO_2 , and corrosion rate changed to 0.5-1 mm/y immediately when 4 mbar H_2S was added. This similar trend was also observed by numerous other researchers[18], [44], [86]–[88] (Smith *et al.*, Sardisco *et al.*, John Lee *et al.*, Nyborg *et al.*, and Omar *et al.*), and was attributed to the formation of a very thin, coherent film of iron sulfide.

Several research studies have shown that the increase of pH₂S could either cause acceleration or retardation of the corrosion of carbon steel, depending on the partial pressure of H₂S, pH, temperature and exposure time [74], [89]. The experimental data reported by Sun, et al., [11] showed that the corrosion rate slightly increases with increasing pH₂S under particular conditions. Smith and Pacheco [17] found that when pH₂S increases from low pressure (8×10^{-4} bar to 3×10^{-3} bar) to high pressure (between 0.04 and 0.12 bar), the weight loss corrosion rate, after 3 days, decreases from approximately 5 mm/y to 1-2 mm/y. Sardisco and Wright [90] conducted experiments with a wider range of H₂S partial pressures from 0 to 0.5 bar. They found that at the beginning, when pH₂S was increased, the corrosion rate remained constant or increased only slightly. Once a certain level of pH₂S was reached, the corrosion rate increased. Kvarekval and Nyborg [91] also performed experiments with higher pH₂S (1.38 to 4.14 bar). They reported that pH₂S in the range of 1.38 and 4.14 bar does not show a significant effect on the sour corrosion rate. Research conducted by Omar, et al.,[88] showed that, in 3 week experiments, the corrosion rate does not change significantly between 10 bar and 30 bar at room temperature. Sun, et al., [92] investigated the effect of pH₂S at the 121°C condition. The results show when pH₂S was increased from 0.1 to 1 bar, no significant increase in corrosion rate was observed; however, when pH_2S was increased from 1 to 35 bar, the corrosion rate in one day tests increased significantly

The increase of corrosion rate with increased pH_2S is probably related to the additional cathodic reaction provided by H_2S (*i.e.*, either direct reduction of H_2S or the extra hydrogen ion source provided by H_2S dissociation). The decrease of corrosion rate

compared with no significant increase in corrosion rate in seven day tests.

is probably due to iron sulfide formation, which can act as a diffusion barrier or provide a coverage affect, leading to reduction of the corrosion rate. H_2S plays dual roles here. First, H_2S is a corrosive species accelerating the corrosion rate. Second, H_2S is also a protective species reacting with the steel to form a layer that decreases corrosion rate. Consequently, during short term tests, the initial corrosion rate can be high because the layer protectiveness is not yet fully established, and thus, is overwhelmed by the accelerating role of the H_2S . However, during long reaction times such as 7 days or longer, the formation of a protective iron sulfide layer is promoted by extending the reaction time, and the sulfide layer seemed to exert a decisive influence.

Figure 6, as reported by Sun, *et al.*,[93] shows an effect of H_2S concentration on corrosion of steel. The results show the corrosion rate initially increased with increasing H_2S concentrations, then slowly decreased with further increasing H_2S concentrations to a high level. Yin, *et al.*,[94] also reported that the corrosion rate increased as pH₂S increased, and that the CR reached a maximum value (0.36 mm/a) at a pH₂S of 0.04 vol.% and decreases with a further pH₂S increase. Ren, *et al.*, [95] found a relationship between corrosion rate and partial pressure of H₂S at a temperature of 100°C. The rate of general corrosion was accelerated when pH₂S increased from 0 to 0.0025 MPa, and decreased when pH₂S increased to 0.01 MPa.



Figure 6. Effect of H_2S on corrosion at bottom of tubing condition, 93.3 °C, 3000 ppm Cl-, 6 Week Data, (Reproduced with permission from [93], © NACE international 2011).

2.2.4.2 Effect of pH

The solution pH indicates the concentration of the free hydrogen ions. First, it can accelerate the cathodic reaction by providing more cathodic reaction species. When H_2S concentration is low, the cathodic reaction is dominated by H⁺ reduction. As a result, pH can affect the corrosion rate significantly. It is noted that the corrosion rate decreased nearly linearly with increasing pH when trace amounts of H_2S were present. When H_2S concentration is higher, the cathodic reaction may be dominated by aqueous H_2S species, and the pH might have less of an effect on the corrosion rate.

Another significance of pH is that it influences the formation of iron sulfide corrosion product layers by affecting the saturation of iron sulfide. Higher pH of the solution leads to the increase in sulfide species concentration and helps the formation of iron sulfide, which would change the corrosion rate.

2.2.4.3 Effect of flow

Flow plays an important role in a corrosion process. First, flow can affect corrosion rate through the mass transport processes involved in H₂S corrosion especially when there is no corrosion product layer formed. It is known that H⁺ reduction is mass transfer controlled while H₂CO₃ reduction is controlled by slow hydration of CO₂ at higher current densities. The flow effect on H₂S reduction is still under investigation. Morris, *et al.*, [46] reported that a limiting current density in an acidic solution gradually disappears as the concentration of H₂S is increased, which indicated H₂S reduction is charge transfer controlled. Electrochemical experiments using a rotating cylinder electrode in pure H₂S solution were conducted by Galvan-Martinez and coworkers [96]. The results showed that the rotation rate can accelerate cathodic processes and further increase corrosion rate. Sun, *et al.*, [92] reported that flow could significantly accelerate general corrosion rate. Corrosion rate was found to increase from 0.45 mm/y to 2 mm/y with an increase in velocity from 0.5 m/s to 5 m/s at 25 °C, pH₂S 13.8 bar, and pCO₂ 3.4 bar.

On the other hand, when there is a protective iron sulfide layer formed on the steel surface, the corrosion rate was found to be insensitive to flow rate, similar to CO_2 corrosion. Sun, *et al.*, [19] investigated the effect of velocity by using a rotating cylinder electrode and found that velocity had a significant effect on the initial corrosion rate and had a negligible effect on the final corrosion rate after 1 day of exposure. Omar, *et al.*, [88] also studied the effect of flow on H₂S corrosion using a flow loop and no clear effects of flow under their test conditions were observed. More interesting results were reported by Bonis, *et al.*, [1]. They reviewed over 100 distinct sour field cases and found

that low flow velocities were present in most of the field cases with medium or severe corrosion, which is in contrast to laboratory findings.

Flow can also affect the formation of a protective iron sulfide layer. Species transport in turbulent flow affects the surface concentration of species and consequently the precipitation rate of iron sulfide. A protective iron sulfide layer is not easily formed at high flow conditions. In cases where flow velocities are extremely high, it is conceivable that flow can mechanically destroy the iron sulfide protective layer already in place, resulting in an increase of corrosion rate.

2.2.4.4 *Effect of temperature*

Temperature has a significant influence on corrosion rates. An increase of temperature in the corroding system has three main effects:

1. Temperature accelerates all the processes involved in H_2S corrosion including electrochemical reactions, chemical reactions including iron sulfide precipitation and transport of species.

2. The solubility of gases in the water is decreased. It means the aqueous H_2S concentration will decrease at the same partial pressure of H_2S .

3. The solubility of corrosion products may also change, resulting in different corrosion products.

Depending on these effects, especially acceleration of corrosion product layer formation rate, temperature can either increase or decrease the corrosion rate. In the case of corrosion where protective iron sulfide does not form (typically at very low pH), corrosion rate increases with increasing temperature. On the other hand, when at a condition when a protective iron sulfide layer is likely to form then temperature accelerates both the rates of corrosion as well as corrosion product formation rate, so it is believed there will be a corrosion rate peak at a given temperature. Yin, *et al.*, [94], found that the maximum corrosion rate occurred at the temperature of 100°C, while at the temperature over 100°C the corrosion rate decreased. Sun, *et al.*, [11] also reported that there is a peak corrosion rate when increasing the temperature at a fixed pH₂S. Omar, *et al.*, [88] conducted flow loops tests at high pH₂S (~10 bar), the corrosion rate slightly increased with an increase of temperature except for the data at V=3 m/s..

2.3 Corrosion Models

Corrosion models are a very useful tool to determine corrosion allowances, make predictions of facilities remaining life, and provide guidance in corrosion management. A model is generally defined to be a representation of an understanding of an object or a system. There is no uniform terminology to classify models. Nešić, *et al.*, [97] (1997) have categorized models as mechanistic, semi-empirical, and empirical based on how firmly the models are grounded in theory.

Mechanistic models have a strong theoretical background, and most of the constants in these models have some physical meaning. When calibrated against a reliable experimental database, this type of model should produce an accurate prediction in the validation range. Moreover, these models can also extrapolate for conditions out with the validation range and remain accurate to a reasonable degree. Representative types of such models were developed by Gray *et al.* [21], [37], Nešić *et al.* [6], [8], Pots [98], and Dayalan *et al.*,[99], [100]. Pure empirical and semi-empirical models usually have no or minimal theoretical background. Most of the constants have little physical meaning and are just best-fit parameters to the available experimental data. These types

of models usually provide reasonable predictions in their validation range and poor predictions out of this range. There are several empirical and semi-empirical models available in the literature such as the de Waard model [101], [102], and the Norsok model [103].

The mechanism of CO_2 corrosion is well understood through laboratory investigations. Software packages for CO_2 corrosion have been developed in the past, ranging from those based on semi-empirical correlations to mechanistic models describing the different processes involved in CO_2 corrosion of carbon steel, namely Multicorp[©], Electronic Corrosion Engineer[©] (ECE), Hydrocorr[©], Norsork, and the OLI model. Recently, Nyborg [10] has overviewed several CO_2 corrosion models based on features relating to pH determination, the effect of iron carbonate layers, oil wetting, fluid flow, H₂S, top-of-the line corrosion, and acetic acid.

In the case of H_2S corrosion, there are numerous experimental studies; however, the mechanism of H_2S corrosion is still unclear, and only a few models have been developed and published in the open literature for pure H_2S or mixed CO_2/H_2S corrosion. It was observed that the corrosion rate will be reduced even in very small concentrations of H_2S (1 mbar or even smaller). Some models just use a factor related to H_2S concentration to correct the sweet (CO_2) corrosion. Anderko, *et al.*,[104] (1999) presented a mechanistic model to simulate the corrosion rates of carbon steel in a mixed CO_2/H_2S environment. The model consists of a thermodynamic part used to predict corrosion product layer composition and an electrochemical model to simulate the rate of cathodic and anodic processes on the metal surface. However, the electrochemical model was simplistically correlated to final steady state corrosion rate data to obtain a good agreement, by using a surface coverage effect by iron sulfide. No mechanistic verification of this approach was done with electrochemical kinetics data, and the steel surface water chemistry was not distinguished from bulk water chemistry in their model. Sun and Nešić [56] (2009) published a mechanistic model based on a mass transfer control mechanism for corrosion in the presence of iron sulfide layers, often seen in H₂S corrosion. This mechanistic model was calibrated to fit a broad range of experimental results and was found to be useful for prediction of transient corrosion rates arising from growth of iron sulfide layers. However, the model includes a number of assumptions which were not explicitly verified. For example, it was universally assumed in the model that mass transfer limits the rate of H₂S corrosion and therefore the electrochemical processes were not defined or included. This is clearly a simplification and limitation of the model which needed improvement.

Above all, there is a need for a comprehensive H_2S corrosion model that takes account of the mechanisms of steel corrosion and iron sulfide formation including their protective effects.

Chapter 3. Objectives

3.1 Research Objectives

The above literature reviews on uniform H_2S/CO_2 corrosion studies and points out a significant gap that needs to be closed related to mechanisms of uniform H_2S corrosion of carbon steel and the development of a new comprehensive uniform H_2S corrosion model including effect of iron sulfide layer growth. As mackinawite is usually the prevalent iron sulfide in H_2S environment and also the precursor to other types of iron sulfides, in the current work, only mackinawite was quantified. The research objectives of this study are set as follows:

- Determine the electrochemical nature of uniform H₂S corrosion (Appendix A)
- Study the electrochemical behavior of carbon steel corrosion in both pure H₂S and mixed H₂S/CO₂ systems without iron sulfide layer growth.
- Develop an electrochemical model of uniform H₂S/CO₂ corrosion of carbon steel without iron sulfide layer growth.
- Analyze the iron sulfide layers formed in the H₂S environment in more detail and investigate how the iron sulfide layers affect the corrosion rate.
- Develop a mechanistic model for uniform H₂S corrosion including the corrosion product layer growth model.

3.2 Work Strategy

First, electrochemical techniques such as potentiodynamic sweep and linear polarization resistance were used to study the electrochemical behavior of carbon steel in both pure H_2S and H_2S/CO_2 systems. An electrochemical model based on charge transfer

current density and mass transfer limiting current density or chemical reaction limiting current density was developed.

Second, a new experimental set up with continuous replenishment of fluid was designed to control and understand the effect of the iron sulfide layer on corrosion. A new iron sulfide layer growth model was built and coupled with the previously developed electrochemical model. Lastly, a comprehensive mechanistic model was calibrated and verified with the experimental results and data from the literature.

Chapter 4. Electrochemical Study and Modeling of Carbon Steel Corrosion in Pure H₂S Environment without Iron Sulfide Layer Growth¹

4.1 Introduction

Despite many studies that have appeared in the literature, many questions still need to be answered regarding the effect of H_2S on mild steel corrosion. Some of the key ones include:

- Is there an additional cathodic reaction direct H₂S reduction? Direct H₂S reduction has been proposed by several authors, but direct evidence for its existence is still not available.
- How does the H₂S affect the anodic reaction of iron dissolution?
- What is the mechanism and kinetics of formation and growth of an iron sulfide layer?
- How does an iron sulfide layer affect the cathodic reactions and the anodic reaction?

The objective of the work in current chapter was to seek answers to the first two questions. Therefore, an experimental study was organized where corrosion of mild steel was examined by electrochemical techniques, in short term experiments, in solutions at various pH and different temperature, under various H_2S/N_2 gas concentration ratios and flow rate conditions, using an X65 mild steel rotating cylinder electrode. The third and fourth questions were partially addressed by the work of Sun and Nešić [56] and will be scrutinized and addressed further in Chapter 6 and Chapter 7.

¹ This chapter has been published as a NACE conference paper in 2013, paper No. 3907 and in Corrosion journal, 70 (4), 351-365
4.2 Experimental

4.2.1 Equipment

Experiments were performed in a 2 liter glass cell (see Figure 7) with a 1 wt% NaCl solution (prepared with deionized water). Gas (mixture of H_2S and N_2) was purged through the solution continuously. A typical three-electrode setup was used. A platinum wire was used as a counter electrode (CE). A saturated silver-silver chloride (Ag/AgCl) reference electrode (RE) was connected to the cell externally via a Luggin capillary. A rotating cylinder electrode (RCE) with a speed controller was taken as the working electrode (WE). The pH was measured with an electrode immersed in the solution. The gaseous concentration of H_2S was adjusted by using a gas rotameter and measured by a gas sample pump with H_2S detector tubes. A carbon scrubber was used to treat the gas coming out of the glass cell to remove the H_2S .

4.2.2 Material

Corrosion of X65 pipeline steel was investigated. The composition of the X-65 steel (as reported by the manufacturer) used in the present experiments is shown in Table 9. The WE was machined from the parent steel material and had a diameter of 1.20 cm and a working surface area of 5.4 cm².

Table 9. Chemical composition of 5LX05 used in the confosion tests (wt/6).										
Cr	Mo	S	V	Si	С	Fe	Ni	Mn	Р	
0.14	0.16	0.009	0.047	0.26	0.13	Balance	0.36	1.16	0.009	

Table 9. Chemical composition of 5LX65 used in the corrosion tests (wt%).



Figure 7. Schematic of the experimental cell.

4.2.3 Procedure

The aqueous solution was initially purged with N₂ gas for at least three hours to remove traces of dissolved oxygen. After the solution was deoxygenated, H₂S was dissolved by purging for at least half an hour to saturate the solution at the required partial pressure of H₂S. H₂S gas concentration was adjusted by purging different ratios of N₂ and H₂S gas, from 100 ppm(v) to 10%(v) H₂S (g), corresponding to a H₂S(g) partial pressure pH₂S = 0.1 mbar and 96.5 mbar, respectively, at 30°C. The pH was adjusted by adding a deoxygenated hydrochloric acid or sodium hydroxide. Prior to immersion, the mild steel specimen surfaces were polished with 400 and 600 grit sandpaper, rinsed with alcohol and dried with an air blower.

Polarization resistance (R_p) measurements were conducted by polarizing the WE ± 5 mV from the free corrosion potential and scanning at 0.125 mV/s. Solution resistance was measured independently using electrochemical impedance spectroscopy (EIS), and

the measured R_p was then corrected. The LPR constant B=23 mV/decade used in this work was determined from longer term weight loss measurements. EIS measurements were carried out by applying an oscillating potential \pm 5 mV around the free corrosion potential of the WE, using the frequency range 3 mHz to 5 kHz. At the end of each experiment, the potentiodynamic sweeps were conducted at a sweep rate of 1 mV/s. The cathodic sweep was performed first by commencing at the OCP; then the electrode was allowed to equilibrate back to the OCP and finally the anodic sweep starting at the OCP was performed. The solution resistance was manually corrected after the measurements. The test matrix for the experimental work is shown in Table 10.

Description	Parameters		
Test Material	API 5L X-65		
Test Solution	1 wt.% NaCl		
Purged Gas(H_2S volume fraction in H_2S/N_2)	0 - 10%(v) (0 - 0.1 bar)		
Rotating Speed / rpm	200 to 4000 rpm		
Total Pressure / bar	1		
Temperature /°C	30°C, 60°C, 80°C		
pH	2.0 - 5.0		
Test Duration	0.5 to 2 h		
Measurement Methods	LPR, EIS, Potentiodynamic		
	Sweeps, Weight Loss		

Table 10. Test matrix for the electrochemical study of carbon steel corrosion in a pure H₂S environment

4.3 **Results and Discussion**

4.3.1 Effect of pH_2S

Effects of H_2S on polarization curves at different pH values and 1000 rpm rotating speed condition are shown in Figure 8, Figure 9, and Figure 10. At pH 4.0, the cathodic polarization curve for a pure N_2 environment (without any H_2S) shows typical

characteristics, consisting of H^+ (hydrogen ion) reduction and H_2O (water) reduction. A mass transfer limiting current plateau is observed. The Tafel slope of H_2O reduction is close to 120 mV/decade. The addition of 100 ppm(v) or 1000 ppm(v) $H_2S(g)$ does not change the cathodic polarization curves much, but it results in a lower H_2O reduction rate, which indicates a retardation effect possibly due to surface coverage by a sulfide species. The H_2O reduction rate in an H_2S saturated aqueous environment is found to be approximately 20 times lower than in the same solution without H_2S . This retardation effect of H_2O reduction is observed at all experimental conditions with H_2S , even at a lower pH level, i.e., pH 2.0, where iron sulfide should be unable to form. Therefore, the retardation effect of the H_2O reduction reaction is not considered related to iron sulfide formation.

At the same pH 4.0, when 1%(v) or 10%(v) H₂S(g) was introduced, the cathodic polarization curves show a higher limiting current (plateau) at more cathodic potentials, often referred to as "the second wave". It is hypothesized here that this is an indication of the direct reduction of H₂S on the steel surface according to:

$$H_2S_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2HS_{(aq)}^-$$
 (55)



Figure 8. Effect of H_2S on polarization curves at pH 4.0, 30°C, total pressure 1 bar, 1 wt% NaCl, 1000rpm.(The repeatability of these results are shown in Appendix B)

Tests conducted at a higher pH 5.0, were able to better distinguish this direct H_2S reduction from H⁺ reduction. From Figure 9, at pH 5.0 in a N₂ environment (no H₂S), the cathodic contribution from H⁺ reduction becomes smaller and the direct H₂O reduction is the dominant cathodic reaction. The cathodic polarization curve appears almost as a straight line; no mass transfer limiting current plateau is observed. With 100 ppm(v) H₂S(g), the additional contribution from H₂S is still not clearly seen. However, in the presence of 10%(v) H₂S(g), the contribution of H₂S reduction to the total corrosion current becomes dominant. The existence of an additional electrochemical reaction - direct H₂S reduction seems to be clear. More evidence and detailed kinetics of this electrochemical reaction was investigated using a 316L stainless steel electrode. The results are shown in Appendix C.



Figure 9. Effect of H_2S on polarization curves at pH 5.0, 30°C, total pressure 1 bar, 1 wt% NaCl, 1000rpm.



Figure 10. Effect of H_2S on polarization curves at pH 3.0 and pH 2.0, 30°C, total pressure 1 bar, 1 wt% NaCl, 1000rpm.



Figure 11. Effect of flow rate on polarization curves at 1%(v) H₂S(g), pH 4.0, 30° C, total pressure 1 bar, 1 wt% NaCl. Vertical lines are corrosion currents measured by LPR using B = 23 mV/ decade.

The effect of H_2S on the anodic iron dissolution reaction can also be seen in these polarization curves. At pH 4.0 (Figure 8), with 100 ppm(v) and 1000 ppm(v) $H_2S(g)$, the anodic polarization curves shift to the left as compared with the one in the N_2 environment, which indicates a retardation effect due to H_2S . With 1%(v) and 10%(v) $H_2S(g)$, the anodic polarization curve shifts to the right suggesting an accelerating effect due to H_2S . This accelerating effect of H_2S on the anodic reaction of iron dissolution can be observed more clearly from the anodic polarization curves obtained at more acidic conditions, pH 2.0 and pH 3.0 (Figure 10). This observation also agrees with previous researchers [14], [46], [47]. The accelerating effect seems to be related to sulfide adsorption. From the results discussed above, it can be summarized that the presence of H_2S affects both anodic and cathodic reaction. There is a complex effect of H_2S on the anodic dissolution of iron and an appearance of a new additional cathodic reaction: direct H_2S reduction.

4.3.2 Effect of Flow/Mass Transfer Rate

To further elucidate the electrochemical corrosion mechanisms in the presence of H_2S , mass transfer conditions were altered by changing the turbulent flow conditions. The effect of flow/mass transfer rate on the polarization curves for the 1%(v) $H_2S(g)$ condition is shown in Figure 11. At this condition, the dominant cathodic reactions are: H^+ reduction, direct H_2S reduction, and H_2O reduction. The mass transfer limitation for H^+ and H_2S reduction gives rise to two "waves" in the cathodic curve, denoting two limiting current plateaus. Water reduction is under charge transfer control, which is flow/mass transfer independent. The reduction rates of H^+ and H_2S are influenced by the diffusion of reactants to the surface, so that, at a given flow rate, the total mass transfer limiting current i_{lim} for mild steel in an H_2S saturated solution can be described by the additive contribution of two components:

$$i_{lim} = i_{lim,H^+} + i_{lim,H_2S} \tag{63}$$

where i_{\lim,H^+} and i_{\lim,H_2S} are the limiting current densities obtained in turbulent flow conditions for H⁺ ions and H₂S molecules, respectively. The limiting current density for the newly identified cathodic reaction – H₂S reduction, which can be seen clearly in Figure 11, is found to be in good agreement with the theoretical mass transport limiting current calculated by using the Eisenberg mass transfer correlation [105], which is described in the model validation part below.

From Figure 11, a clear Tafel behavior was observed for all the anodic curves, with a 40 -50 mV /decade Tafel slope. No effect of flow on the anodic reaction was noticed, as expected.

Polarization curves for the solution purged with 10%(v) H₂S(g) at pH 4.0 are shown in Figure 12. The overall shape of the curves was slightly different compared to those in the experiments with 1%(v) H₂S(g). The second "wave" on the cathodic polarization curves is not as clearly observed as it was at 1%(v) H₂S(g). This is because the bulk concentration of H₂S is 10 times higher than before, and thereby the limiting current "wave" from H₂S reduction is masking the much smaller limiting current "wave" from H⁺ reduction. Therefore, the mass transfer limiting current in this case is mostly attributed to the reduction of H₂S. The magnitude of the mass transfer limiting current density for reduction of H₂S obtained in this test is also in good agreement with the prediction made by the Eisenberg mass transfer correlation [105].



Figure 12. Effect of flow rate on polarization curves at 10%(v) H₂S(g), pH 4.0, 30° C, total pressure 1 bar, 1 wt% NaCl. Vertical lines are representing the magnitude LPR corrosion currents derived from polarization resistance measurements by using B = 23 mV/ decade.



Figure 13. Effect of pH on polarization curves in the solution purged with N_2 , 1000rpm, 30°C, total pressure 1 bar, 1 wt% NaCl.

Both the tests at 1%(v) H₂S(g) and 10%(v) H₂S(g) confirmed that the direct reduction of H₂S is flow sensitive. All the cathodic curves displayed the mass transfer limiting currents, which could be calculated by using mass-transfer correlations. Morris, *et al.* concluded that a limiting current density gradually disappears as the concentration of H₂S increased in an acidic solution [46]. However, from review of their data, it appears that they hadn't polarized the steel low enough (in the cathodic direction) to see the appearance of the mass transfer limiting current. The current work extends their results to show that the limiting current density does increase as the concentration of H₂S is increased.

Moreover, from Figure 11 and Figure 12, it is seen that the corrosion currents i_{corr} measured by LPR (shown as vertical lines) are much smaller than the mass transfer limiting currents, which indicates that the H₂S corrosion is not always under mass transfer control as previously assumed by Sun and Nešić [56].

4.3.3 Effect of pH

4.3.3.1 Solution without H_2S

The effect of pH in a solution without H_2S is shown in Figure 13. The i_{lim,H^+} values measured at 1,000 rpm are directly proportional to the H⁺ concentration. Over the whole pH range, the Tafel line for H_2O reduction stayed approximately at the same the position, with a Tafel slope of ≈ 120 mV/decade. This agreed with the findings of Nešić, *et al.* [6]

The analysis of anodic polarization curves showed that the Tafel line for anodic dissolution of iron maintained the slope of 40 - 50 mV/decade over the whole pH range tested. The increase of the anodic exchange current density was significant from pH 2.0

to pH 4.0 and much less between pH 4.0 and pH 5.0, which is in agreement with findings of Bockris, *et al.* [27]

4.3.3.2 Solution with H_2S

The effect of pH in a solution saturated with 10%(v) H₂S(g) is shown in Figure 14. The decrease in limiting current is much less from pH 3.0 to pH 5.0 than expected accounting for an order of magnitude change in H⁺ concentration. This suggests that the cathodic reaction was not solely comprised of H⁺ reduction. The reason in this case is that the main contribution for the cathodic limiting current from pH 3.0 to pH 5.0 is from the H₂S species, whose concentration is independent of pH value. The exception is pH 2.0 where the main contribution for the cathodic limiting current is from H⁺, while only a small "bump" on the limiting current plateau can still be observed due to the additional H₂S.

From Figure 14, it can be seen that the H₂O reduction curve at 10%(v) H₂S(g) stayed approximately the same over the whole pH range, except at pH 5.0 which was most likely caused by an experimental error. Figure 14 also shows that pH had a smaller effect on the anodic dissolution reaction at 10%(v) H₂S(g), especially from pH 3.0 to pH 5.0 which is different from the results obtained without H₂S. According to the finding of Cheng, *et al.* [14], anodic dissolution current (i_a) is independent of pH and pH₂S when $c_{H_2S} / c_{H^+} > 10^{1.5}$.

Actually, the ratio of c_{H_2S} / c_{H^+} is equal to c_{HS^-}/K_{hs} , according the equilibrium expression of the first dissociation of H_2S in the solution, as Equation (37) shown. The anodic dissolution current will reach a maximum value when HS^- exceeds a specific

concentration at a specific temperature. The current experimental results in Figure 8 and Figure 14 also support this point.



Figure 14. Effect of pH on polarization curves in the solution purged with 10%(v) H₂S(g), 1000rpm, 30°C, total pressure 1 bar, 1 wt% NaCl.

4.3.4 Effect of Temperature

In order to investigate the effect of temperature in the presence of H₂S, experiments were conducted at the same aqueous H₂S concentration, c_{H_2S} , using different gas concentrations of H₂S at each temperature (30°C, 60°C, and 80°C) to maintain an approximate $c_{H_2S} = 8.3 \times 10^{-4}$ mol/L.

Corrosion rate measured from LPR increased from 1.6 mm/year at 30°C to 5.0 mm/year at 80°C. This change of corrosion rate can be explained from the polarization curves obtained at different temperatures as shown in Figure 15. Temperature is known to accelerate most of the chemical, electrochemical and transport processes occurring in the

system and both cathodic reactions and anodic currents, which were measured, increased with increasing temperature. The increase of anodic current is not as significant as the one stemming from cathodic reactions. The water reduction current and the limiting current also increase with increasing temperature.



Figure 15. Polarization curves at pH 4.0 for temperatures 30°C, 60°C, and 80°C, $[H_2S]aq = 8.3 \times 10^{-4} \text{ mol/L}$, 1000rpm, total pressure 1 bar, 1 wt% NaCl.

4.4 Electrochemical Model

4.4.1 Physicochemical Model

4.4.1.1 Cathodic Reactions

When H_2S is not present in the water, the main cathodic reaction is hydrogen evolution *via* the reduction of H^+ ions:

$$2H_{(aq)}^{+} + 2e^{-} \rightarrow H_{2(g)}$$
 (28)

This is the most important cathodic reaction in an acidic solution (pH < 4). In the case of mild steel corrosion, this reaction is usually limited by the mass transport rate of H^+ ions from the bulk solution to the steel surface (mass transfer limitation).

As the availability of H^+ ions decreases, in more neutral solutions (pH > 5), hydrogen evolution via the direct reduction of water may become important:

$$2H_2O_{(l)} + 2e^- \to H_{2(g)} + OH_{(aq)}^-$$
(30)

When H_2S is present in the water, the following additional reactions occur: H_2S gas dissolves in water to form aqueous H_2S :

$$H_2S_{(g)} \rightleftharpoons H_2S_{(aq)} \tag{34}$$

Aqueous H₂S is a mild acid which partly dissociates in two steps:

$$H_2S_{(aq)} \rightleftharpoons H_{(aq)}^+ + HS_{(aq)}^-$$
(36)

$$\mathrm{HS}_{(\mathrm{aq})}^{-} \rightleftharpoons \mathrm{H}_{(\mathrm{aq})}^{+} + \mathrm{S}_{(\mathrm{aq})}^{2-} \tag{38}$$

This provides additional H^+ ions and accelerates the H^+ reduction. However, as it has been experimentally proven in this work, adsorbed H_2S can also be an electron acceptor [49], and the evolution of hydrogen can occur via the so called direct reduction of H_2S :

 $(\mathbf{n} \mathbf{n})$

(0 1)

$$H_2S_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2HS_{(aq)}^-$$
 (55)

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This reaction has a limiting current which is controlled by a mass transfer rate of H_2S from bulk solution to the steel surface, and is therefore sensitive to flow.

4.4.1.2 Anodic Reaction

Bockris *et al.* [27] proposed the following mechanism of anodic iron dissolution in strong acids (pH \leq 4) which applies here to cases when H₂S was not present in the system:

$$Fe_{(s)} + OH_{(aq)}^{-} \rightleftharpoons FeOH_{(ad)} + e^{-}$$
 (24)

$$\operatorname{FeOH}_{(\mathrm{ad})} \xrightarrow{\operatorname{RDS}} \operatorname{FeOH}_{(\mathrm{ad})}^+ + e^-$$
 (25)

$$FeOH_{(ad)}^{+} \rightarrow Fe_{(aq)}^{2+} + e^{-}$$

$$\tag{26}$$

This mechanism suggests that the reaction order with respect to OH⁻ ions is 1, which is proven to be valid in acidic solutions; it has also been found that iron dissolution proceeds with little influence of pH for solutions where pH is approximately above pH 4 [27].

In a solution containing H_2S , the anodic reaction rate is related to HS^- ions adsorption. The mechanism is similar to the one proposed by Bockris *et al.* [27] and is shown [48]:

$$Fe + H_2S \rightleftharpoons FeSH_{(ad)} + H^+$$
 (49)

$$\operatorname{FeSH}_{(\operatorname{ad})}^{-} \rightleftharpoons \operatorname{FeSH}_{(\operatorname{ad})}^{-} + e^{-}$$
 (50)

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$$\operatorname{FeSH}_{(ad)} \leftarrow \operatorname{FeSH}_{(ad)} + e^{-}$$

$$\operatorname{FeSH}_{(ad)} \xrightarrow{RDS} \operatorname{FeSH}_{(ad)}^{+} + e^{-}$$
(50)
(51)

$$\operatorname{FeSH}_{(\mathrm{ad})}^{+} + \mathrm{H}^{+} \rightleftharpoons \operatorname{Fe}^{2+} + \mathrm{H}_{2}\mathrm{S}$$

$$\tag{52}$$

4.4.2 Mathematical Model

In order to mathematically and numerically describe the physicochemical model, the measured cathodic and anodic reactions reported above are used as a basis.

4.4.2.1 H^+ Reduction

For H⁺ reduction, in order to describe the effect of charge transfer and mass transfer on H⁺ reduction, the current density for reduction of H⁺ can be thought of as consisting of two components: charge transfer current and mass transfer limiting current. Total current density is calculated using the equation below[6]:

$$\frac{1}{i_{H^+}} = \frac{1}{i_{\alpha,H^+}} + \frac{1}{i_{\lim,H^+}^d}$$
(64)

where i_{μ^+} is total current density of H⁺ reduction (A/m²), i_{α,H^+} is the charge transfer current density (A/m²), and i_{lim,H^+}^d is the diffusion limiting current density.

The charge transfer current density can be calculated using the Tafel equation as:

$$i_{\alpha,H^+} = i_{0,H^+} \times 10^{-\frac{\eta}{b_c}}$$
(65)

where i_{0,H^+} is the exchange current density (A/m²), b_c is the cathodic Tafel slope (V/decade), η is the over potential (V), which is equal to the difference between the operating (actual) potential and the reversible potential.

The cathodic Tafel slope b_c can be calculated from:

$$b_c = \frac{2.303RT}{\alpha_c F} \tag{66}$$

According to Bockris, *et al.*, [27] for H⁺ reduction, $\alpha_c = 0.5$ giving $b_c \approx 0.120$ V/decade at 30°C. This agreed well with the present findings.

The reversible potential of hydrogen reduction can be calculated as:

$$E_{_{rev(H^+)}} = -\frac{2.303RT}{F} pH - \frac{2.303RT}{2F} \log p_{_{H_2}}$$
(67)

where the partial pressure of hydrogen normally is assumed to be close to zero. The only unknown model parameter for calculating the charge transfer current density is the exchange current density, i_{0,H^+} . According to Nešić *et al.* [8], i_{0,H^+} can be calculated by:

$$i_{0,H^{+}} = i_{0}^{ref} \left(\frac{c_{H^{+}}}{c_{H^{+}ref}}\right)^{0.5} \times e^{-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{Tref})}$$
(68)

where i_0^{ref} is the reference exchange current density at a reference temperature, T_{ref} (K) and reference concentration of H⁺. ΔH is the enthalpy of activation for the H⁺ reduction reaction (J/mol).

The i_0^{ref} for H⁺ reduction was taken as 0.03 A/m² at a reference temperature of 20°C and reference H⁺ concentration of 1×10⁻⁴ mol/L. The enthalpy of activation was taken as 30 kJ /mol[8]. No effect of H₂S on H⁺ reduction was found in our experiments.

The diffusion limiting current in Equation (64) is calculated with:

$$i_{\lim,H^+}^d = k_{m,H^+} F c_{H^+}$$
(69)

where k_{m,H^+} represents H⁺ mass transfer coefficient (m/s) and c_{H^+} represents the bulk concentration of H⁺ (mol/m³).

The mass transfer coefficient of H^+ can be calculated from a rotating cylinder correlation described by Eisenberg *et al.* [105]:

$$Sh = \frac{k_{m,H^+} d_{RCE}}{D_{H^+}} = 0.0791 \times \text{Re}^{0.7} \times Sc^{0.356}$$
(70)

where *Sh* is Sherwood number; d_{RCE} : pipe diameter (m); D_{H^+} is diffusion coefficient of hydrogen ion (m²/s); *Re* is Reynolds number = $\rho u d_{RCE} / \mu$; and *Sc* is Schmidt number = $\mu / \rho D_{H^+}$.

The diffusion coefficient of species in a dilute solution can be calculated by the Stokes-Einstein equation below

$$D_{H^+} = D_{ref(H^+)} \times \frac{T_k}{T_{ref}} \times \frac{\mu_{ref}}{\mu}$$
(71)

where $D_{ref(H^+)}$ represents the reference diffusion coefficient at a reference temperature, and was taken as $9.31 \times 10^{-9} \text{ m}^2/\text{s}$ [106]. μ represents the water viscosity in kg/m·s and μ_{ref} is the reference viscosity at a reference temperature and was taken as 1.002 kg/(m·s) [107].

The temperature dependence of water density and water viscosity can be given as:

$$\rho = 1152.3 - 0.5116 \times T_k \tag{72}$$

$$\mu = \mu_{ref} \times 10 \frac{1.3272(20 - T_c) - 0.001053(20 - T_c)^2}{T_c + 105}$$
(73)

Where T_C , T_K is temperature in °C and Kelvin respectively.

4.4.2.2 Direct H₂S Reduction

 H_2S plays role in the corrosion process by two main ways. First, by chemical dissociation of the aqueous H_2S , an additional source of H^+ can be provided and reduced on the steel surface. Secondly, the aqueous H_2S can be reduced on a steel surface directly and further enhance the corrosion.

$$\frac{1}{i_{H_2S}} = \frac{1}{i_{\alpha,H_2S}} + \frac{1}{i_{\lim_{m,H_2S}}^d}$$
(74)

where i_{H_2S} , i_{α,H_2S} and i_{\lim,H_2S}^d are total current density, charge transfer current density and mass transfer limiting current density of H₂S reduction in A/m², respectively.

Charge transfer current density of H_2S reduction can be calculated using the equation:

$$i_{\alpha,H_2S} = i_{0,H_2S} \times 10^{-\frac{\eta}{b_c}}$$
(75)

Where i_{o,H_2S} represents the exchange current density in A/m², b_c represents the cathodic Tafel slope in V/decade for H₂S reduction, and η represents the over potential in V, which is equal to the difference between the operating (actual) potential and the reversible potential.

From the experiments, the cathodic Tafel slope b_c for H₂S reduction in Equation (71) was found to be close to 120 mV/decade at 30°C, which is the same as the value used for H⁺ reduction. The value of b_c can be calculated from Equation (66).

From the best fit to experimental results at different concentration of H_2S at pH 4, the order *n* of the reaction with respect to C_{H_2S} is found to be:

$$\frac{\partial \log i_{0,H_2S}}{\partial \log c_{H,S}} \approx 0.5 \tag{76}$$

The same reaction order of 0.5 was also suggested by J. Kittel *et al.* [108]. It is similar to the one associated with the exchange current density of H⁺ reduction. Morris *et al.* [46] and Cheng *et al.* [14] stated that corrosion reaction order with H₂S: $n = \partial(\log i_{corr}/\partial \log c_{H_2S}) = 0.2$. However, i_{corr} includes both contributions from H⁺ and H₂S reduction. Under their experimental conditions (pH from 0.75 to 4), the contribution from H⁺ is dominant and would not allow an accurate calculation of the H₂S reduction reaction order.

Therefore, the exchange current density can be calculated as:

$$i_{0,H_2S} = i_0^{ref} \left(\frac{c_{H_2S}}{c_{H_2Sref}}\right)^{0.5} \left(\frac{c_{H^+}}{c_{H^+ref}}\right)^{-0.5} \times e^{-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{Tref})}$$
(77)

Where the i_0^{rel} for H₂S reduction is taken as 0.00015 A/m² at a reference temperature of 293.15K and a reference H⁺ concentration of 1×10⁻⁴ mol/L, and a reference H₂S concentration of 1×10⁻⁴ mol/L. This means that the H₂S reduction rate is about 200 times slower than the H⁺ reduction rate (0.03 A/m²) at the same condition. The enthalpy of activation was taken as 60 kJ/mol from the best fit to experimental results.

The two electrochemical reactions, the reductions of H_2S and H^+ , are equivalent thermodynamically and have the same reversible potential given by Equation (67).

Calculation of limiting current density for H_2S reduction is similar to that for H^+ reduction. The mass transfer limiting current density of this reaction is given by:

$$i_{\lim,H_2S}^d = k_{m,H_2S} F c_{H_2S}$$
(78)

$$Sh = \frac{k_{m,H_2S} d_{RCE}}{D_{H_2S}} = 0.0791 \times \text{Re}^{0.7} \times Sc^{0.356}$$
(79)

$$D_{H_2S} = D_{ref(H_2S)} \times \frac{T_k}{T_{ref}} \times \frac{\mu_{ref}}{\mu}$$
(80)

where $D_{ref(H_2S)}$ was taken as 1.61×10^{-9} m²/s at reference temperature (293.15 K) [109]. The concentration of H₂S can be calculated from the water chemistry model in section 2.2.1.

4.4.2.3 H₂O Reduction

Since water molecules are readily available at the metal surface, it can be assumed that at all times the reduction rate of H_2O is controlled by the charge-transfer process, and hence, the Tafel equation is used:

$$i_{H_2O} = i_{0,H_2O} \times 10^{-\frac{\eta}{b_c}}$$
(81)

Tafel slope for this reaction in all experiments at 30 $^{\circ}$ C was found to be close to 120 mV/decade, which is the same as that for H⁺ reduction. Tafel slope for H₂O reduction is given by Equation (66).

Since the electrochemical reduction of H_2O and H^+ are equivalent thermodynamically, the reversible potential of H_2O reduction were assumed to be the same as for H^+ reduction, which is calculated by Equation (67).

When H_2S is not present, the exchange current density for H_2O reduction is given by:

$$i_{0,H_2O} = i_0^{ref} \left(\frac{c_{H^+}}{c_{H^+_{ref}}} \right)^{-0.5} e^{-\frac{\Delta H}{R} (\frac{1}{T} - \frac{1}{Tref})}$$
(82)

The i_{0ref} for H₂O reduction was taken as 2×10^{-5} A/m² at reference temperature 293.15K and reference H⁺ concentration 1×10^{-4} mol/L. The enthalpy of activation was taken as 30 kJ/mol [6].

When H_2S is present, apparently it can retard the H_2O reduction, resulting in rates about 20 times lower than that seen in environments without H_2S , suggesting competitive adsorption at the steel surface. From the current experimental results, the reaction order $\log i_{0,H2O}/\log c_{H2S}$ is close to 0.1. The exchange current density is given by:

$$i_{0,H_2O} = i_0^{ref} \left(\frac{c_{H^+}}{c_{H^+_{ref}}}\right)^{-0.5} \left(\frac{c_{H_2S}}{c_{H_2Sref}}\right)^{-0.1} e^{-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{Tref})}$$
(83)

In an H₂S environment, the i_0^{ref} for H₂O reduction was taken as 1×10^{-6} A/m² at reference temperature 293.15K, the reference H⁺ concentration of 1×10^{-4} mol/L, and the

reference H_2S concentration of 1×10^{-4} mol/L. The enthalpy of activation was taken as 90 kJ/mol from the best fit to experimental results, which would suggest that H_2O reduction in an H_2S environment is more sensitive to temperature.

4.4.2.4 Anodic Dissolution of Iron

In the present experiments, the anodic dissolution of iron was under charge transfer control. Thus, pure Tafel behavior can be assumed close to the corrosion potential:

$$i_{Fe} = i_{0,Fe} \times 10^{\frac{\eta}{b_a}}$$
 (84)

The Tafel slopes of anodic reaction in a H_2S environment or environment without H_2S are all close in the range of 40-50 mV/decade. The introduction of H_2S did not have any effect on the Tafel slope, so for anodic iron dissolution the Tafel slope is given as:

$$b_a = \frac{2.303RT}{\alpha_a F} \tag{85}$$

According to Bockris, *et al.*, [27] the apparent symmetry coefficient for the anodic reaction of Fe dissolution was taken as 1.5, giving $b_a = 40 \text{ mV}$ at 30°C, which is close to our experimental results. The reversible potential of X-65 steel was taken[6] to be - 0.488 V.

When H_2S is not present, according to the mechanism proposed by Bockris *et al.* [27], the reaction order with respect to OH^- ions is 1, which is only valid in acidic solutions. When the solution pH is above approximately 4, it has been found that iron dissolution proceeds with little influence of pH. It is assumed that the exchange current density is proportional to the surface coverage of OH⁻ (θ_{OH-}) and it follows the Frumkin adsorption model:

$$i_{0,Fe} = i_{0,Fe}^{*} \theta_{OH^{-}} e^{-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{Tref})}$$
(86)

$$K_{1}c_{OH^{-}} = \frac{\theta_{OH^{-}}}{1 - \theta_{OH^{-}}}e^{(-f\theta_{OH^{-}})}$$
(87)

According to the current experimental results and Bockris *et al.* [27], the best-fit values in Equation (86)and (87) are $i_{0,Fe}^* = 0.25$, $K_1 = 1.56 \times 10^9$ and f = 3.83. Actually when *f* is equal to 0, the Frumkin adsorption model becomes the Langmuir adsorption model. The reference temperature is 293.15K. The activation energy ΔH was set to be 37.5 kJ/mol, which is taken from the finding of Nešić *et al.* [8].

The concentration of OH⁻ can be calculated by the water chemistry model in section 2.2.1.

When H₂S is present, according to the mechanism proposed previously, Equations (49) to (52), the exchange current density for iron dissolution is related to HS⁻ concentration. Even at low concentrations of H₂S, such as 100 ppm(v) H₂S (0.1 mbar) and pH 4, the concentration of HS⁻ is much higher (1×10⁻⁸ mol/L) than the concentration of OH⁻ (1×10⁻¹⁰ mol/L). Therefore, the contribution of OH⁻ to the anodic reaction kinetics was ignored. It can be assumed that the exchange current density is only related to the surface coverage of HS⁻ (θ_{HS} -) and that it follows the Langmuir adsorption model:

$$i_{0,Fe} = i_{0,Fe}^{*'} \theta_{HS^{-}} e^{-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{Tref})}$$
(88)

$$\theta_{HS^{-}} = \frac{K_2 c_{HS^{-}}}{1 + K_2 c_{HS^{-}}}$$
(89)

The best fit values for $i_{0,Fe}^{*'}$ and K_2 in Equation (88) and (89) are $i_{0,Fe}^{*'} = 0.33$, $K_2=3.5\times10^6$. The reference temperature is 293.15 K. The activation energy ΔH was assumed to be the same as that for an environment without H₂S (37.5 kJ/mol). c_{HS^-} is the concentration of HS⁻, which is given by the water chemistry model in section 2.2.1.

4.4.3 The Mixed Potential Theory

The model requires as input: temperature, pH, p_{H_2S} , and the hydrodynamic parameters: in this case the rotating cylinder diameter, and the rotational velocity. The corrosion potential then can be calculated by solving the charge balance equation:

$$\sum i_a = \sum i_c \tag{90}$$

which here takes the form:

$$i_{Fe} = i_{H_2S} + i_{H^+} + i_{H_2O} \tag{91}$$

Once the corrosion potential is known, the corrosion current and rate can be found from the anodic current (or the sum of cathodic current) at the corrosion potential. The individual and total cathodic and anodic curves, and predicted potentiodynamic sweeps can be then readily generated.

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4.4.4 Model Verification

Performance of the model was validated by comparing the predictions with experimental results described above. Even if the same empirical data are used which formed a basis for calibrating the constants in the model, the complexity of the physicochemical phenomena present a real challenge for the mechanistic model. Good agreement across the different conditions can be expected only if the fundamental assumptions underlying the model are correct, and of course, if the calibration was done properly. Further testing with the model using external data was done and described in the following sections.

4.4.4.1 Effect of pH_2S

Figure 16 shows that the predicted corrosion rates from the electrochemical model are in good agreement with experimental results, which suggests that the electrochemical model captured the main effects of H_2S corrosion of mild steel in the absence of iron sulfide.

Figure 17, Figure 18, Figure 19 show cathodic and anodic polarization curves changing with H_2S concentration for the different pH aqueous environments. The model prediction successfully captures the anodic reaction change in the low pH range (Figure 18, for pH 3.0) and the cathodic reaction change in high pH environments (Figure 19, for pH 5.0) due to the additional cathodic reaction: H_2S reduction. Predicted potentiodynamic sweeps are in good agreement with experimental results for individual reactions generated with the present model.

Using this kind of model, the cathodic polarization curves can be deconvoluted to show the contribution from three individual cathodic reactions $(H^+$ reduction, H_2S

reduction and H_2O reduction). It can be seen, for example, that when increasing the H_2S concentration, the H^+ reduction doesn't change; that the H_2S reduction curve moves to the higher values of the current (on the right of the graph), and that H_2O reduction changes only a little; see Figure 17, Figure 18, and Figure 19.



Figure 16. Comparison of corrosion rate predictions with LPR experimental results and experimental OCP at pH 4.0 and different H_2S concentration, total pressure=1.0 bar, 1000rpm 30°C, B = 23 mV/ decade. Here the error bars represent standard deviation of mean value, which calculated from the multiple LPR measurements. The error bars in the following text were obtained with the same method.



Figure 17. Comparison of predicted polarization curves with experimental results at different H₂S concentration, pH 4.0, total pressure=1.0 bar, 1000rpm, 30°C. Solid line: experimental curves. Dashed line: predicted curves. Black: 0 ppm(v) H₂S(g), Red: 100 ppm(v) H₂S(g), Dark blue: 1000 ppm(v) H₂S(g), Pink: 1%(v) H₂S(g), purple: 10%(v) H₂S(g).



Figure 18. Comparison of predicted polarization curves sweeps with experimental results at different H₂S concentration, pH 3.0, total pressure=1.0 bar, 1000rpm, 30°C. Solid line: experimental curves. Dashed line: predicted curves. Black: 0 ppm(v) H₂S(g), red: 100 ppm(v) H₂S(g), purple: 10%(v) H₂S(g).



Figure 19. Comparison of predicted polarization curves with experimental results at different H₂S concentration, pH 5.0, total pressure=1.0 bar, 1000rpm, 30°C. Solid line: experimental curves. Dashed line: predicted curves. Black: 0 ppm(v) H₂S(g), red: 100 ppm(v) H₂S(g), purple: 10%(v) H₂S(g).

4.4.4.2 Effect of Flow Rate

The effect of flow rate on both cathodic reaction and anodic reaction at 1%(v) and 10%(v) H₂S(g) is depicted in Figure 21 and Figure 22. Increasing flow (rotating speed) does not affect the anodic reaction and H₂O reduction which are both under charge transfer control, but accelerates the cathodic reaction due to the increase of mass transfer rate related to H⁺ reduction and H₂S reduction. Except for the case of the limiting current density at 200 rpm rotating speed, all the predicted polarization curves agree well with the experimental results. Corrosion rate predictions are shown in Figure 20. The predicted corrosion rates are close to the experimental results.



Figure 20. Comparison of predicted corrosion rate with LPR experimental results at different rotational speed, pH 4.0, total pressure=1.0 bar, 30° C, points: experimental results, solid lines: predicted curves, B = 23 mV/ decade.



Figure 21. Comparison of predicted polarization curves with experimental results at different rotated speed, pH 4.0, 1%(v) H₂S(g), total pressure=1.0 bar, 30° C. Solid line: experimental curves. Dashed line: predicted curves. Dark: 200rpm, red: 1000rpm, pink: 4000rpm.



Figure 22. Comparison of predicted polarization curves with experimental results at different rotated speed, pH 4.0, 10%(v) H₂S(g), total pressure=1.0 bar, 30° C. Solid line: experimental curves. Dashed line: predicted curves. Dark blue: 200rpm, red: 1000rpm, pink: 4000rpm.

4.4.4.3 Effect of pH

Comparison between predicted polarization curves and experimental polarization curves in solution without H_2S are shown in Figure 23. A good agreement is found at each pH. From Figure 23, H^+ reduction curves shift to the higher current values on the right with pH decreasing while anodic reaction curves move to lower values on the left with pH decreasing.

When 100 ppm(v) $H_2S(g)$ is present, the prediction of polarization curves is shown in Figure 24. Due to the low concentration of H_2S in solution, no obvious effect on the cathodic polarization curve is observed. As mentioned previously, the anodic reaction is related to the HS⁻ concentration. At the same gas concentration of H_2S , [HS⁻] is inversely proportional to the pH, so the anodic reaction rate increases with pH increase. The experimental and predicted polarization curves were found to be in very good agreement.



Figure 23. Comparison of predicted polarization curves with experimental results at different pH, 1000rpm, 0ppm(v) H_2S (g), total pressure=1.0 bar, 30°C. Solid line: experimental curves. Dashed line: predicted curves. Pink: pH 5.0, Dark blue: pH 2.0, black: pH 3.0, red: pH 4.0, pink: pH 5.0.

For 10%(v) $H_2S(g)$ present, the comparison of the predicted polarization curves with the experimental results is shown in Figure 25. It is evident that the predicted polarization curve at each pH is in good agreement with the experimental result. When the H_2S concentration is higher the H_2S reduction affects the overall cathodic polarization curves significantly. Anodic polarization curves are not sensitive to pH in Figure 25 due to the high concentration of HS⁻.

Corrosion rate prediction at a different pH is shown in Figure 26. The electrochemical model predictions are in good agreement with experimental results,

which means the electrochemical model captured the main features of H₂S corrosion at a different pH.



Figure 24. Comparison of predicted polarization curves with experimental results at different pH, 1000rpm, 100ppm(v) $H_2S(g)$, total pressure=1.0 bar, 30°C. Solid line: experimental curves. Dashed line: predicted curves. Pink: pH 5.0, Dark blue: pH 2.0, black: pH 3.0, red: pH 4.0, pink: pH 5.0.



Figure 25. Comparison of predicted polarization curves with experimental results at different pH, 1000rpm, 10%(v) H₂S(g), total pressure=1.0 bar, 30° C. Solid line: experimental curves. Dashed line: predicted curves. Dark blue: pH 2.0, black: pH 3.0, red: pH 4.0, pink: pH 5.0.



Figure 26. Comparison of predicted corrosion rate with experimental results at different pH, different H₂S concentration, 1000rpm, total pressure=1.0 bar, 30°C, point: experimental results, solid line: predicted curves. LPR constant B = 23 mV/ decade.

4.4.4.4 Effect of Temperature

The effect of temperature on both cathodic reaction and anodic reaction at $c_{H_2S} = 8.3 \times 10^{-4}$ M is depicted in Figure 27. Increasing temperature has a small influence on the anodic reaction, but accelerates the cathodic reaction greatly. H⁺ reduction, H₂S reduction and H₂O reduction rate increase with temperature increase. All the predicted sweeps agree with experimental results well.

Corrosion rate predictions are shown in Figure 28. This electrochemical model captures well the corrosion rate change with temperature.


Figure 27. Comparison of predicted polarization curves with experimental results at different temperature, 1000rpm, $c_{H_2S} = 8.3 \times 10^{-4} \text{mol/L}$, total pressure=1.0 bar, 30°C. Solid line: experimental curves. Dashed line: predicted curves. Red: 30°C, Dark blue: 60°C, pink: 80°C.



Figure 28. Comparison of predicted corrosion rate with experimental results at different temperature, 1000rpm, $c_{\text{H}_2\text{S}} = 8.3 \times 10^{-4} \text{mol/L}$, total pressure=1.0 bar, 30°C, Point: experimental results, solid line: predicted curves. LPR constant B = 23 mV/ decade.

4.5 Conclusions

During aqueous corrosion of mild steel, the presence of dissolved H_2S in water affects both the cathodic reactions and the anodic reaction. An additional cathodic reaction, direct H_2S reduction, was clearly observed. This reaction is flow sensitive and a mass transfer limiting current density was identified. The Tafel slope was observed to be close to 120 mV/decade at 30°C. The reaction order with concentration of H_2S , C_{H_2S} , is estimated to be close to 0.5. A retardation of H_2O reduction in the presence of H_2S was observed at all experimental conditions, even at pH 2.0.

Anodic dissolution of iron was either accelerated or retarded due to the presence of H_2S in acidic solutions dependent on the pH. This effect is related to the chemisorption of HS⁻ ions. The effect can be modeled by using the Langmuir adsorption model. The Tafel slope for the anodic dissolution of iron was 40~50mV/ decade. When [HS⁻] reached a saturation value, the anodic reaction current reached a maximum and became independent of both [HS⁻] and pH.

A new electrochemical model has been developed which can be used to simulate the effect of pH_2S , flow, temperature, and pH on corrosion of mild steel in an H_2S environment in the absence of iron sulfide layers.

Chapter 5. Electrochemical Study and Modeling of Carbon Steel Corrosion in Mixed H₂S/CO₂ Environment without Iron Sulfide Layer Growth²

5.1 Introduction

In Chapter 4, an electrochemical model of carbon steel corrosion in pure H_2S system was described and verified with electrochemical kinetics experiments. It accounts for the effect of pH₂S, flow rate, pH and temperature on H₂S corrosion. An additional cathodic reaction, direct H_2S reduction, was identified and included in the model. However, in reality CO_2 is ubiquitous, so it is of key importance to extend this electrochemical model to cover mixed H_2S/CO_2 systems and include validation with more literature data. The results of this work are presented below.

5.2 Experimental

The experimental set-up, specimens and procedure are the same as the pure H_2S experiments in Chapter 4. N_2 gas was replaced with CO_2 gas. The test matrix for the experimental work is shown in Table 11.

Description	Parameters
Test Material	API 5L X-65
Test Solution	1 wt% NaCl Solution
Purge Gas(H_2S volume fraction in H_2S/CO_2)	0 - 10%(v) (0 - 0.1 bar)
Rotating Speed / rpm	1000
Total Pressure / bar	1
Temperature /°C	30
pH	4.0, 5.0
Test Duration/ hour	0.5 to 2
Measurement Methods	LPR, EIS, Sweeps

Table 11. Test matrix for the electrochemical study of carbon steel corrosion in mixed H_2S/CO_2 environment

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5.3 **Results and Discussion**

5.3.1 Effect of pH_2S

Table 12 shows the unit conversion of ppm (part per million) or % to mbar for H_2S concentration in the gas phase. The unit of ppm or % used here is based on a volume fraction (volume H_2S in the total mixture of H_2S/CO_2 gas). Only the dry gas mixture of H_2S and CO_2 without water vapor was metered before purging into glass cell system. There is always some water vapor in the gas phase in any system containing liquid water. When converting ppm or % to partial pressure of H_2S , the water vapor pressure needs to be considered, especially in high temperature environments.

Table 12. The unit conversion of ppm or % to mbar for H_2S in gas phase at 30°C, 1 bar total pressure

H_2S gas volume fraction in the total	100ppm	500ppm 0.65%	0.65%	6%	10%
mixture H ₂ S/CO ₂ gas			0.0370		
H ₂ S partial pressure / mbar	0.1	0.5	6.3	58.2	96.5

Corrosion rates at different H_2S concentrations in the H_2S/CO_2 mixture, pH 4.0, and 1000 rpm rotating speed condition are shown in Figure 29. The corrosion rate under a pure CO_2 environment (zero H_2S concentration) at pH 4.0 was about 2.7 mm/year. When H_2S gas concentration was increased to 100 ppm and 500 ppm, the corrosion rates were reduced to 1.4 and 1.5 mm/year and then increased again to 2.4 mm/year at 10% H_2S gas concentration. Similar behavior was observed at pH 5.0 (Figure 30).



Figure 29. Effect of H_2S gas concentration in the H_2S/CO_2 mixture at total pressure 1 bar, on corrosion rates of X65 mild steel at pH 4.0, 30°C, 1 wt% NaCl, 1000 rpm rotating speed, exposure time < 2 hours, B = 23 mV/decade.



Figure 30. Effect of H_2S gas concentration in the H_2S/CO_2 mixture at total pressure of 1 bar, on corrosion rates of X65 mild steel at pH 5.0, 30°C, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours, B = 23 mV/decade.

The effect of H_2S on cathodic potentiodynamic sweeps at pH 4.0 and pH 5.0 are shown in Figure 31 and Figure 32. At pH 4.0, the cathodic polarization curve in a pure CO_2 aqueous environment (without any H_2S) has the same shape as previously reported by others [6]. It shows a limiting cathodic current region in the range of -720 mV to -900 mV, which consists of the diffusion limited current of H⁺ reduction and chemical reaction controlled current of H_2CO_3 reduction. At a more negative potential a charge transfer current region is seen corresponding to direct H_2O reduction. When 100 ppm or 500 ppm H_2S was introduced, the mass transfer limiting current did not change compared with a pure CO_2 purged environment, but the H_2O reduction rate was slowed down; this agreed with the observation reported previously for a H_2S environment (without CO_2) in Chapter 4. As the H_2S gas concentration increased (to 0.65% and higher to 10%), the cathodic limiting current plateau moved to higher currents and a second "wave" in the limiting current at more cathodic potential also appeared, which is due to the direct reduction of H_2S on the steel surface according to:

$$H_2S_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2HS_{(aq)}$$
 (55)

At pH 5.0, the same trend was observed. The mass transfer limiting current did not change at 100 ppm H_2S , but increased at 10% H_2S . The water reduction rate was retarded at pH 5.0 as well.

The effect of H_2S concentration on the anodic iron dissolution reaction at pH 4.0 and pH 5.0 can also be seen in the potentiodynamic sweeps (Figure 31 and Figure 32). At pH 4.0 (Figure 31), with 100 ppm and 1000 ppm H_2S , the anodic potentiodynamic sweeps shifted to lower currents as compared with a pure CO_2 environment, which indicates a retardation effect due to H_2S . As H_2S gas concentration increased to 6% and 10% in the H_2S/CO_2 mixture, the anodic reaction rate increased, and eventually reached the same rate as in a pure CO_2 environment. At pH 5.0 (Figure 32), the similar behavior of the anodic potentiodynamic sweeps was observed. These also agreed with the observations in a pure H_2S environment in Chapter 4. According to the finding of Bockris *et al.*, in the strong acid solution, iron dissolution rate is contributed to OH⁻ adsorption on the iron surface. When H_2S is present, HS^- can be strongly chemisorbed on the iron and displace adsorbed OH⁻, and slow down the iron dissolution rate. However, analogous to the OH⁻ accelerated mechanism of iron dissolution, HS^- can also accelerate this process with the increase of H_2S gas concentration.

To summarize the experimental findings, the presence of H_2S in a CO_2 dominated aqueous environment affects both the cathodic and anodic reactions, and may lead to either acceleration or retardation of the corrosion rate of the steel, depending on H_2S concentration. A new cathodic reaction is direct reduction of H_2S . The H_2O reduction rate is slowed down in the presence of the H_2S . The effect of H_2S on the charge transfer kinetics of H_2CO_3 reduction is not as clear from the potentiodynamic sweeps because of the interference by the iron dissolution anodic reaction and the mass transfer limiting current. However, based on the corrosion rate measurements, it appears that H_2CO_3 reduction is also slowed down in the presence of the H_2S , making it similar to what was observed for H_2O reduction. For the anodic reaction, the same phenomena was observed as seen in pure H_2S environments in Chapter 4, which is dependent primarily on H_2S



Figure 31. Effect of H_2S gas concentration in the H_2S/CO_2 mixture at total pressure 1 bar on potentiodynamic sweeps of X65 mild steel corrosion at pH 4.0, 30°C, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours.



Figure 32. Effect of H_2S gas concentration in the H_2S/CO_2 mixture at total pressure 1 bar on potentiodynamic sweeps of X65 mild steel corrosion at pH 5.0, 30°C, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours.

5.3.2 Effect of pH

5.3.2.1 Solution without H_2S

The effect of pH in an aqueous solution saturated with CO_2 (without any H₂S) on potentiodynamic sweeps is shown in Figure 33. The change of pH from pH 4.0 to pH 5.0 agrees with the previous findings of Nešić, *et al.* [6] The limiting current density decreased by a factor 2-3, and not 10, because of the additional contribution from direct H₂CO₃ reduction. Figure 33 also shows a very small effect on the anodic reaction from pH 4.0 to pH 5.0.



Figure 33. Effect of pH on potentiodynamic sweeps of X65 mild steel corrosion in the solution purged with pure CO_2 at 30°C, total pressure of 1 bar, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours.

5.3.2.2 Solution with H_2S

The change of the potentiodynamic sweeps from pH 4.0 to pH 5.0 in an aqueous solution purged with 100ppm H_2S in the gas mixture (Figure 34) has the same trend as that in a pure CO_2 gas purged solution for both cathodic and anodic parts.



Figure 34. Effect of pH on potentiodynamic sweeps of X65 mild steel corrosion in the solution purged with 100 ppm H₂S in the H₂S /CO₂ gas mixture at total pressure of 1 bar, 30° C, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours.



Figure 35. Effect of pH on potentiodynamic sweeps of X65 mild steel corrosion in the solution purged with 10% H_2S in the H_2S /CO₂ gas mixture at total pressure of 1 bar, 30°C, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours.

When H_2S concentration increased to 10%, the effect of pH on potentiodynamic sweeps is shown in Figure 35. The limiting current was almost the same at pH 4.0 and pH 5.0, which is a different behavior from a three-fold change in pH seen in a "CO₂ only" environment. The reason is that the main contribution to the cathodic limiting current at 10% H_2S concentration is from the aqueous H_2S species, whose concentration is independent of pH.

Both Figure 34 and Figure 35 show that pH had a smaller effect on the anodic dissolution reaction in the range of conditions studied.

5.4 Electrochemical Model

5.4.1 Anodic Reaction

The only anodic reaction is iron dissolution from the steel surface, as reaction (23) shows. This reaction is already described in Chapter 4 for both strong acid solution and H_2S/N_2 purged solution, and will be further extended to a pure CO_2 and a mixed H_2S/CO_2 environment.

$$Fe_{(s)} \to Fe_{(aq)}^{2+} + 2e^{-}$$
 (23)

The detailed model of iron dissolution in a CO_2 environment without H_2S has been reported by Nešić *et al.* [6] This reaction is under charge transfer control. Thus, pure Tafel behavior can be assumed close to the corrosion potential.

$$i_{Fe} = i_{0,Fe} \times 10^{\frac{\eta}{b_a}}$$
 (84)

The reference exchange current density $i_{o,Fe}^*$ at room temperature, 293.15K is 1 A/m² for X-65 steel. The activation energy ΔH was found to be 37.5 kJ/mol. The Tafel slope is $b_a = \frac{2.303RT}{1.5F}$. The reversible potential of X-65 steel was taken to be – 0.488 V[6], [8].

When in a mixed H_2S/CO_2 environment, the anodic reaction rate is observed to mostly depend on H_2S concentration, as shown in Figure 31 and Figure 32. This behavior is modeled as proposed in Chapter 4, where the exchange current density is related to the surface coverage by HS⁻ ions (θ_{HS}) and follows the Langmuir adsorption model, as Equation (88), (89) show.

$$i_{0,Fe} = i_{0,Fe}^{*'} \theta_{HS^-} e^{\frac{\Delta H}{R} (\frac{1}{T} - \frac{1}{Tref})}$$
(88)

$$\theta_{HS^{-}} = \frac{K_2 c_{HS^{-}}}{1 + K_2 c_{HS^{-}}}$$
(89)

5.4.2 Cathodic Reactions

There are four cathodic reactions in a mixed CO_2/H_2S aqueous system. The details of H⁺ reduction, H₂S reduction, and H₂O reduction have been described in Chapter 4 which covers these same reactions for a pure H₂S system, and no change is made in the present work for a mixed CO_2/H_2S aqueous system. However, modeling of H₂CO₃ reduction with and without H₂S is an additional work and will be addressed below.

Direct H₂CO₃ reduction is represented by:

$$2H_{2}CO_{3_{(aq)}} + 2e^{-} \rightarrow H_{2(g)} + HCO_{3_{(aq)}}^{-}$$
(29)

Modeling of H_2CO_3 reduction for a pure CO_2 aqueous system (without H_2S) has been clearly described clearly by Nešić *et al.* [6] The total current density of H_2CO_3 reduction is given by:

$$\frac{1}{i_{H_2CO_3}} = \frac{1}{i_{\alpha,H_2CO_3}} + \frac{1}{i_{\lim_{m,H_2CO_3}}^r}$$
(92)

where $i_{H_2CO_3}$, i_{α,H_2CO_3} and $i_{\lim,H_2CO_3}^r$ are the total current density, the charge transfer current density and the mass transfer limiting current density of this reaction in A/m², respectively.

Charge transfer current density of this reaction can be calculated using the equation:

$$i_{\alpha,H_2CO_3} = i_{0,H_2CO_3} \times 10^{-\frac{\eta}{b_c}}$$
(93)

Tafel slope and reversible potential can be calculated from Equations (66) and (67).

$$b_c = \frac{2.303RT}{\alpha_c F} \tag{66}$$

$$E_{rev} = -\frac{2.303RT}{F} pH - \frac{2.303RT}{2F} \log p_{H_2}$$
(67)

 $\alpha_{\rm c} = 0.5$ giving $b_{\rm c} \approx 0.120$ V/decade at 30°C, and the $p_{\rm H_2}$ is set to 1 bar.

The exchange current density can be calculated by:

$$i_{0,H_2CO_3} = i_0^{ref} \left(\frac{c_{H_2CO_3}}{c_{H_2CO_3\,ref}}\right)^{0.5} \left(\frac{c_{H^+}}{c_{H^+ref}}\right)^{-0.5} \times e^{\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{Tref})}$$
(94)

From Nešić *et al.* [6], [8], the i_{0ref} for H₂CO₃ reduction was taken to be 0.018 A/m² at 293.15K reference temperature and 1×10⁻⁴ mol/L reference H₂CO₃ concentration. The enthalpy of activation in Equation (94) is set to 50 kJ/mol.

The CO₂ hydration reaction limiting current density can be calculated using [110]:

$$i_{\lim(H_2CO_3)}^r = f \times Fc_{co_2} \times \left(D_{H_2CO_3} K_{hyd} k_{hyd}^f \right)^{0.5}$$
(95)

where c_{co_2} is the bulk concentration of dissolved carbon dioxide, which can be obtained from the water chemistry model in the section 2.1.1. k_{hyd}^{f} is the forward hydration reaction constant, which is given as [24]:

$$k_{hyd}^{f} = 10^{329.85 - 110.54 \, ||\log T_{k} - \frac{172654}{T_{k}}} \tag{96}$$

From experimental observation, it was found that when H_2S was present, the H_2O reduction rate was slowed down by approximately 1 or 2 orders of magnitude. Similarly, it is considered here that H_2CO_3 reduction was also slowed due to the presence of H_2S . In an H_2S environment, the i_0^{ref} for H_2CO_3 reduction was taken to be 0.006 A/m² (3 times lower than the 0.018 A/m² used for a pure CO₂ environment without H_2S). The other parameters were taken to be the same as in the model without H_2S .

5.4.3 The Mixed Potential Theory

The model process is similar to that in Chapter 4 except the additional work of modeling H_2CO_3 reduction. The inputs are the same except an additional parameter, the partial pressure of CO_2 (p CO_2). The corrosion potential then can be calculated by solving the charge balance Equation (90), which here takes the form:

$$i_{Fe} = i_{H_2CO_3} + i_{H_2S} + i_{H^+} + i_{H_2O}$$
(97)

Similarly, once the corrosion potential is found, the corrosion current and rate can be found from the anodic current (or total cathodic current) at the corrosion potential. The individual and total cathodic and anodic curves and predicted potentiodynamic sweeps can be generated.

5.5 Model Verification

Performance of the model was validated by comparing the calculations with experimental results described above and with external data obtained from the open literature.

5.5.1 Comparison with Results from the Present Experimental Study

First, the electrochemical model in a pure CO_2 environment without H_2S is validated with the experimental results at pH 4.0 and pH 5.0. Figure 36 and Figure 37 show the comparison of the potentiodynamic sweeps simulated by the model with experimental data. It can be seen that the potentiodynamic sweeps capture the corrosion processes very well, and the calculated results are in a very good agreement with all experimental results. Second, the effect of H_2S addition was simulated with the electrochemical model. Figure 38 and Figure 39 show the comparisons of simulated sweeps with experimental results at pH 4.0 and pH 5.0. Model simulations capture the changes of cathodic and anodic potentiodynamic sweeps with increasing H_2S gas concentration and generally agree with experimental potentiodynamic sweeps at the different H_2S concentration. Figure 40 and Figure 41 show the corrosion rates calculated by the electrochemical model are in good agreement with experimental results, which all suggest the electrochemical model captures the main electrochemical processes underlying H_2S/CO_2 corrosion.



Figure 36. Comparison between predicted potentiodynamic sweeps and experimental results in the solution purged with pure CO_2 at pH 4.0, 30°C, total pressure of 1 bar, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours.



Figure 37. Comparison between predicted potentiodynamic sweeps and experimental results in the solution purged with pure CO_2 at pH 5.0, 30°C, total pressure of 1 bar, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours. Dashed line is for prediction and solid line is for experimental.



Figure 38. Comparison of predicted potentiodynamic sweeps with experimental results in the solution purged with different H₂S gas concentrations in the H₂S/CO₂ gas mixture at pH 4.0, 30°C, total pressure of 1 bar, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours. Solid line: experimental sweeps, dashed line: predicted sweeps. Red: 100 ppm H₂S/CO₂, Dark blue: 500 ppm H₂S, pink: 0.65% H₂S, orange: 6% H₂S, purple: 10% H₂S in the H₂S/CO₂ gas mixture.



Figure 39. Comparison of predicted potentiodynamic sweeps with experimental results in the solution purged with different H₂S gas concentrations in the H₂S/CO₂ gas mixture at pH 5.0, 30°C, , total pressure of 1 bar, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours. Solid line: experimental sweeps. Dashed line: predicted sweeps. Red: 100 ppm H₂S, purple: 10% H₂S in the H₂S/CO₂ gas mixture.



Figure 40. Comparison of corrosion rate predictions with experimental results in the solution purged with different H₂S gas concentrations in the H₂S/CO₂ gas mixture at pH 4.0, 30°C, total pressure of 1 bar, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours.



Figure 41. Comparison of corrosion rate predictions with experimental results in the solution purged with different H₂S gas concentrations in the H₂S/CO₂ gas mixture at pH 4.0, 30°C, total pressure of 1 bar, 1 wt% NaCl, 1000rpm rotating speed, exposure time < 2 hours.

5.5.2 Comparison with Results from External Experimental Studies

The electrochemical model was also validated with external data obtained from the open literature. Model performance was examined first in low partial pressure of H_2S (pH₂S ranged from 0.05 mbar to 0.33 mbar, corresponding to 55 ppm to 340 ppm in the gas phase at 1 bar CO₂), where the experiments were conducted by Lee [86]. Figure 42 shows the corrosion rates change with H_2S partial pressure. It shows even a very low concentration of H_2S (50 ppm or 0.05 mbar) can reduce the CO₂ corrosion rate, which is greater than 1 mm/y in the absence of H_2S . The model clearly captures this effect.



Figure 42. Comparison of corrosion rate predictions with experimental results in the solution purged with different partial pressures of H_2S gas in the H_2S/CO_2 gas mixture at total pressure of 1.0 bar, at pH 5.0, 20°C, 1 wt% NaCl, 1000 rpm, exposure time <1 h. Data taken from Lee [86].

Corrosion experiments at a somewhat higher concentration of H_2S (pH₂S ranging from 1 mbar to 9.8 mbar, corresponding to 1000 ppm to 10,000 ppm H₂S in the mixed H_2S /CO₂ gas phase) was reported by Choi [61]. Model predictions are compared with the experimental results in Figure 43. Corrosion rates do not change much with H_2S concentration from 1 mbar to 9.8 mbar, which is broadly captured by the model.



Figure 43. Comparison of corrosion rate predictions with experimental results in the solution purged with different partial pressures of H_2S gas in the H_2S/CO_2 gas mixture at total pressure of 1.0 bar, at pH 4.0, 25°C, 1 wt% NaCl, stagnant solution (0.01 m/s used in model), exposure time <1 hour. Data taken from Choi *et al.* [61].

The effect of temperature on corrosion rate was investigated by Abayarathna *et al.* [111] where corrosion rates increased with temperature at different H_2S concentration conditions. The experiments were simulated using the present CO_2/H_2S model and it was found that the model can predict the measured corrosion rate change, as shown in Figure 44.



Figure 44. Comparison of corrosion rate predictions with experimental results for different temperatures; experimental data shown as points, model predictions shown as lines; total pressure = 1 bar, exposure <1 hour, pH 4.2 (4.5 at 90°C, CO₂), stirring condition. Assumed model parameters: volume ratio for mixture $CO_2/H_2S=1:1$, flow velocity 0.3 m/s. Data taken from Abayarathna *et al.* [111].



Figure 45. Parity plot showing a direct comparison of predicted and experimental corrosion rates; data taken from Bich and Goerz [112], $pCO_2 = 3$ bar to 12.8 bar, $pH_2S = 3$ bar to 12.2 bar, pH 5.0, v = 0.1 m/s. The solid line represents perfect agreement of experimental and calculated corrosion rates. The dashed lines represent a factor of 2 deviation.

A corrosion case at more severe conditions was reported by Bich and Goerz [112]. The experimental condition includes high partial pressures of CO_2 (p $CO_2 = 3$ bar to 12.8 bar) and H_2S (p $H_2S = 3$ bar to 20 bar). The predicted corrosion rates are within a factor of 2 of the measured data points as Figure 45 shows.



Figure 46. Comparison of corrosion rate predictions with experimental results for different velocities; experimental data shown as points, present electrochemical model predictions shown as lines; exp. 1: 19 days, p = 40 bar, $pCO_2 = 3.3$ bar, $pH_2S = 10$ bar, $80^{\circ}C$, pH 3.5, v = 1 m/s to 5 m/s; exp. 2: 21 days, p = 40 bar, $pCO_2 = 3.3$ bar, $pH_2S = 10$ bar, $25^{\circ}C$, pH 3.5, v = 1 m/s to 5 m/s; exp. 3: 10 days, p = 40 bar, $pCO_2 = 10$ bar, $pH_2S = 30$ bar, $80^{\circ}C$, pH 3.2, v = 1 m/s to 5 m/s; experimental data taken from Omar, *et al.* [88].

Long-term flow loop experiments (15 - 21 days) at high partial pressure of H₂S $(pH_2S = 10 \text{ bar to } 30 \text{ bar})$ and high partial pressure of CO₂ $(pCO_2 = 3.3 \text{ bar to } 10 \text{ bar})$ was conducted by Omar, *et al.* [88]. Figure 46 shows a comparison between the present electrochemical model prediction and experimental results. The model over-predicts the corrosion rate by a large factor, by 10 to 50. This is due to the formation of iron sulfide

layers on the surface, which are not accounted for in the current model. Sun and Nešić's mass transfer based model [56] considers the effect of iron sulfide corrosion product layers and makes a better prediction for long term experiments, as Figure 47 [56] shows. Further extension of the current electrochemical model to include mass transfer effects and coverage effect due to iron sulfide layer formation, such as was partly done by Sun and Nešić, is addressed in Chapter 6 and Chapter 7.



Figure 47. Comparison of corrosion rate predictions with experimental results for different velocities; experimental data shown as points, Sun and Nešić's mass transfer model (Sun's model) predictions shown as lines; exp. 1.: 19 days, p = 40 bar, $pCO_2 = 3.3$ bar, $pH_2S = 10$ bar, $80^{\circ}C$, pH 3.5(calculated), v = 1 m/s to 5 m/s; exp. 2.: 21 days, p = 40 bar, $pCO_2 = 3.3$ bar, $pH_2S = 10$ bar, $25^{\circ}C$, pH 3.5 (calculated), v = 1 m/s to 5 m/s; exp. 3.: 10 days, p = 40 bar, $pCO_2 = 10$ bar, $pH_2S = 30$ bar, $80^{\circ}C$, pH 3.2 (calculated), v = 1 m/s to 5 m/s; expression of model matrix of m/s; experimental data taken from Omar, *et al.* [88].

5.6 Summary

- A mechanistic study of H₂S corrosion kinetics for X65 steel in short term exposure was extended to include the effects seen in a mixed H₂S/CO₂ environment.
- The effect of H₂S on the anodic dissolution of iron was the same as previously observed behavior in a pure H₂S environment and included retardation or acceleration depending on the H₂S concentration.
- An order of magnitude retardation of H₂O reduction due to the presence of H₂S was observed in all experimental conditions; it is postulated that the presence of H₂S also slows down the charge transfer kinetics of H₂CO₃ reduction approximately by a factor of 3.
- An electrochemical model of aqueous H₂S corrosion of X65 steel was extended to cover H₂S/CO₂ saturated solutions. The model has been calibrated to fit the new experimental results and was compared with external data found in the open literature. A good agreement with the experimental data has been obtained for short term exposures where the effect of iron sulfide corrosion product layers can be ignored.

Chapter 6. Mechanistic Study of H₂S Corrosion of Carbon Steel with Iron Sulfide Layer Growth³

6.1 Introduction

In Chapter 4 and Chapter 5, an electrochemical model of H_2S corrosion without iron sulfide layer growth has been developed to address the initial stages of the corrosion process, avoiding the complex issues associated with formation and growth of an iron sulfide layer. However, long term H_2S corrosion experienced in lab or field conditions is dominated by the formation of iron sulfide corrosion product layer. The corrosion product layer can be very protective for a long time, but there are also some reports of localized corrosion related to iron sulfide corrosion products failures. The magnitude of the corrosion attack is very dependent on the nature of the iron sulfide corrosion product layer [19]. The protective layer is usually dense and has a good adherence to the steel surface. The less protective layer is usually porous, flaky, and non-adherent to the steel surface and may lead to localized corrosion and failures.

The mechanism of H_2S corrosion of carbon steel under corrosion product layer forming condition is a complex process that still lacks a comprehensive understanding. A few years ago, a predictive model for H_2S corrosion was developed by Sun *et al.* [56], who proposed an inner 1-10 nm thin mackinawite film acting as a solid state diffusion barrier and a porous outer iron sulfide layer formed by spalling of the inner iron sulfide film. Due to the presence of these two layers, the corrosion rate is always under masstransfer control, Sun *et al.* [56] hypothesized. The proposal that two different iron sulfide

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layers formed on the steel surface, which is the key for understanding H_2S corrosion, is well accepted in the corrosion community. However, the mechanism of the formation of the two layers is still under debate.

A somewhat similar but better defined and more strongly researched alternative hypothesis is proposed by the author in the present thesis. The inner very thin iron sulfide film of mackinawite is primarily formed *via* a chemisorption process, *i.e.*, by a direct reaction of exposed surfaces of Fe with H_2S [50]. This film forms rapidly and its presence can be determined, based on the thermodynamic arguments for chemically adsorbed species; see the appropriate stability diagrams developed by P. Marcus, *et al.* [113]. The second outer layer of iron sulfide is formed by precipitation on the initially formed layer of mackinawite, a preferred nucleation surface. The formation of this outer layer depends on the saturation value for iron sulfide on the steel surface. This layer may be dense and protective or porous and non-protective depending on the competition between the precipitation rate and the corrosion rate (the undermining rate). In the current study, the objective is to verify this proposal about the nature and role of iron sulfide corrosion product layers on H_2S corrosion

6.2 Experimental Method

6.2.1 Equipment

In the literature, many corrosion tests have been conducted in closed systems with a limited inventory of fluids. Solution Fe²⁺ concentration and pH may vary significantly with exposure time and affect the iron sulfide layer formation and corrosion rates. Therefore, a new approach with continuous replenishment of fluid was developed to understand the effect of iron sulfide layer on corrosion. The experiment apparatus is shown in Figure 48. The system consists of four main components: the pre-conditioning vessel for N_2 pre-purged solution, the test cell (Figure 49), the gas scrubber, and the chemical scrubber.

The vessel for N_2 pre-purged solution can hold up to 20 L and is equipped with four ports:

- 1. Gas inlet
- 2. Gas outlet
- 3. A port for pH probe and the addition of solution
- 4. An outlet port connecting a line to the gear pump.

The pH of solution in the pre-conditioning vessel was adjusted manually by a deoxygenated hydrochloric acid (HCl) or sodium hydroxide (NaOH) solution to the desired value, which is dependent on the water chemistry conditions in the test cell. The pump rate for transferring solution from the pre-conditioning vessel to the test cell also depends on the pH change of the solution in the test cell, which is related to corrosion rate. When the corrosion rate is high, Fe²⁺ release is faster and pH increases quickly, so the pump rate was set to a higher value (3-6 ml/min), and vice versa, when corrosion rate is low, pump rate was set to a lower value (1-2 ml/min). The pH of the solution in the test cell is continuously monitored and the pump rate is adjusted accordingly.

The test cell is similar to the standard three electrode glass cell, as introduced in Chapter 4. The counter electrode was a platinum wire. The reference electrode was Ag/AgCl in the saturated KCl electrolyte. The working electrode was a cylindrical carbon steel specimen with a surface area of *ca*. 5.4 cm². However, several improvements were made to address the specific research needs. First, in order to investigate the growth of

iron sulfide layer, several square specimens (1.2cm×1.2cm×0.2cm, carbon steel) were hung from nylon string into the solution in the test cell. These were recovered for surface analysis and weight loss measurements at the different exposure times.

Second, a magnetic stirrer at the bottom was used to simulate flowing conditions instead of a rotating cylinder electrode (RCE). The RCE can be inserted only as a single specimen, which is mostly used for electrochemical measurement and is not as suitable for surface analysis and weight loss measurements. The other specimens put in the solution with the RCE are in an almost stagnant flow condition, which is considerably different from the flow condition for the RCE. When a magnetic stirrer was used, the flow condition for all the specimens was similar. The effect of flow on iron sulfide layer growth and corrosion rate was investigated by using this experimental set-up. Since this is a hydrodynamically unique setup, unlike the RCE, a correlation between stirring rate and the mass transfer coefficient was developed and described in Appendix D.

Third, another feature of this test cell was the addition of two extra ports: one port at the top for the inflow of fresh solution added from the pre-conditioning vessel and one side port at the bottom for the solution exiting to the gas scrubber. The solution level of the test cell was controlled by the U-shaped tube connected between the test cell and gas scrubber.

The exhaust gas scrubber (in the form of a glass cell) was used to collect the solution out of the main test cell. N_2 gas was purged to remove H_2S left in the solution and prevent O_2 contamination to the solution in the test cell. The addition of concentrated NaOH as a scrubbing liquid at the bottom was also used to neutralize H_2S left in the solution according to Equation (98).

The liquid water scrubber (a high volume container) was used to collect the solution out of the gas scrubber. Solid NaOH was also put inside to remove the dissolved H_2S .

$$H_2S + 2NaOH \rightarrow 2H_2O + Na_2S \tag{98}$$



Figure 48. Schematic of the experimental set-up for long tern H_2S corrosion tests, courtesy of Cody Shafer.



Figure 49. Schematic of the test cell for the long term H_2S corrosion test, courtesy of Cody Shafer.

6.2.2 Material

Corrosion of X65 pipeline steel was investigated. The composition of the X-65 steel is shown in Table 9. One single RCE and multiple hanging specimens machined from the parent steel material were used. The RCE has a diameter of 1.20 cm and a working surface area of 5.4 cm^2 . The hanging specimen dimensions are $1.2 \text{ cm} \times 1.2 \text{ cm} \times 0.2 \text{ cm}$, with a surface area of around 3.8 cm^2 .

6.2.3 Procedure

All experiments were performed in the test cell with the solution saturated with a H_2S/N_2 mixture at atmospheric pressure. The test cell can hold 2 L of 1 wt% NaCl electrolyte. The solutions in both the test cell and the pre-conditioning cell were both purged with N_2 at least three hours (usually overnight), to remove oxygen. After the solution was deoxygenated, the designated H_2S/N_2 mixed gas was introduced to the solution in the test cell by purging for at least half an hour to saturate the electrolyte. The

solution pH in both the test cell and pre-conditioning cell were adjusted to the set value by adding deoxygenated aqueous HCl or NaOH. Prior to immersion, the carbon steel specimen surfaces were polished with 400 and 600 grit silicon-carbide paper, rinsed with isopropyl alcohol and dried in air. Experimental conditions are summarized in Table 13.

X65
1 wt.% NaCl
25 °C, 80 °C
1 bar
60, 600rpm
4.0, 5.0, 6.0
10% H ₂ S/N ₂ 4-7 days

 Table 13. Test matrix for studying the effect of iron sulfide layer on corrosion

 Parameter
 Description

Corrosion rates for carbon steel were determined using both the electrochemical and weight loss techniques. During the test, LPR and EIS were used to monitor the corrosion rate. LPR measurements were conducted in a range of ± 5 mV from free open circuit potential with a scan rate of 0.125 mV/s. EIS measurements were performed from 5 kHz to 3 mHz, with an alternating current signal amplitude of 5 mV(rms) with respect to OCP. The Clarke solution [114] was used to clean the corrosion product layer from the specimens surface for weight loss corrosion rate calculation. After the experiments, the specimens were evaluated through additional ex situ analyses. The surface morphology and compositions of corrosion products were analyzed using a scanning electron Microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD).

6.3 Results and Discussion

6.3.1 Discussion of the Formation of the Inner Thin Iron Sulfide Film and Its Effect on H₂S Corrosion

At the introduction of this chapter, an argument was made that there is a thin inner iron sulfide layer on the steel surface. This layer was explained by Sun *et al.* [19], [56] to form by 'solid state' reaction which reduces the corrosion rate by acting as a solid state diffusion barrier. However, it is more likely that this layer forms by a chemisorption process and retards the corrosion rate by interfering with the kinetics of different electrochemical reactions. The evidence will be listed in the text below and its effect on corrosion is also discussed. There are two main pieces of evidence for the existence of this chemisorbed sulfide film.

First, the formation of the inner adsorbed sulfide film is not only found on an iron substrate, a similar adsorbed sulfide film is also observed on other metal substrates, such as platinum (Pt), gold (Au), nickel (Ni), and copper (Cu) [70]. Jiang and Carter [50], [51] predicted HS⁻ can be strongly chemisorbed on the iron surface using density functional theory (DFT). Marcus [70] also confirmed that the dissolved H₂S species such as H₂S, HS⁻ can be specifically adsorbed on the metal surface and form a chemisorbed layer. The layer forms rapidly and its presence is dependent on the thermodynamic stability of the adsorbed sulfide layer on Fe or other substrates at the given conditions. A E-pH diagram is the most typical way to represent the thermodynamic stability of different species for the REDOX process. Marcus *et al.* [113] developed an E-pH diagram for sulfur species

adsorbed on iron to predict the formation of this chemically adsorbed layer, as Figure 50 shows. The condition for this diagram is 25 °C, 10^{-4} mol/kg total S concentration and 10^{-4} mol/kg Fe²⁺ concentration. The red line at the bottom is the transition line between the H₂O adsorbed layer and sulfide adsorbed layer (sulfide adsorbed layer coverage $\theta_{s(ads)} = 0.99$, H₂O adsorbed layer coverage $\theta_{H_2O(ads)} = 0.01$). Above this red line, a surface coverage of the sulfide adsorbed layer is higher than 0.99 and H₂O coverage is less than 0.01, which means the sulfide adsorbed layer is stable. Vice versa, below this red line, the adsorbed sulfide layer is unstable. The blue square area represents the range of potential (-0.3 to -0.6 V) and pH (2 to 7) for the common corrosion conditions for mild steel in an upstream oil and gas pipeline. Comparing the blue square area with the stability domain of the adsorbed sulfide layer in Figure 50 shows the adsorbed sulfide layer is very stable at these conditions except for some very extreme conditions (low pH and low potential). It is also found that sulfide adsorbed film can exist under conditions in which no bulk iron sulfide (Mackinawite) is stable



Figure 50. E-pH diagram for sulfur adsorbed on Fe (25°C, Total sulfur concentration= 10⁻⁴ mol/kg) (Reproduced with permission from Marcus and Protopopoff [113], Copyright ©1990, The Electrochemical Society).

Second, not only is the dissolved H_2S species found to be easily adsorbed on an iron surface, other sulfur species such $HS_2O_3^-$, $S_2O_3^{2-}$ and thiols (R-SH) can also be specifically adsorbed on an iron surface. Comparison between H_2S and thiol adsorption is performed here. Similar adsorption binding energy has been observed for thiols [64] and aqueous H_2S [61] on an iron substrate. Volmer, *et al.* [115] and Lay *et al.* [116] have proposed the adsorption mechanism of thiols on a metal surface. The sulfur atoms in thiols are covalently bonded to the metal surface. The bond from chemisorption of a thiol to the metal surface can only be formed by cleavage of the S-H bond. This mechanism can be interpreted to be the same for aqueous H_2S , because H_2S can be thought of as the smallest of thiols, and an analogy between aqueous H_2S and thiol adsorption on mild steel can be accepted.

However, a question remains about how does this sulfide adsorbed layer affect the electrochemical reaction of H₂S corrosion? It was proven that chemisorption of H₂S on
the platinum can slow down the hydrogen evolution rate (HER) [117], which is the most important electrochemical reaction in the corrosion process. As Figure 51 shows, the exchange current density of the hydrogen evolution rate (HER) on Pt decreases with an increase in surface coverage by sulfides. The sulfide coverage was measured by Auger spectroscopy, low energy electron diffraction (LEED), and ³⁵S radiotracer techniques. In addition, if an analogy between aqueous H₂S and thiol adsorption on mild steel can be built, the observations of the retardation effect of thiols adsorption on electrochemical reactions can be taken as the evidence. Stratmann, et al. [118] have reported that during thiol adsorption the sulfide adsorbed layer was established within 10 s, yielding a film with a lateral size of 10-20 nm. This adsorbed layer can cause a decrease of capacitance due to the pushing apart of the double layer, and affect the charge transfer reaction. Volmer, et al. [64] stated that both propanethiol (C_3H_7SH) and decanethiol ($C_{10}H_{21}SH$) chemisorb onto metallic iron and form 10-nm-thick multilayer films, which shows excellent retardation of oxygen reduction. Thiols or other sulfur containing compounds (such as thiosulfate), have been used as corrosion inhibitors for carbon steel corrosion [119].



Figure 51. Exchange current density of HER on Pt (111) vs. the sulfur coverage. The curved dash line is calculated according to $i_0=i_{0(\theta_s=0)}(1-\theta_s)$, with $i_{0(\theta_s=0)}=1.4\times10^{-4}$ A cm⁻². (Reproduced with permission from Marcus *et al.* [117], Copyright ©1987, American Vacuum Society).

Moreover, the retardation effect of the first sulfide layer on the charge transfer reactions, especially the anodic reaction and H_2O reduction is also observed in potentiodynamic sweeps as shown in Chapter 4 and Chapter 5. Figure 52 shows a comparison of potentiodynamic sweeps between a H_2S saturated aqueous environment and a non- H_2S environment. The anodic reaction and the H_2O reduction current density are retarded with addition of H_2S . Actually a similar retardation effect on anodic reaction from HAc was also observed by Crolet *et al.* [120], Sun *et al.* [121], and Gulbrandsen and Bilkova [122].



Figure 52. Comparison of potentiodynamic sweeps for H_2S environment and non- H_2S environments.

The mechanism of the retardation effect coming from H_2S can be explained by the change of the double layer. The thickness of the first inner sulfide film was reported to be 10 nm [61], which is approaching the same order of magnitude as the double layer (10-100 nm) [123]. The double layer is constructed by adsorption of H_2O molecules at the metal/solution interface. The adsorption of sulfide species can be considered to be a replacement reaction in which sulfide species replace H_2O molecules adsorbed at the metal/solution interface and affect the capacitance of the double layer. Therefore, this adsorbed sulfide layer is part of the double layer and can be treated as the boundary condition in the corrosion product layer growth model.

In summary, the existence of the first inner sulfide layer has been demonstrated in the literature for different substrates (Fe, Pt, and Au electrodes) and is formed by chemisorption. The chemically adsorbed sulfide layer can slow down the charge transfer reaction kinetics. The previous electrochemical corrosion model already includes the influence of the first inner sulfide adsorbed layer on corrosion by slowing the charge transfer exchange current density.

6.3.2 Study of the Effect of the Outer Iron Sulfide Layer on Corrosion

As the introduction stated, the second outer iron sulfide layer formed by precipitation, may be present, or not, depending on the surface saturation value for iron sulfide, in relation to the precipitation reaction:

$$\operatorname{Fe}_{(\mathrm{aq})}^{2+} + \operatorname{S}_{(\mathrm{aq})}^{2-} \rightleftharpoons \operatorname{FeS}(\mathrm{s})$$

$$(60)$$

The saturation value for iron sulfide formation is calculated based on Equation (61).

$$S_{\text{FeS}} = \frac{c_{\text{Fe}^{2+}}c_{\text{S}^{2-}}}{K_{\text{spFeS}}}$$
(61)

By knowing the concentration of Fe^{2+} and S^{2-} ions at the steel surface, the formation of iron sulfide can be determined. When $S_{FeS} > 1$, the multiple of the concentrations of Fe^{2+} and S^{2-} ions exceeds the solubility limit, iron sulfide can precipitate on the steel surface. When S_{FeS} is smaller than 1, iron sulfide can be dissolved from the steel surface. The saturation value can be used to determine if an iron sulfide layer forms or not. Importantly, the corrosion rate is more related to the protective properties of the iron sulfide layer and depends on the surface scaling tendency (SST) which describes the relative rate of precipitation with respect to corrosion rate (undermining rate) at the steel surface as Equation (99) shows.

$$SST = \frac{Precipitation Rate (PR)}{Corrosion rate (CR)}$$
(99)

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When SST ≥ 1 , the rate of precipitation at the steel surface equals or exceeds the rate of corrosion (film undermining), the condition is favorable for formation of dense, protective iron sulfide layers which can cause corrosion rate reduction. *Vice versa* when SST<1, the corrosion process undermines the newly formed corrosion product layer faster than precipitation can fill in the voids. A porous and non-protective iron sulfide layer forms, which can be very thick.

In order to verify the hypothesis of the effect of the outer iron sulfide layer on H₂S corrosion and check the validity of surface scaling tendency as an effective indicator of protective film formation, three series of controlled corrosion tests in the presence of iron sulfide were designed. Test series #1 concerns the effect of pH. As previously known, precipitation rates increase and corrosion rates decrease with increasing pH, so the SST will be higher. This is favorable for protective iron sulfide layer formation. Test series #2 is related to the effect of flow. Species transport in turbulent flow affects the surface concentration of species. Lower flow can cause the increase of surface pH [68], making the surface condition more favorable for iron sulfide precipitation and increase SST. The protective layers form more readily. Test series #3 regards the effect of temperature. Increased temperature accelerates the precipitation kinetics and aids in formation of a protective layer.

6.3.2.1 Test series #1 pH Effect

6.3.2.1.1 Corrosion behaviors

Corrosion rates from LPR measurement at different pH values are shown in Figure 53. The pH has a strong influence on the corrosion rate. At pH 4.0, the increase of corrosion rate with time can be attributed to the presence of a carbide network left after corrosion. It has been reported that iron carbide can accelerate the corrosion rate due to the increase of the cathodic reaction area. At pH 5.0 and pH 6.0, the decrease of corrosion rate is the result of the protective iron sulfide layer formed on the steel. It is also shown that the iron sulfide layer formed at pH 6.0 is more protective compared with pH 5.0, due to the high SST at pH 6.0.



Figure 53. Corrosion rate with time at different pH, $P_{total} = 1$ bar, 10% H_2S/N_2 (0.05 bar H_2S), 80 °C (Data of pH 6.0, 400rpm taken from Ning [124]).



Figure 54. Corrosion rate, pH, [Fe²⁺] and $S_{FeS,bulk}$ with time for an initial solution pH 4.0, $P_{total} = 1$ bar, 10% H₂S /N₂ (0.05 bar H₂S), 80 °C, 600 rpm

Figure 54 shows the detail of corrosion study including pH, [Fe²⁺] and the saturation of FeS in the bulk solution ($S_{FeS,bulk}$) at the initial of pH 4.0. It shows an increase in corrosion rate with time to a stable value after approximately 3 days. The pH fluctuated between 3.9 and 4.2. The increase of $S_{FeS,bulk}$ with time can be explained from the mass balance equation for Fe²⁺:

$$\frac{\partial c_{Fe^{2+}}}{\partial t} = R_{Fe^{2+}(CR)} - R_{Fe^{2+}(PR)} - R_{Fe^{2+}(out)} + R_{Fe^{2+}(in)}$$
(100)

Here, $R_{Fe^{2+}(CR)}$ represents the rate of $c_{Fe^{2+}}$ change due to the release of Fe²⁺ from corrosion. $R_{Fe^{2+}(PR)}$ is the rate of $c_{Fe^{2+}}$ change due to the consumption of Fe²⁺ form precipitation. $R_{Fe^{2+}(out)}$ and $R_{Fe^{2+}(in)}$ represent the rate of $c_{Fe^{2+}}$ change due to the inflow and outflow of the solution. In the experimental system, Fe²⁺ inflow rate, $R_{Fe^{2+}(in)}$, is zero, and Fe²⁺ outflow rate, $R_{Fe^{2+}(out)}$, is constant if the outflow rate and $c_{Fe^{2+}}$ is constant (assuming 1 ml/min outflow rate, 20 ppm $c_{Fe^{2+}}$ and 20 cm² corrosion area, $R_{Fe^{2+}(out)}$ is calculated to be equivalent to approximately 0.7 mm/year metal loss). When steady state is achieved, any increase in iron concentration due to corrosion should be balanced by a decrease in the iron concentration due to precipitation. From Figure 54, the corrosion rate increases, so the precipitation rate also needs to increase, and this requires the iron sulfide saturation value S_{FeS,bulk} to increase from 1.5 to 3.9.

Figure 55 and Figure 56 show the detail of the corrosion behaviors at pH 5.0 and pH 6.0. The corrosion rate was reduced at both pH 5.0 and pH 6.0 due to the formation of iron sulfide protective layers. $S_{FeS,bulk}$ was observed to decrease with time, the result of the reduction in corrosion rate. According to Equation (100) and the explanation in the above paragraph, the precipitation rate will also decrease with the reduction in the $S_{FeS,bulk}$ value. If the corrosion rate goes to almost zero, as is the case at pH 6.0, the precipitation rate will be very close to zero, and $S_{FeS,bulk}$ will be equal to 1.



Figure 55. Corrosion rate, pH, [Fe²⁺] and S_{FeS,bulk} with time at pH 5.0, $P_{total} = 1$ bar, 10% H₂S /N₂ (0.05 bar H₂S), 80 °C, 600 rpm.



Figure 56. Corrosion rate, pH, [Fe²⁺] and S_{FeS,bulk} with time at pH 6.0, $P_{total} = 1$ bar, 10% H₂S /N₂ (0.05 bar H₂S), 80 °C, 400 rpm, data from Ning, 2013 [124]

6.3.2.1.2 Corrosion product layers

Figure 57 shows the surface morphology and cross section of the corrosion product layer changed with pH after a one day exposure. Top view SEM images show that a surface layer had formed on all specimens after one day of corrosion.

At pH 4.0, the surface layer has a very open and porous structure, as shown in Figure 57 (a), (d), so the product cannot provide any protection against corrosion. The layer thickness is about 4.5 μ m, which is much smaller than the average of 10 μ m of metal lost due to corrosion. That is probably due to the layer being too loose and detached from the steel surface, so it could be easily removed by flow shear stress.

At pH 5.0, the top surface layer displayed a "lettuce leaf-like" structure. Parts of the layer had spalled off and revealed the presence of much smaller crystallites under the outer layer. From the cross section analysis, the corrosion product is also composed of two parts: a dense and adherent layer covering the steel surface with a thickness on average of about 5 μ m and a second very porous layer on top of the underlying one. By comparison, the steel thickness loss due to corrosion is about 5 μ m, which corresponds roughly to the thickness of the dense layer. It is most likely this layer is the result of the immediate precipitation of Fe²⁺ released from corrosion. The second porous layer has most likely formed through a slow precipitation from Fe²⁺ in the bulk solution. This second porous layer is not as well attached and probably corresponds to the lettuce leaf like features observed in the top view SEM image.

At pH 6.0, the surface was mostly covered with a much denser layer of slightly distorted crystals. Similar to the specimen at pH 5.0, small crystals were observed on areas where the outer layer had peeled off. From the cross section image, a thin dense and

seemingly adherent layer covers the steel surface with a thickness around 1 μ m, which is close to the metal loss thickness (0.7 μ m).



Figure 57. SEM image (left column) and cross section (right column) of corrosion product layer at various pH conditions, $P_{total} = 1$ bar, 10% H₂S /N₂ (0.05 bar H₂S), 80 °C, duration 1 day, results of pH 6.0 from Ning [124].

The surface morphology of the corrosion product layer and cross section analysis after 6 days corrosion is shown in Figure 58. The structure of the corrosion product layers present the same characteristics as were observed after one day of corrosion. That is the cause that corrosion rates remaining the same from 1 day to the end of the tests.



Figure 58. SEM image (left column) and cross section (right column) of corrosion product layer at various pH conditions, $P_{total} = 1$ bar, 10% H₂S /N₂ (0.05 bar H₂S), 80 °C, duration 6 day, results of pH 6.0 from Ning [124].

At pH 4.0, a thick, porous and very detached layer covers the steel surface, which does not provide any protective effect. At pH 6.0, a thin, dense and adherent layer is present on the steel surface, which plays a very good protective role against corrosion. The protectiveness of the iron sulfide layer at pH 5.0 is intermediate with respect to the layers at pH 4.0 and pH 6.0. The corrosion layer was somewhat protective, as the final steady-state corrosion rates were much lower than the initial corrosion (3.2 mm/y to 1.0 mm/y), but was still around 1 mm/y.

Moreover, the corrosion product layers after 6 days of corrosion at different pH values are much thicker than those after 1 day of corrosion, but corrosion rates do not change from 1 day to 6 days. This is indicative that the thickness of corrosion product layers plays little role in corrosion rate reduction. Lack of correlation of layer thickness and associated corrosion rate has also been observed in CO_2 corrosion in the presence of iron carbonate layers [125]. The corrosion rate is mostly likely related to the porosity and morphology of the corrosion product layer and how well it is attached to the steel surface, rather than the layer thickness.

6.3.2.2 Test series #2 Flow Effect

6.3.2.2.1 Corrosion behaviors

Turbulent flow usually affects the surface water chemistry by changing mass transfer rate of species moving from the bulk to the steel surface or *vice versa*. At low flow rate, the surface concentration for most of the species is different from bulk concentrations. The surface pH has been shown to be 1 to 2 units higher than the bulk solution pH [68], [125]. When surface pH is higher, the condition is more favorable for

iron sulfide formation on the steel surface, precipitation rate will be higher, and the corrosion rate will be lower; therefore the SST will be higher and the protective corrosion product layer is easier to form.

Figure 59 shows corrosion rates from LPR measurement at a different flow rate at pH 4.0. At the higher flow rate (600 rpm stirring rate), corrosion rate increases with time, meaning that no protective layer formed on the steel surface. At the lower flow rate (60 rpm stirring rate), the corrosion rate reduces from 2.2 mm/y to about 1.5 mm/y, which is due to the formation of the somewhat protective layer on the surface. The bulk water chemistry is exactly the same in these two cases. The different roles of the corrosion product layer resulted from the difference in surface water chemistry caused by the flow rate.



Figure 59. Effect of flow rate on corrosion rate change with time at pH 4.0, $P_{total} = 1$ bar, 10% H₂S /N₂ (0.05 bar H₂S), 80 °C.

Similar to the role of flow rate at pH 4.0, the same effect was observed at pH 5.0 as shown in Figure 60. A lower flow rate was observed to be favorable for the protective corrosion product layer formation.



Figure 60. Effect of flow rate on corrosion rate change with time at pH 5.0, $P_{total} = 1$ bar, 10% H₂S /N₂ (0.05 bar H₂S), 80 °C.

6.3.2.2.2 Corrosion Product Layers

Figure 61 shows the effect of the flow on the surface morphology and cross section of the corrosion product layers at pH 4.0. At 600 rpm (high flow rate), the surface layer has a very open and porous structure and is detached from the steel surface, as shown in Figure 61 (a), (b). Consequently, the corrosion product layer cannot provide any protection against further corrosion. At 60 rpm (low flow rate), a more dense and adherent layer covering the steel surface with a thickness on average of about 20 μ m was observed, which corresponds roughly to the thickness of steel loss (22 μ m). The corrosion product layer was slightly more protective than that at 600 rpm (high flow

rate), as the final steady-state corrosion rate (1.5 mm/y) was lower than the initial corrosion rate (2.2 mm/y). However, it is still high.



(a) SEM image of corrosion product layer at 600rpm (high flow rate)



(b) Cross section of steel specimen with corrosion product layer at 600rpm (high flow rate)



(c) SEM image of corrosion product layer at 60rpm (low flow rate)



(d) Cross section of steel specimen with corrosion product layer at 60rpm (high flow rate)

Figure 61. Effect of flow on the surface morphology and cross section of corrosion product layers at pH 4.0, $P_{total} = 1$ bar, 10% H_2S / N_2 (0.05 bar H_2S), 80 °C.

Figure 62 shows the effect of the flow on the surface morphology and cross section of the corrosion product layers at pH 5.0. The results have a similar dependence on flow rate as observed for pH 4.0. At a low flow rate (60 rpm), the rate of precipitation at steel the surface is much higher than the corrosion rate, leading to a high surface scaling tendency, and tends to form a more protective corrosion product layer, which is dense and adherent to the steel surface, as Figure 62(d) shows.



(a) SEM image of corrosion product layer at 600rpm (high flow rate)



(b) Cross section of steel sample with corrosion product layer at 600rpm (high flow rate)



(c) SEM image of corrosion product layer at 60rpm (low flow rate)



(d) Cross section of steel sample with corrosion product layer at 60rpm (high flow rate)

Figure 62. Effect of flow on the surface morphology and cross section of corrosion product layers at pH 5.0, $P_{total} = 1$ bar, 10% H_2S / N_2 (0.05 bar H_2S), 80 °C.

6.3.2.3 Test series #3 Temperature Effect

In the absence of any precipitation and corrosion product layer formation (i.e., at the initial stage of the corrosion), temperature accelerates the kinetics of all the processes involved in a corroding system: electrochemical reactions, chemical reactions, transport processes, etc. Hence, the initial corrosion rate also increases with temperature as indicated in Figure 63.

When the formation of the corrosion product layer occurs by precipitation, it is known that increased temperature aids the iron sulfide layer formation by accelerating the kinetics of precipitation. At 25 °C the kinetics of iron sulfide precipitation is very much slower than that at 80 °C. Only the porous layer formation can be detected, as shown in Figure 64 (c) and (d), which does not provide a good protection against corrosion (the corrosion rate is fairly constant from 0.4 mm/y to 0.3 mm/y). Figure 64 (a) and (b) show a thin, dense and adherent iron sulfide layer formed on the steel surface, which provides a very good protectiveness against corrosion, reducing corrosion rate from 1.1 mm/y to 0.1 mm/y. In summary, higher temperatures make the initial corrosion rate higher, but make the final corrosion rate lower, which is shown in Figure 63.



Figure 63. Effect of temperature on corrosion rate change with time at pH 6.0, $P_{total} = 1$ bar, 10% H₂S /N₂, 80 °C, data provided by Ning [124].



(a) SEM image of corrosion product layer at 80 °C (high temperature)



(b) Cross section of steel specimen with corrosion product layer at 80°C (high temperature)



(c) SEM image of corrosion product layer at 25 °C (low temperature)



(d) Cross section of steel specimen with corrosion product layer at 25 °C (low temperature)

Figure 64. Effect of temperature on the surface morphology and cross section of corrosion product layers at pH 6.0, $P_{total} = 1$ bar, 10% H₂S /N₂, 80 °C, image provided by Ning [124].

6.3.2.4 Composition of corrosion product

EDS and XRD were used to characterize the composition of the corrosion product layer on the steel surface. XRD results show mackinawite is the dominant corrosion product except at pH 4.0. At pH 4.0, iron carbide is the dominant corrosion product after one day of exposure. Other iron sulfides such troilite and pyrrhotite appear at the end of the tests. The details of the EDS and XRD results are shown in Appendix E.

6.4 Summary

In summary, the hypothesis regarding protectiveness of the outer iron sulfide corrosion product layer on H_2S corrosion has been verified by three sets of tests. The results show that the balance between iron sulfide precipitation and the undermining process can lead to a variety of corrosion outcomes depending on the environmental parameters such as temperature, pH, and flow rate. The protective corrosion product layer and low corrosion rate were observed at high pH, temperature and low flow rate due to formation of dense corrosion product layers. The present results also confirm that the concept of scaling tendency is a good indicator for assessing the likelihood of the formation of protective iron sulfide layer.

Chapter 7. Mechanistic Model of H₂S Corrosion of Carbon Steel with Iron Sulfide Layer Growth⁴

7.1 Introduction

Since the mechanistic study of iron sulfide layer growth has been described in Chapter 6, the next step described in this chapter is the modeling of iron sulfide layer growth and its complex interaction with CO_2/H_2S corrosion.

As noted above, a large amount of research effort has been made to understand uniform H_2S corrosion over the past few decades, but the comprehensive understanding of the many aspects of uniform H_2S corrosion is still not achieved. This is mostly due to the complexity of iron sulfide layer formation. Iron sulfide precipitation is usually very fast and related to water chemistry, especially the water chemistry at the steel surface. This refers to the concentration of different species in the restricted volume close to steel surface where conventional equipment cannot easily be used for measurement, and it can be very different from the water chemistry in the bulk solution. Therefore, for the purpose of simulating the process of iron sulfide layer growth, it would be necessary to obtain the physicochemical properties near the steel surface by using a mechanistic approach.

In Chapter 4 and Chapter 5, an electrochemical model of H_2S corrosion without iron sulfide layer growth has been developed to address the corrosion process on a bare steel surface, avoiding the complex issues associated with formation and growth of iron sulfide. Actually, this model is very similar to the corrosion model called FREECORP [126], which was developed by the Institute for Corrosion and Multiphase Technology

⁴ Portions of the work presented in this Chapter have been published in a NACE conference paper in 2015, paper No. 6146 and also submitted to journal

(ICMT). The difference between this model and FREECORP is the addition of a new electrochemical reaction: a direct H_2S reduction and additional effects H_2S has on the other electrochemical reactions. Unfortunately, the FREECORP type of model is rather simple and is based on bulk water chemistry and therefore does not enable explicit calculation of surface water chemistry, which is required to calculate the iron sulfide layer growth.

FREECORP is a simple electrochemical corrosion model where the mass transport of species from the bulk solution to the steel surface is accounted for by using mass transfer coefficients. The charge transfer and mass transfer/chemical reaction limiting current density for each electrochemical reaction are determined separately, and then linked together to obtain the total current density. The corrosion rate is then determined by a charge neutrality equation, balancing the total cathodic current density with the total anodic current density. The advantage of FREECORP is that the simulation is very fast and gives a reasonable corrosion rate prediction in many conditions. The problem is that all the calculations are based on the bulk water chemistry, and the water chemistry at the steel surface remains unknown, where the precipitation reaction occurs. If the surface water chemistry was calculated by using a balance of mass transfer rate and charge transfer reaction rate, the electrical charge neutrality and chemical reaction equilibrium would be violated at the steel surface.

Fortunately, an advanced one-dimensional finite-difference numerical model has been developed in the ICMT, called MULTICORP, which can calculate the parameters in the whole boundary layer, i.e., in any control volume, however small, including the restricted volume close to the steel surface. The physicochemical process and the numerical methods of the MULTICORP model were described in the paper by Nešić *et al.* [8]. This model covers the electrochemical reactions, diffusion of species and homogenous chemical reactions including iron carbonate precipitation. A uniform grid from the steel surface to the bulk solution is defined as shown in Figure 65, therefore allowing the water chemistry, the electrochemical reactions (occurs only at the steel surface), mass transport, and iron carbonate layer formation to be simulated at every control volume according to the corresponding physicochemical laws. This model is a more realistic description of the corrosion process. The concentrations, the potential, and the chemical reaction terms including iron carbonate precipitation are predicted in every control volume; therefore, an additional chemical reaction (iron sulfide precipitation) and an additional electrochemical reaction (direct H_2S reduction) can be easily incorporated into the existing MULTICORP model.

However, this model has its own advantages and known problems. The known problem is that MULTICORP is so complex and sometimes slow to get the answer. As Figure 65 shows, if 10 species and 300 grid points were considered, it would be necessary to solve 3000 linear equations at the same time in each time step. And coupling this model with the corrosion product layer growth model would just make it even more complex. Considering that the time scale for oil and gas fields as years, it may take a very long time to get an answer. For this reason, a simple corrosion model could be developed to address this issue via faster calculations.



Figure 65. Sketch of the computational grid for MULTICORP model, the lines from left to right or right to left represent the mass transport process, the arrow lines from top to bottom or bottom to top represent the chemical reaction including the precipitation reaction.

Actually, some of the main physicochemical processes described in both the FREECORP model and MULTICORP model are the same except for the corrosion product layer formation, which is not considered in FREECORP. Both of these models calculate electrochemical reactions at the steel surface, mass transfer of species from the bulk solution to the steel surface and homogenous chemical reactions in the solution. The main difference is the mathematical method or the numerical techniques used to simulate the corrosion process. The MULTICORP model uses multiple nodes (currently around 300 nodes) and a finite-difference method to solve complex partial differential equations at every control volume within the boundary layer. The physicochemical laws (chemical reaction kinetics, mass conservation law, charge neutrality) are applied to every control volume to obtain the concentration and the potential profile between two boundary conditions (the steel surface and bulk solution).

FREECORP is a more simplified model as compared to MULTICORP. It only considers two nodes: the bulk solution and the metal surface. As it stands today, in

FREECORP the chemical reaction terms and charge neutrality are applied only to the bulk solution node, but not to the node of the steel surface. Therefore, the surface water chemistry was not calculated explicitly in the model, but it is implicitly included by coupling pure charge transfer and mass transfer/chemical reaction limiting current density. The mass transfer process is calculated by using mass transfer coefficients for each species independently, which ignore the interaction between the chemical and diffusion processes in the boundary layer.

Here a new corrosion model is developed here based on both the existing FREECORP with only two nodes considered: the bulk solution and the steel surface, by using some of the MULTICORP model strategy: all the physicochemical laws are not only applied to the node of the bulk solution, but also apply to the node of the steel surface, which is different from FREECORP and more similar to MULTICORP. However, MULTICORP considers the chemical reaction processes in the boundary layer between these two nodes, which is ignored in the current model. The transport of species is treated to independently diffuse through the boundary layer without interacting with each other. The concentration gradient from the bulk solution and the steel surface is calculated to be linear. These two nodes are only connected by a diffusion flux calculated by the mass transfer coefficient and a linear concentration gradient. The surface water chemistry is explicitly obtained from the water chemistry in the bulk solution and mass transfer flux. The iron sulfide and iron carbonate precipitation rate at the steel surface can now be calculated and incorporated into the corrosion model.

From the description above, this type of corrosion model is inherently transient, which is related to the corrosion product layer growth over time. In practical terms, a steady-state or end-state model is required in addition to a transient model. Here, an additional steady-state mechanistic H_2S/CO_2 corrosion model with the same theoretical foundations as the transient model has been derived based on the concept of surface scaling tendency (the ratio of precipitation rate and corrosion rate) to address this issue.

In the following text, the physicochemical processes included in the model are outlined. Two models (a transient corrosion model and a steady-state corrosion model) are presented using different ways to address the effect of corrosion product layers. Model verifications and parametric studies for both models are then given to discuss how different key parameters affect the uniform H_2S/CO_2 corrosion. Moreover, comparisons of these two models and model limitations are then presented at the end of the chapter.

7.2 Physicochemical Processes Included in the Model

Based on the previous experimental study and an analogy with iron carbonate formation in CO_2 corrosion, a comprehensive uniform aqueous H_2S corrosion model can now be described.

We can start the description with H₂S diffusing to a bare steel surface where a very thin adsorbed iron sulfide layer forms very rapidly as suggested by Marcus, *et al.*, [113] and using the mechanism proposed by Smith and Wright [127]

$$Fe_{(s)} + H_2S_{(aq)} \rightarrow FeS_{(ad)} + 2H_{(ad)}$$
(101)

The research by Marcus *et al.* [113] indicates that sulfur adsorbs very strongly to a steel surface and can displace adsorbed H_2O and OH^- . This action results in slowing down the kinetics of electrochemical reactions like Fe dissolution, H_2O reduction, and carbonic acid reduction by affecting the double layer. However, electrochemical reactions (anodic and cathodic reactions) continue to occur despite an existing adsorbed H_2S layer, albeit at a slower rate.

When the surface concentrations of Fe^{2+} and S^{2-} ions exceed the solubility limit of iron sulfide (mackinawite), and iron sulfide is thermodynamically stable, this means that iron sulfide will precipitate on the steel surface:

$$\operatorname{Fe}_{(\mathrm{aq})}^{2+} + \operatorname{S}_{(\mathrm{aq})}^{2-} \Leftrightarrow \operatorname{FeS}_{(\mathrm{s})}$$
 (60)

This iron sulfide layer can retard the corrosion rate by providing a surface coverage effect and a via mass transfer effect (acting as diffusion barrier).

The current transient corrosion model is somewhat similar but also quite different from the model proposed by Sun *et al.* [56] A comparison between Sun's model[56] and the current model is listed in Table 14.

Sun's model (2009)	Current model
An inner 1-10 nm thin mackinawite film acting as a solid state diffusion barrier.	A thin adsorbed iron sulfide film affecting the kinetics of different electrochemical reactions (retardation offect)
A porous outer iron sulfide layer formed	An outer iron sulfide layer is growing via
by <u>spalling of the inner layer</u> .	a precipitation mechanism.
Corrosion rate is <u>always under mass-</u> <u>transfer control</u> due to the porous outer	Corrosion rate is <u>not always under mass-</u> <u>transfer</u> control depending the coupling
and inner iron sulfide layers.	of mass transfer process and electrochemical reactions.

Table 14. Comparison between Sun's model and the current model

7.3 Model Construction

The model describes H_2S/CO_2 corrosion in terms of three main parts: a water chemistry model in the bulk solution, an electrochemical corrosion model including the mass transport from bulk to the surface, and corrosion product formation and growth models for iron carbonate and iron sulfide.

7.3.1 Water Chemistry Model

A water chemistry model is built to calculate the concentrations of different chemical species in the bulk solution for given conditions of CO_2 partial pressure, H_2S partial pressure and temperature. These models have been addressed in the literature separately for CO_2 and H_2S corrosion [8], [128], shown in section 2.1.1 and section 2.2.1. The principles of the water chemistry will be introduced briefly.

All the reactions in the bulk solution are listed in Table 1 and Table 3, and it is assumed that all chemical reactions are at chemical equilibrium in the bulk solution.

In an open system, the amount of gaseous CO_2 and H_2S is much larger than that of water, like flow loop system or glass-cell system by continuous purging of gaseous H_2S/CO_2 , so pH₂S and pCO₂ is constant and known. There are 9 unknowns, the concentrations of different species (c_{H_2S} , c_{HS^-} , $c_{S^{2^-}}$, c_{CO_2} , $c_{H_2CO_3}$, $c_{HCO_3^-}$, $c_{CO_3^{2^-}}$, c_{OH^-} , c_{H^+}) in the aqueous solution. One can get 8 equations from equilibrium equations in Table 1 and Table 3, leaving one more equation necessary to find the solutions (9 unknowns need 9 equations to solve). Since the aqueous solution is always charge neutral, the electro-neutrality equation must follow, as Equation (102) shows:

$$c_{H^+} = c_{HS^-} + c_{S^{2^-}} + c_{HCO_3^-} + 2c_{CO_3^{2^-}} + c_{OH^-}$$
(102)

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Therefore, the concentration for all the chemical species can be calculated by these 9 equations. Equation (102) is valid only for an ideal H_2S/CO_2 -saturated aqueous solution without other species. If other ions are introduced in the aqueous solution, such as Fe²⁺ produced by corrosion of steel or Na⁺ or Cl⁻, then Equation (102) must be changed to include these species, as Equation (103) shows.

$$c_{H^+} + 2c_{Fe^{2+}} + c_{Na^+} = c_{HS^-} + c_{S^{2-}} + c_{HCO_3^-} + 2c_{CO_3^{2-}} + c_{OH^-} + c_{Cl^-}$$
(103)

However, in a closed system, the amount of gaseous H_2S/CO_2 is limited (like an autoclave), and the pressures of gaseous CO_2 and H_2S are no longer constant and known. Based on the water chemistry model developed above, two additional equations are thus required to account for two additional unknowns: pH_2S and pCO_2 . For a closed system, the total amounts of carbonic species (in moles) and sulfide species are conserved. Accordingly, two more equations are added as follows:

$$N_{CO_{2}(g)} + N_{CO_{2}(aq)} + N_{H_{2}CO_{3}} + N_{HCO_{3}^{-}} + N_{CO_{3}^{2^{-}}} = constant$$
(18)

$$N_{H_{2S_{(g)}}} + N_{H_{2S_{(aq)}}} + N_{HS^{-}} + N_{S^{2-}} = constant$$
(44)

The mole of species in the gas phase can be calculated based on an Equation of State, such as ideal gas law, $N_i=PV_g/RT$. The mole of species in liquid phase can be

calculated via $N_i = V_{l*}C_i$. The ratio between the volume of the gas phase and the liquid phase is also necessary to know. With this information, the concentrations of each species in both the gas phase and the aqueous solution can be calculated in a closed system.

The water chemistry model is the foundation for the electrochemical corrosion model and the corrosion product layer growth model. It is very important to predict concentrations accurately. This is much more difficult for the solution at the high pressure, high temperature, and high salt concentrations [129], [130], because of the non-ideal behavior in the system.

7.3.2 Electrochemical Corrosion Model

As stated in the introduction of this chapter, two nodes were used in the electrochemical corrosion model: one for the bulk solution and the other for the thin water layer adjacent to the steel surface (called "surface water layer" in the following text). The concentrations of different chemical species in the bulk solution can be calculated as shown in the previous section describing the water chemistry model. The calculation node for the bulk solution did not require modification from previous models, but the second node for the surface water layer needs to be addressed to include physicochemical processes related to the corrosion. The physicochemical processes (Figure 66) occurring in the surface water layer next to the steel surface are listed as follows:

- 1. Homogenous chemical reactions in the surface water layer
- Electrochemical reactions at the steel surface, which cause the flux in or out of the surface water layer

 Transport of species to and from the bulk, including convection and diffusion through the boundary layer as well as migration due to establishment of potential gradients.

These three physicochemical processes are interconnected together with a material balance or mass conservation equation at the surface water layer.

$$\frac{\partial c_{\text{surface},j}}{\partial t} = \frac{N_{in,j} - N_{out,j}}{\Delta x} + R_j$$
(104)

where $c_{\text{surface},j}$ is the concentration and R_j the production due to homogeneous chemical reactions for species *j*. N_{in} is the flux of species due to mass transfer from the bulk solution to the surface water layer. N_{out} is the flux of species due to electrochemical reactions at the steel surface.



Figure 66. Illustration of computation domain and governing equation for mass transport simulation.

7.3.2.1 Homogenous Chemical Reactions

The homogenous reactions considered in the current model are all listed in Table 1 and Table 3. The equilibrium constants to determine species dissociation are listed in Table 2 and Table 4.

It should be noted that chemical reactions are sometimes very rapid compared to other processes involved in corrosion, such as species transport from the bulk solution to the steel surface and electrochemical reactions at the steel surface, thus preserving chemical equilibria throughout the solution. On the other hand, in the case of slow chemical reactions (such as the CO_2 hydration reaction (4)), other faster processes can lead to local non-equilibrium conditions in the surface water layer. Therefore, chemical reactions can significantly affect the rates of electrochemical processes at the steel surface and the ultimately – the corrosion rate.

In order to better understand how the rates of homogenous chemical reactions are calculated, one can refer to the research done by Nešić, *et al.* [125].

7.3.2.2 Electrochemical Reactions at the Steel Surface

Electrochemical reactions considered in this model include:

$$Fe_{(s)} \to Fe_{(aq)}^{2+} + 2e^{-}$$
 (23)

$$2H_{(aq)}^{+} + 2e^{-} \rightarrow H_{2(g)}$$
 (28)

 $\langle \mathbf{n} \mathbf{n} \rangle$

$$2H_2CO_{3(aq)} + 2e^- \rightarrow H_{2(g)} + HCO_{3(aq)}$$
 (29)

$$H_2S_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2HS_{(aq)}$$
 (55)

 $2H_2O_{(1)} + 2e^- \rightarrow H_{2(g)} + OH_{(aq)}^-$ (30)

The Tafel equation used to calculate the current densities (rate) of various electrochemical reactions listed above is described in detail in the previously developed electrochemical corrosion model in Chapter 4 and Chapter 5:

$$i = i_o \times 10^{\pm \frac{E - E_o}{b}} \tag{105}$$

Where i_o represents a reference current density in A/m², *i* represents the current density in A/m², E_o represents a reference potential in V, *E* represents the potential on the steel surface in V, and *b* represents the Tafel slope in V/decade.

In this model, the current density for each electrochemical reaction depends on the surface concentration of species, which is not explicitly known and needs to be calculated, as explained below. For a spontaneous corrosion process, the unknown corrosion potential of the steel, E can be calculated from the charge balance equation at the steel surface. Details of this calculation have already been explained elsewhere in Chapter 4 and Chapter 5. Then the flux at the steel surface can be determined from:

$$N_{out,j} = \pm \frac{i_j}{n_j F} \tag{106}$$

where n_j is the number of moles of electrons exchanged per mol of species *j* participating in a particular electrochemical reaction. For species *j* consumed by electrochemical reactions at the steel surface, the positive sign is applied. For species *j* produced by electrochemical reactions at the steel surface, the negative sign is applied. For those species *j* that are not involved in the electrochemical reactions, $i_j = 0$. Once the corrosion potential (*E*) is found, the partial current (i_j) for a given species *j* is readily calculated from Equation (105).

7.3.2.3 Species Surface Concentration and Mass transfer

Ten (10) minor species (H₂S, HS⁻, S²⁻, CO₂, H₂CO₃, HCO₃⁻, CO₃²⁻, OH⁻, H⁺, Fe²⁺) and two (2) major species (Na⁺ and Cl⁻) were considered to calculate the mass transfer flux from the bulk solution to the surface water layer. The homogenous chemical reactions are not considered in the water solution between the bulk solution and the surface water layer. The change in concentration for each species is linear over this region as defined by a corresponding mass transfer coefficient ($k_{m,j}$).

The mass transfer flux from the bulk solution to the surface water layer can be calculated for each of the minor species.

$$N_{in,j} = k_{m,j} * (c_{bulk,j} - c_{surface,j})$$
(107)

Here $c_{bulk, j}$ is the concentration of the species in the bulk solution, $c_{surface, j}$ is the concentration of the species in the surface water layer. $k_{m,j}$ is the mass transfer coefficient. The mass transfer coefficient can be calculated from well-known hydrodynamic relations among Re, Sc and Sh number. The mass transfer coefficient for a rotating cylinder electrode (RCE) was calculated by the correlation described by Eisenberg [105]:

$$Sh = 0.0791 \times Re^{0.7} \times Sc^{0.356} \tag{70}$$

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The mass transfer coefficient for turbulent single phase pipe flow can be calculated by a straight pipe correlation of Berger and Hau [131]:

$$Sh = 0.0165 \times Re^{0.86} \times Sc^{0.33} \tag{108}$$

A magnetic stirrer was used in the previous experiments (Chapter 6), and a custom mass transfer coefficient correlation was developed (shown in Appendix D):

$$Sh = 1.48822 \times Re^{0.5511} \times Sc^{0.1905}$$
(109)

For the major species (Na⁺ and Cl⁻), ion electro-migration needs to be considered which adds an additional term to the equation for mass transfer flux from the bulk solution to the surface water layer:

$$N_{in,j} = k_{m,j} * \left(c_{bulk,j} - c_{surface,j} \right) + k_{m,j} * \frac{z_j F}{RT} c_{bulk,j} \Delta \Phi$$
(110)

Here, z_j is the electric charge of the species, $\Delta \Phi$ represents a small electrical potential difference between the bulk solution and the surface water layer. $c_{bulk,j}$ is used in the second term at the right to make the equation become linear. Actually the average value of the bulk solution and surface concentrations should be used, but the difference

between of the bulk solution and surface concentrations is negligible (on the order of the concentration of minor species) due to an excess of supporting electrolyte..

Substitution of flux density due to electrochemical reactions and mass transfer processes into mass conservation equation of Equation (104):

$$\frac{\partial c_{\text{surface},j}}{\partial t} = \frac{N_{in,j} - N_{out,j}}{\Delta x} + R_j$$
(104)

yields Equation (111) for the minor species:

$$\Delta x \frac{\partial C_{surface,j}}{\partial t} = -\frac{i_j}{n_j F} + k_{m,j} * \left(C_{bulk,j} - C_{surface,j} \right) + \Delta x * R_j$$
(111)

For the major species, this same procedure yields (112):

$$\Delta x \frac{\partial c_{surface,j}}{\partial t} = k_{m,j} * \left(c_{bulk,j} - c_{surface,j} \right) + k_{m,j} * \frac{z_j F}{RT} c_{bulk,j} \Delta \Phi$$
(112)

There are 13 unknowns (10 unknown surface minor species concentrations, 2 unknown surface major species concentrations and 1 unknown potential $\Delta \Phi$), but only 12 mass conservation equations were obtained above. One more equation is needed. Since the aqueous solution is always charge neutral, the electro-neutrality equation must be followed:
$$\sum z_j c_{surface,j} = 0 \tag{113}$$

Therefore, the concentration for all the chemical species in the surface water layer can be calculated by these 13 equations. At the same time, corrosion current, the corrosion potential, corrosion rate, and the rates (currents) for each of the electrochemical reactions can also calculated from Equations (105).

From the description above, the equations for the minor species are independent from the equations for the major species and the electrical potential. According to Newman [132], the first step should be to solve the equations for the concentrations of the minor species in the solution and then, secondly, to solve the equations for the concentrations of the major species and the electrical potential gradient $\Delta \Phi$.

7.3.2.4 Numerical Implementation

Theoretically the 13 equations can be easily solved, but there are two numerical difficulties that need to be addressed.

First, the equations for the minor species are highly non-linear due to the presence of chemical reactions term, by which various species concentrations are linked together. An example can be shown using the H_2S dissociation reaction.

$$H_{2}S \underset{k_{b,hs}}{\overset{k_{f,hs}}{\Leftrightarrow}} H^{+} + HS^{-}$$
(36)

The net reaction rates for HS⁻ species can be expressed as the equation below.

$$R_{hs} = k_{f,hs} c_{H_2S} - k_{b,hs} c_{H^+} c_{HS^-}$$
(114)

Here, the non-linear term is the multiplication of two concentrations, i.e. $k_{b,hs}c_{H^+}c_{HS^-}$. In MULTICORP, the nonlinear chemical reaction rates are linearized by using a Taylor series expansion around the known solution concentrations in the previous time step. Actually, if the concentration of c_{H^+} is known, then all of the chemical reaction terms will become linear. Therefore, one of the most stable calculation methods, the bisection method, was used in the current model to find a c_{H^+} value to satisfy the equations. The details of the calculation process are shown in Appendix F.

The second numerical difficulty is related to the magnitude of the chemical reaction rate constants, which make the equation set "stiff" i.e. difficult to solve. In MULTICORP, this issued is also solved by using linearized Taylor series expansion around the known solution in the previous time step and by keeping only the constant and the linear term. Pots [98] proposed two ways to solve these issues in his CO₂ corrosion model. One way was to decrease the chemical reaction rate, but keep it faster than other processes. An alternative way was to calculate the concentrations of HCO_3^- , CO_3^{2-} , and OH^- directly from the equilibrium constants and then calculate the H⁺ concentration from the charge electro-neutrality equation. All the carbonic species (H₂CO₃, HCO₃⁻, and CO_3^{2-}) are then lumped together into one mass transport equation. In the current model, a method similar to this second method Pots proposed [98] was used.

For the sulfide species group (H_2S , HS^- , and S^{2-}), three mass conservation equations were developed. Because chemical reaction rates for the first and second

dissociation of H_2S are fast, these three mass conservation equations can become one mass conservation equation for total sulfide species and two more chemical equilibria equations. Therefore, chemical reaction rate terms could be discarded. A similar strategy was used for carbonic species (aqueous CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-}), but because CO_2 hydration is a slow reaction, the mass conservation equation for the aqueous CO_2 , species must be kept. Therefore, 4 mass conservation equations for aqueous CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-} become one mass conservation equation for all aqueous carbonic species, 1 mass conservation equation for all aqueous carbonic species, 1 mass conservation equations become 2 more chemical equilibria equations for carbonic acid dissociation rate terms with the expression from H^+ and OH^- species, 2 mass conservation equations become 2 new equations. One is obtained by substituting all the chemical reaction rate terms with the expression from other mass conservation equations to a H^+ species mass conservation equation. The other is the chemical equilibria equation for H_2O dissociation. These transformations are also shown in Appendix F.

7.3.3 Corrosion Product Growth Model

From the previous electrochemical corrosion model, the surface water chemistry (the concentration of different chemical species at the steel surface) can be obtained. Based on the concentrations of different species at the steel surface, a thermodynamic model based on research by Ning [12] and Tanupabrungsun [133] can be used to predict which solid corrosion product should form on the steel surface. If no solid corrosion product is expected to form, the corrosion process will continue to occur unimpededly. If a corrosion product layer forms on the steel surface, the growth and thickness of the corrosion product layer will affect the corrosion process. Therefore, a corrosion product

growth model, which focuses on kinetics of iron sulfide and iron carbonate formation, was developed to address these issues.

In the previous electrochemical corrosion model at section 7.3.2, two nodes, the steel surface water layer and the bulk solution were considered. Because of the corrosion product layer, one more node needs to be added, as shown in Figure 67. Additional physicochemical processes like iron sulfide and iron carbonate corrosion product formation and growth were added on top of the previous three physicochemical processes: chemical reaction, electrochemical reaction, and mass transport.



Figure 67. Sketch of corrosion process with corrosion product layer.

The mass conservation equation in the surface water layer becomes:

$$\frac{\partial \mathscr{E}_{surface,j}}{\partial t} = \frac{N_{b,j} - N_{out,j}}{\Delta x} + R_j$$
(115)

here, $_{s}$ is the porosity of the corrosion product layer. R_{j} is for chemical reactions of species *j* (production and consumption) due to homogeneous chemical reactions and also heterogeneous chemical reactions like iron sulfide precipitation and iron carbonate precipitation. $N_{b,j}$ is the flux of species due to mass transfer from the layer surface water layer to the surface water layer, which is related to the transport properties of the corrosion product layer (diffusion effect). $N_{out,j}$ is the flux of species due to electrochemical reactions at the steel surface, which change due to the coverage effect of the corrosion product layer. How these three terms, R_{j} , $N_{b,j}$ and $N_{out,j}$ change with corrosion product layer growth is addressed below.

7.3.3.1 Heterogeneous Chemical Reactions

Homogenous reactions have been addressed in the previous section. The focus here is to deal with two heterogeneous reactions: iron sulfide formation and iron carbonate formation.

7.3.3.1.1 Iron Carbonate Formation

Iron carbonate precipitation acts as a sink for Fe^{2+} and CO_3^{2-} . When saturation of iron carbonate, as defined in (19), is higher than 1, net iron carbonate precipitation occurs and consumes Fe^{2+} and CO_3^{2-} .

Equation (116) describes the kinetics of iron carbonate precipitation proposed by Sun, *et al.* [19], which is used in the present model.

$$R_{FeCO_3(s)} = e^{28.20 - \frac{64.85}{RT}} \frac{S}{V} K_{spFeCO_3} (S_{FeCO_3} - 1)$$
(116)

where $R_{FeCO_3(s)}$ is the precipitation rate in mol/m³.s; $\frac{s}{v}$ is the surface volume ratio of the iron carbonate in 1/m. K_{spFeCO_3} represents the solubility limit of iron carbonate in (mol/L)², which is given by Equation (117) [19].

$$logK_{spFeCO_3} = -59.3498 - 0.041377T - \frac{2.1963}{T} + 24.5724logT + 2.518I^{0.5} - 0.657I$$
(117)

where T is the temperature in K and I is the ionic strength in mol/L.

7.3.3.1.2 Iron Sulfide Formation

The iron sulfide layer forms when the product of the concentrations of Fe^{2+} and S^{2-} ions exceeds the solubility limit according to:

$$\operatorname{Fe}_{(\operatorname{aq})}^{2+} + \operatorname{S}_{(\operatorname{aq})}^{2-} \rightleftharpoons \operatorname{FeS}(\operatorname{s}) \tag{60}$$

The precipitation kinetics is much faster for iron sulfide than for iron carbonate and the solubility for iron sulfide is much lower than iron carbonate. So in the current model, when an iron sulfide layer can precipitate (S_{FeS} >1), iron carbonate precipitation is excluded. Although some researchers [55], [134] have investigated the precipitation kinetics of iron sulfide, no expression of the precipitation kinetics of iron sulfide has been developed. Lee [86] suggested an expression for iron sulfide precipitation kinetics based on Harmandas's experimental results:

$$R_{FeS(s)} = e^{16.2584 - \frac{9520.648}{T} \frac{S}{V}} (S_{FeS}^{0.5} - 1)^2$$
(118)

but the expression ignores the basic finding in this study that the apparent activation energy for the precipitation of iron sulfide is about 40 kJ /mol. According to these results a new expression is developed, which is similar to the iron carbonate precipitation kinetics:

$$R_{FeS(s)} = e^{A - \frac{40000}{RT}} \frac{s}{V} K_{sp,S^{2-}} (S_{FeS} - 1)$$
(119)

In this expression, the constant A value was calibrated with the experimental results from the present study and Harmandas *et al.* [134]. S_{FeS} is the saturation value of iron sulfide defined as Equation (61). $K_{sp,S^{2-}}$ is the solubility limit of iron sulfide in $(mol/L)^2$, which can be calculated from Benning *et al.* [135]:

$$K_{sp,S^{2-}} = 10^{\left(\frac{2848.779}{T}\right) - 6.347} \times K_{hs} \times K_{bs}$$
(120)

7.3.3.2 Electrochemical Reactions

The electrochemical reactions are mainly affected by coverage effect from the corrosion product layer. Assuming the coverage is equal to the porosity of the corrosion product layer, the current density of each electrochemical reaction is calculated by:

$$i = \varepsilon \times i_o \times 10^{\pm \frac{E - E_o}{b}} \tag{121}$$

Based on the change in the current density, the flux $N_{out,j}$ at the steel surface can be calculated.

7.3.3.3 Mass Transfer Process

The governing equations to quantify the mass transfer process for the different species are the same as described in section 7.3.2. The critical need is to address the change of mass transfer coefficients for the transportation through the corrosion product layer, i.e., the diffusion retardation effect. This effect depends on the morphology of the corrosion product layer, such as the thickness, porosity and tortuosity of the layer. Considering the models available in the literature [136]–[139], the mass transfer coefficient $k_{s,j}$ through the corrosion product layer is selected as a function of the diffusion coefficient (D_j), porosity (ε), tortuosity (τ) and thickness (δ_s) of the corrosion product layer.

$$k_{s,j} = \frac{\varepsilon \tau D_j}{\delta_s} \tag{122}$$

Here, τ tortuosity is set to be square root of porosity, in an analogy with the theory of porous electrodes [140]. Only the precipitation of corrosion product in the surface water layer was considered, while the increment in corrosion product layer thickness δ_s is calculated as follows for the two distinct cases:

- when iron sulfide layer forms:

$$\Delta \delta_s = \frac{\Delta x R_{FeS(s)} M_{FeS} \Delta t}{\rho_{FeS} (1 - \varepsilon)}$$
(123)

- when iron carbonate layer forms:

$$\Delta \delta_s = \frac{\Delta x R_{FeCO3(s)} M_{FeCO_3} \Delta t}{\rho_{FeCO3} (1 - \varepsilon)}$$
(124)

Here M_{FeS} and M_{FeCO_3} represent the molecular weight of iron sulfide and iron carbonate (kg/mol); Δt is the time step; ρ_{FeS} and ρ_{FeCO_3} are the density of iron sulfide and iron carbonate (kg/m³).

Substituting the flux density due to mass transfer through corrosion product layer and electrochemical reactions on the steel surface, the mass conservation equations in the surface water layer can be given:

- for the minor species:

$$\Delta x \frac{\partial \varepsilon C_{surface,j}}{\partial t} = -\frac{i_j}{n_j F} + k_{s,j} * \left(c_{scale,j} - c_{surface,j} \right) + \Delta x * R_j$$
(125)

- for the major species:

$$\Delta x \frac{\partial \varepsilon C_{surface,j}}{\partial t} = k_{s,j} * \left(c_{scale,j} - c_{surface,j} \right) + k_{s,j} * \frac{z_j F}{RT} c_{bulk,j} \Delta \Phi_s$$
(126)

where $\Delta \Phi_s$ is the potential gradient from the corrosion product layer surface to the steel surface.

The mass conservation equations in corrosion product surface water layer is given:

- for the minor species:

$$\Delta x \frac{\partial c_{scale,j}}{\partial t} = -k_{s,j} * \left(c_{scale,j} - c_{surface,j} \right) + k_{m,j} * \left(c_{bulk,j} - c_{scale,j} \right) + \Delta x * R_j$$
(127)

- for the major species:

$$\Delta x \frac{\partial c_{scale,j}}{\partial t} = -k_{s,j} * \left(c_{scale,j} - c_{surface,j} \right) + k_{m,j} * \left(c_{bulk,j} - c_{scale,j} \right) -k_{s,j} * \frac{z_j F}{RT} c_{bulk,j} \Delta \Phi_{s} + k_{m,j} * \frac{z_j F}{RT} c_{bulk,j} \Delta \Phi_{m}$$
(128)

where $\Delta \Phi_m$ is the potential gradient from the corrosion product layer surface to steel surface.

Two more electro-neutrality equations for the solution in the surface water layer and the corrosion product layer surface layer are also needed.

Using the same numerical techniques as introduced in section 7.3.2., all 26 equations can be solved at the same time if porosity ε at the surface water layer is known.

Here porosity ε is calculated explicitly by a corrosion product layer growth model developed by Nešić *et al.* [7], as shown in Equation (129) and Equation (130). The detail of these equations is explained in the original paper and will not be repeated here.

- for iron carbonate layer:

$$\frac{\partial \varepsilon}{\partial t} = -\frac{M_{FeCO_3}}{\rho_{FeCO_3}} R_{FeCO_3} - CR \frac{\partial \varepsilon}{\partial x}$$
(129)

- for iron sulfide layer:

$$\frac{\partial \varepsilon}{\partial t} = -\frac{M_{FeS}}{\rho_{FeS}} R_{FeS} - CR \frac{\partial \varepsilon}{\partial x}$$
(130)

Here M_{FeCO_3} and ρ_{FeCO_3} are the molecular weight and density of iron carbonate respectively. M_{FeS} and ρ_{FeS} are the molecular weight and density of iron sulfide, respectively. CR represents the corrosion rate in proper units, ε is the porosity.

Since the corrosion process continuously creates voids underneath the corrosion product layer, ε is taken to be 1 at the interface between corrosion product layer and steel surface. The initial porosity was set as 0.99, which can be changed according to the concentration of carbide network in the carbon steel. Equation (129) and Equation (130) will become:

$$\frac{\partial \varepsilon}{\partial t} = -\frac{M_{FeCO_3(S)}}{\rho_{FeCO_3(S)}} R_{FeCO_3(S)} + CR \frac{1-\varepsilon}{\Delta x}$$
(131)

$$\frac{\partial \varepsilon}{\partial t} = -\frac{M_{FeS(S)}}{\rho_{FeS(S)}} R_{FeS(S)} + CR \frac{1-\varepsilon}{\Delta x}$$
(132)

The procedure for the calculation in this model is done in successive time steps and implemented. First, the initial corrosion rate, including surface water chemistry, is determined by the electrochemical corrosion model previously developed without the corrosion product layer present. Then, a corrosion product prediction model based on thermodynamic framework is used to determine whether a corrosion product layer forms or not on the steel surface. If a corrosion product layer doesn't form, the calculation is over. If a corrosion product layer forms, a corrosion product layer growth model is invoked. The porosity for the corrosion product layer is calculated from Equation (131) or Equation (132), and the thickness of layer is obtained from Equation (123) or Equation (124) depending on which corrosion products forms. Finally, the mass conservation equations for each species are solved. Therefore, the concentration for all the chemical species in both the surface water layer and the corrosion product layer surface water layer can be obtained. The corrosion current, corrosion potential, corrosion rate, potential gradient and the rates (currents) for each of the cathodic reactions and the anodic reaction are calculated.

7.4 Model Verification

Although the present model targets H_2S corrosion primarily, it also has the capability of predicting pure CO_2 corrosion. Since the entire mathematical model was

revised, this new model needs to be compared with other models and verified against a large number of experimental data points.

7.4.1 Verification of Corrosion Model without Corrosion Product Layer

7.4.1.1 Comparisons with Other Models

As described above, specific procedure for calculations was followed in the present model in order to compare it with other multi-node models, i.e., MULTICORP [7], [125] and NUMCOR [98].

First, the comparisons were conducted for a pure CO_2 environment. The predicted corrosion rate, surface pH and CO_3^{2-} concentration at 25 °C from these different models are shown in Figure 68. Reasonably good agreement was obtained.



Figure 68. Comparison between the current and other models (MULTICORP and NUMCOR) with velocities up to 8 m/s at 25 °C, $[Fe^{2+}]=1$ ppm, pH 4.0, 1bar CO₂, D_P= 0.1 m, 1 wt% NaCl.

Second, the comparisons in an H_2S environment were performed. The results are shown in Figure 69. A very good agreement between the present model and NUMCOR was achieved.



Figure 69. Comparison between the current model and NUMCOR at 25 °C, pH 4.0, 0.05-8 m/s, 0.1bar H_2S , D_P : 0.1 m, 1 wt% NaCl.

7.4.1.2 Comparisons with Experimental Results

A model cannot be used with confidence before its performance is compared with experimental results. Various comparisons with laboratory data are presented below. Figure 70 shows the comparisons between the current model and experimental data for a N_2 environment without CO_2 or H_2S at pH 4.0 and various velocities. The predictions from the present model fairly agree with experimental results.

In a CO_2 environment, the comparisons between the model predictions and experimental results for two important parameters, pH and velocity are shown in Figure 71. Good agreement is evident under all conditions.

In an H_2S environment, Figure 72 shows the present model captures the effect of H_2S concentration, flow rate and pH as well as FREECORP.

Moreover, Figure 73 shows that the surface pH predicted from the current model generally agrees with the measured surface pH values at different bulk pH.



Figure 70. Comparisons between model and experiments for N₂ environment, 20°C, $[Fe^{2+}] < 1$ ppm, pH 4.0, D_P: 0.01 m and various velocities. Data from ICMT database.



Figure 71. Comparisons between model predictions and experiment results at 1 bar CO₂, 20°C, various pHs, and various velocities. Data from ICMT database.



Figure 72. Comparisons between model predictions and experiment results for 30° C, 1 bar total pressure and various H₂S concentrations, velocities and pHs.



Figure 73. Comparisons of surface pH between model and experiments for 25 °C, 0.1 bar H_2S and pH 3.0 through pH 5.0, Experimental data from Ning [68].

7.4.2 Verification of Corrosion Model in Iron Carbonate Layer Forming Condition

Figure 74 shows the comparisons of the model predictions with experiments conducted in a glass cell with 1000 rpm rotating speed flowing conditions. Predictions are in the range of the variation of experimental data, which indicates the model is capable of simulating the kinetics of iron carbonate layer growth and its effect on the corrosion process.



Figure 74. Comparisons between the model predictions and the experiment results for iron carbonate layer forming condition at pH 6.6, 80°C, 0.53 bar CO₂, and 1000rpm rotating speed, (a) 10 ppm bulk Fe^{2+} , (b) 50 ppm bulk Fe^{2+} .

7.4.3 Parameter Study and Verification of Corrosion model in Iron Sulfide Layer Forming Condition

7.4.3.1 Effect of pH_2S

The partial pressure of H_2S , which directly relates to the H_2S concentration in the solution, is an important factor that contributes not only the increase of H_2S reduction rate, but also to the iron sulfide layer formation. H_2S plays dual roles here. First, H_2S is a corrosive species accelerating the corrosion rate by enhancing the cathodic reaction rate. Second, H_2S also promotes the rate of the iron sulfide precipitation that decreases the general corrosion rate.

Figure 75 illustrates the predicted effect of pH_2S on the corrosion rate calculated by the current model. The initial corrosion rate increases with increasing pH_2S , because no corrosion product layer protectiveness is accounted for at the initial time (time zero), the system is overwhelmed by the accelerated role of H_2S . However, during longer reaction time, such as 1 day, the formation of a protective iron sulfide layer is promoted by extending the reaction time. The dual roles make the corrosion rates after 1 day increase with pH_2S , and then slowly decrease with further increasing pH_2S . The best example of the dual roles of H_2S is that at 10 bar pH_2S , the initial corrosion rate is the highest, but the corrosion rate after 24 hours is the lowest.



Figure 75. The predicted effect of pH_2S on the corrosion rate from current model for pH 5.0, T=80°C, V=1 m/s.

The predicted effect of pH_2S on the corrosion rate from Sun's model is illustrated in Figure 76. Sun's model does not predict the dual roles of H_2S , and only the accelerated effect shows up in Figure 76. That is because, in Sun's model, the corrosion product layer formation rate is not directly related to H_2S concentration, but correlated as half of the corrosion rate.

Both the current model and Sun's model were also compared with the experimental data to the performance of the models.

First, the condition at low partial pressures of H_2S was examined. The test was conducted by Sun [56] at H_2S gas partial pressures from 0.54 mbar to 54 mbar. Figure 77 and Figure 78 show that both the current model and Sun's model capture the corrosion rate change well.



Figure 76. The predicted effect of p_{H_2S} on the H_2S corrosion rate from Sun's model for pH 5.0, T=80°C, V=1 m/s.



Figure 77. Corrosion rate changing with time at different H_2S partial pressure from current model; points: experimental data, lines: model predictions; conditions: total pressure = 1 bar, H_2S gas partial pressure from 0.54 mbar to 54 mbar, 80°C, experiment duration 1 h to 24 h, pH 5.0 to 5.5, stagnant. Experimental data taken from Sun [56].



Figure 78. Corrosion rate changing with time at different H_2S partial pressure from Sun's model; points: experimental data, lines: model predictions; conditions: total pressure = 1 bar, H_2S gas partial pressure from 0.54 mbar to 54 mbar, 80°C, experiment duration 1 h to 24 h, pH 5.0 to 5.5, stagnant. Experimental data taken from Sun [56].

Corrosion experiments at higher pH_2S ($pH_2S=16.1$ bar in the mixed H_2S/N_2 environment) were reported by Liu [141] and model predictions are compared with the experimental results in Figure 79. The current model performs much better than Sun's model at this condition.

A similar range of H_2S partial pressures were reported by Bich, *et al.* [112] with the main difference being the presence of CO₂. Figure 80 shows the comparison between the model prediction and experimental results in a mixed H_2S/CO_2 environment. The current model captures the corrosion rate change with time, but Sun's model tends to over predict the corrosion rate.



Figure 79. Corrosion rate changing with time, points: experimental data, lines: model predictions; conditions: 16.1 bar H_2S , 90°C, 2L autoclave, stagnant. Experimental data taken from Liu, *et al.* [141].



Figure 80. Corrosion rate changing with time, experimental data = points, model predictions = lines; conditions: 12.2 bar H_2S , 3.5 bar CO_2 , 65°C. Experimental data taken from Bich *et al.* [112].

7.4.3.2 *Effect of pH*

The solution pH is the measurement of the concentration of the free hydrogen ions. These free hydrogen ions accelerate the cathodic reaction by providing more cathodic reaction species. Another significance of the concentration of hydrogen ions is their influence on the formation of the iron sulfide corrosion product layer by affecting the saturation value (S_{FeS}). A higher pH indicates a lower hydrogen ion concentration, so both HS⁻ and S²⁻ concentrations will be higher at the constant concentration of aqueous H₂S. This increases the formation rate of iron sulfide layer and decreases the corrosion rate. The predicted effect of a change in pH on the corrosion rate from the current model is demonstrated in Figure 81. Corrosion rate increases with a decrease in pH. The decrease of corrosion rate with time is much faster at pH 6.0 due to the formation of a denser iron sulfide layer.

The predicted effect of pH on the corrosion rate from Sun's model is demonstrated in Figure 82. Corrosion rates do not change with pH, because under these environmental conditions, the model predicts that H_2S is the dominant corrosive species.

Comparisons between model predictions and experimental results are shown in Figure 83. The current model captures the corrosion rate change much better than Sun's model. The experimental LPR corrosion rates are much higher than the model prediction at pH 4.0. This is probably due to the iron carbide remaining on the metal surface from corrosion at pH 4.0, which can accelerate the corrosion rate by providing a more cathodic reaction area [142], [143]. This effect is not included in the current model.



Figure 81. The predicted effect of pH on the corrosion rate from current model for 0.054 bar pH_2S , balance N_2 , T = 80°C, stirring rate: 600 rpm



Figure 82. The predicted effect of pH on the corrosion rate from Sun's model [56] for 0.054 bar pH₂S, balance nitrogen, $T = 80^{\circ}C$, stirring rate: 600 rpm



Figure 83. Corrosion rate changing with time, points: experimental data, lines: model predictions; conditions: 0.054 bar pH₂S, balance nitrogen, $T = 80^{\circ}$ C, stirring rate: 600 rpm.

7.4.3.3 Effect of Flow

Fluid flow and turbulence play an important role in the corrosion process. First, higher flow can increase the corrosion rate through enhancing the mass transport process, especially when there is no corrosion product layer formed. Second, flow can also affect the formation of the protective iron sulfide layer. Species transport in turbulent flow affects the surface concentration of species and, consequently, changing the precipitation rate of iron sulfide.

The predicted effect of flow on the corrosion rate from the current model is illustrated in Figure 85 and Figure 86. Figure 85 shows that the corrosion rate increases with an increase in velocity, especially the initial corrosion rate when the corrosion product layer is not established. The reduction of the corrosion rate that occurs with time is due to the iron sulfide layer growth. The decrease process is much faster at a low velocity. That is because that the surface condition at a low velocity is more favorable for iron sulfide layer formation. Moreover, Figure 86 illustrates that the corrosion rate after 300 hours is almost the same at different velocities. That is because most of the mass transfer resistance is from transport processes through the iron sulfide layer which built-up with the long time exposure. This is similar to Sun's model which assumes that the corrosion process is always under mass transfer control due to the iron sulfide layer on the steel surface and no effect of velocity will be predicted, as shown in Figure 86.

Figure 87 shows the comparisons between model predictions and experimental results at different stirring rates (e.g., flow velocities). The current model is generally able to predict the change of the corrosion rate with the different stirring rates.



Figure 84. The predicted effect of velocity on the corrosion rate from current model for pH 5.0, T=80 $^{\circ}$ C, pH₂S = 0.54 bar (30 hours).



Figure 85. The predicted effect of velocity on the corrosion rate from current model for pH 5.0, T=80 $^{\circ}$ C, pH₂S = 0.54 bar (300 hours).



Figure 86. The predicted effect of velocity on the corrosion rate from Sun's model for pH 5.0, T=80 $^{\circ}$ C, pH₂S = 0.54 bar, balance N₂.



Figure 87. Corrosion rate vs. time, points: experimental data, lines: model predictions; conditions: $pH_2S = 0.54$ bar, balance N₂, T=80 °C, pH 5.0.

7.4.3.4 Effect of Temperature

Figure 88 illustrates the predicted effect of temperature on corrosion rate from the current model. The initial corrosion rate increased with increasing temperature, because no precipitated iron sulfide layer was accounted for at time zero (when the bare metal is first exposed to the environmental conditions), and corrosion process was dominated by the accelerating role of temperature. However, during longer reaction times, such as one day, the formation of a protective iron sulfide layer is promoted. The effect of protective iron sulfide layer formation is actually accelerated by an increase in temperature; therefore, the corrosion rate decreases with temperature. The best example of the effect of temperature is at 80 °C in Figure 88, where the initial corrosion rate is the highest as compared to similar calculations for lower temperatures, but the corrosion rate after 24 hours is the lowest.

Figure 89 demonstrates the predicted effect of temperature on corrosion from Sun's model. Temperature does not affect the corrosion rate. That is because mass transfer control of the corrosion process was assumed in Sun's model, and the mass transfer process is not as sensitive as the reaction process to temperature change.

Comparisons between model prediction and experimental results at different temperatures are shown in Figure 90 and Figure 91. The current model predicted the corrosion rate much better than Sun's model in most cases.



Figure 88. The predicted effect of temperature on the corrosion rate from current model for pH 5.0, T=80 $^{\circ}$ C, pH₂S = 0.54 bar, V=1 m/s.



Figure 89. The predicted effect of temperature on the corrosion rate from Sun's model for pH 5.0, T=80 $^{\circ}$ C, pH₂S = 0.54 bar, V=1 m/s.



Figure 90. Corrosion rate vs. time, points: experimental data, lines: model predictions; conditions: $pH_2S = 0.54$ bar, pH 6.0, 400 rpm stirring rate. Experimental data taken from Ning [124].



Figure 91. Corrosion rate vs. time, points: experimental data, lines: model predictions; conditions: total pressure= 1 bar, $pH_2S=0.3$ bar at 90 °C, $pH_2S=0.88$ bar at 50 °C pH 4.2-4.7, Stirring condition. Experimental data taken from Abayarathna, *et al.* [111].

7.5 A Steady State Model

7.5.1 Theory behind the Model

The steady state model is based on the same theoretical foundations as the previously described transient model, i.e. the water chemistry model and the electrochemical corrosion model. The difference is related to the way of accounting for the effect of the corrosion product layer. Two assumptions were made here. First, only the surface coverage or blockage effect by the iron sulfide corrosion product layer was considered while the diffusion effect through the iron sulfide layer was neglected. Second, it is assumed that a steady state is reached when the corrosion rate is equal to the corrosion product layer formation rate.

7.5.2 Mathematic Model

The mass transfer coefficient for the transport process of each species from the bulk solution to the steel surface water layer is represented by $k_{m,j}$, which has already been described in the section regarding the electrochemical corrosion model. The total mass transfer coefficient from the bulk solution to the steel surface is represented by $k_{T,j}$, which is the function of $k_{m,j}$ and $k_{s,j}$. Actually, if assuming there is no chemical reaction in the corrosion product layer, then $k_{T,j}$ can be expressed in relation to $k_{m,j}$ and $k_{s,j}$ as shown:

$$\frac{1}{k_{T,j}} = \frac{1}{k_{s,j}} + \frac{1}{k_{m,j}}$$
(133)

As a first assumption of the steady state model, the reduction in diffusion through the iron sulfide layer is neglected, so $k_{T,j} = k_{m,j}$. Therefore the mass conservation equations for the surface water layer can be given:

- for the minor species:

$$0 = -\frac{i_j}{n_j F} + k_{T,j} * \left(c_{bulk,j} - c_{surface,j}\right) + \Delta x * R_j$$
(134)

- for the major species:

$$0 = k_{T,j} * \left(c_{bulk,j} - c_{surface,j} \right) + k_{T,j} * \frac{z_j F}{RT} c_{bulk,j} \Delta \Phi_T$$
(135)

The electro-neutrality equation is added:

$$\sum z_j c_{surface,j} = 0 \tag{136}$$

Iron sulfide layer growth equation is:

$$\frac{\partial \varepsilon}{\partial t} = -\frac{M_{FeS(S)}}{\rho_{FeS(S)}} R_{FeS(S)} + CR \frac{1-\varepsilon}{\Delta x}$$
(137)

The first term on the right side of Equation (137) is related to the corrosion product layer formation rate and the second term on the right side is related to the undermining corrosion rate. For the second assumption of the steady state model, the corrosion product layer formation rate is equal to the undermining corrosion rate, so Equation (137) will become a steady state equation:

$$0 = -\frac{M_{FeS(S)}}{\rho_{FeS(S)}} R_{FeS(S)} + CR \frac{1-\varepsilon}{\Delta x}$$
(138)

By solving Equations (134), (135), (136) and (138), the corrosion rate can be obtained.

7.5.3 Model Verification

7.5.3.1 Verification -Pure CO₂ Environment

Figure 92 shows the comparison of the model predicted corrosion rate with the experimental corrosion rates at different Fe^{2+} concentration. The increase of Fe^{2+}

concentration results in a higher iron carbonate saturation, which consequently accelerates the precipitation rate and leads to a higher surface scaling tendency. The corrosion rate will decrease. This change is captured by the steady-state model.

Figure 93 shows the predicted effect of temperature on corrosion rate from the steady state model. When no corrosion product layer forms on the steel surface, the corrosion rate increases with temperature. However, an increase in temperature also aids iron carbonate corrosion product layer formation by accelerating the precipitation kinetics. This causes the corrosion rate to decrease with an increase in temperature. The model predicts the corrosion rate change with temperature for both conditions: without and with corrosion product layer.

Figure 94 demonstrates the predicted effect of velocity on the corrosion rate. Increasing velocity always accelerates the mass transport process in both corrosion product layer free and forming conditions.


Figure 92. Comparison of model prediction with experimental data at different Fe^{2+} concentration, conditions: 1000rpm, 80 °C, 0.54 bar CO₂, 1 wt% NaCl, pH 6.6, data from ICMT database.



Figure 93. The predicted effect of temperature on corrosion rate from current steady state model. Experimental conditions: 1000 rpm, total pressure 1 bar, 1 wt% NaCl, pH 6.6, pCO₂: 0.97 bar (25 °C), 0.8 bar (60 °C), 0.54 bar (80 °C).



Figure 94. The predicted effect of velocity on corrosion rate from current steady state model; conditions: Total pressure= 1 bar, 1%NaCl, pH 6.6, pCO₂: 0.97 bar (25 $^{\circ C}$), 0.8 bar (60 $^{\circ}$ C), 0.54 bar (80 $^{\circ}$ C)

7.5.3.2 Verification $-H_2S$ Environment

Figure 95 shows the corrosion rate at different solution pH values. Decreasing the solution pH can accelerate corrosion rate by providing more H⁺ ions and decelerate the formation of a protective iron sulfide layer. The increase of corrosion with decreasing pH is captured by the current steady state model.

Figure 96 shows the comparison between model predictions and experimental data at different stirring rates (e.g. flow velocities). It is well known that flow can accelerate the mass transport process, so the corrosion rate increases as stirring rate increases.

Figure 97 shows the predicted effect of the pH_2S on the corrosion rate. H_2S can play the dual roles to the corrosion process by not only increasing the amount of H_2S reduced at the surface, but also by increasing the amount of iron sulfide layer formation. Due to these characteristics, a peak corrosion rate should be observed with an increase in pH_2S . The current steady state model predicts this effect of pH_2S on the corrosion rate just below 0.1 bar pH_2S at 80C, in a pH 5.0 solution at 1 m/s flow rate, which also agrees with the finding of Sun *et al.* [93] shown in Figure 6.



Figure 95. Effect of pH on corrosion rate; conditions: $pH_2S = 0.054$ bar, balance with N₂, T=80 °C, stirring rate: 600 rpm.



Figure 96. Effect of velocity on corrosion rate; conditions: $pH_2S = 0.054$ bar, balance with N₂, T=80 °C, pH 5.0.



Figure 97. The predicted effect of temperature on corrosion rate; conditions: 80 °C, 1 m/s, pH 5.0.

7.6 Comparison between Models

A comparison between the steady state corrosion model and the transient corrosion model developed previously was performed in both CO_2 and H_2S environments.

Figure 98 shows the comparison between the steady state corrosion model and the transient corrosion model in a CO_2 environment. The predicted corrosion rate from the steady state corrosion model is close to the transient corrosion model results after 1 day, but is higher than the transient corrosion model after 20 days. This is because the current steady state model does not account for the effect of diffusion through a corrosion product layer. After 20 days, the diffusion through this layer will play an important role for the corrosion rate reduction.

A similar comparison was performed in a pure H_2S environment, as shown in Figure 99. The steady state corrosion model prediction is still close to the transient model prediction after 1 day, but is higher than the transient model prediction after 6 days and 20 days. The reason for this difference is the same as for the CO_2 environment. The effect of diffusion through the corrosion product layer is not accounted for in the current steady state model.



Figure 98. Comparison between steady state model and transient model at CO₂ environments; conditions: 1000rpm, 80 °C, 0.54bar CO₂, 1 wt% NaCl, pH 6.6.



Figure 99. Comparison of steady state model and transient model at H_2S environment; conditions: 0.054 bar H_2S , 1 wt% NaCl, 80°C, 600rpm.

In the steady model above, the diffusion effect through the corrosion product layer is not addressed. If this effect is accounted for by reducing 10 times of the total mass transfer coefficient, $k_{T,j}=0.1*k_{m,j}$, the steady state model will predict more similar results with the transient model. Figure 100 and Figure 101 show the comparison between the steady state model and transient model. It can be seen that the prediction from the steady state model with diffusion effect is close to the transient model prediction after 20 days, which is an expected result.



Figure 100. Comparison between steady state model and transient model at CO₂ environments; conditions: 1000rpm, 80 °C, 0.54bar CO₂, 1 wt% NaCl, pH 6.6.



Figure 101. Comparison of steady state model and transient model at H₂S environments; conditions: 0.054 bar H₂S, 1 wt% NaCl, 80°C, 600rpm.

7.7 Model Limitations

In the current models, there are a number of factors which are not taken into consideration. These limitation need to be pointed out here, to avoid the misuse of the current model. Major limitations of the current model are listed below:

- The current model covers only uniform carbon steel corrosion. It does not predict localized corrosion, but it is a solid foundation for constructing a localized corrosion model.
- Mackinawite is the only iron sulfide corrosion product considered in the current model. The various transformations of mackinawite to other type of iron sulfides are known to happen over time. However, if the kinetics of precipitation and transformations of other types of iron sulfides are known, the new physics can be added easily to the current mechanistic corrosion model.

- The current model does not account for the effect of iron carbide on the corrosion.
- A simple water chemistry was considered in the current model, which means the infinite solution theory and an ideal solution are assumed. Concentrations of different species are used rather than activities.
- The current model ignores the chemical processes though the boundary layer.
 The chemical processes are only considered in the bulk solution and steel surface water layer.
- Empirical mass transfer correlations are used to account for the mass transfer process in this model, making it only take into account the effect of single-phase flow. However, empirical mass transfer correlations in multiphase flow can be easily developed to couple with the current model.
- The effects of high salt concentration, oxygen, elemental sulfur on the corrosion process are not considered in the current model.

7.8 Summary

A mechanistic transient two-node model of uniform CO_2/H_2S corrosion of carbon steel has been developed, which is based on three key elements of the corrosion process:

- Water chemistry in the bulk solution
- Electrochemical corrosion including the mass transport from the bulk solution to the metal surface, and
- Corrosion product formation and growth for iron carbonate and iron sulfide.

The model is able to predict the corrosion rate as well as the surface water chemistry related to all species involved. The model has been successfully calibrated against experimental data in conditions where corrosion product layer do not form and in those where they do. Parametric testing and verification of the model in iron sulfide forming conditions have been performed in order to gain insight into the effect of different environmental parameters on the H_2S/CO_2 corrosion process. The trends shown in the predictions agreed well with the general understanding of the H_2S/CO_2 corrosion process in the presence of iron sulfide.

Moreover, a simple steady-state mechanistic H_2S/CO_2 corrosion model was established to predict the final corrosion rate. The verification shows this simple model can capture the change of corrosion rate at different conditions. The difference between the steady state model and transient model is due to the effect of diffusion through the corrosion product layer. If the diffusion effect is addressed, a good agreement between the steady state model and transient model can be obtained.

Chapter 8. Recommendation for Future Work

Some recommendations for future work are listed as follows:

- Further study of CO₂ /H₂S corrosion in high pH₂S and high temperature conditions. The current mechanistic model needs to be calibrated with more accurate data on CO₂/H₂S corrosion in high pH₂S and high temperature conditions
- Further study on kinetics of iron sulfide precipitation. The kinetics of iron sulfide precipitation used in the current mechanistic H₂S corrosion model is adopted from a single literature source and adjusted to fit current H₂S corrosion experiments. Therefore, a more accurate study on the kinetics of iron sulfide precipitation needs to be conducted in a carefully controlled environment, such as Fe²⁺-H₂S-H₂O system using a platinum substrate.
- Effect of various iron sulfides on the H₂S corrosion. As we know, there are various iron sulfides in H₂S corrosion, and how they affect both uniform corrosion and local corrosion remains unclear and requires further investigation, especially the conductivity of different iron sulfides.

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Appendix A: Examining the Mechanism of H₂S Corrosion: Electrochemical vs.

Non-electrochemical

A.1. Introduction

Two corrosion mechanisms have been proposed: a non-electrochemical reaction mechanism and an electrochemical reaction mechanism.

As an initial starting point, it is important to establish the differences between both mechanisms. In the non-electrochemical reaction mechanism, or calling 'direct reaction' H₂S adsorbs directly on the steel surface and iron sulfide forms at one location. No other species participate and no Fe^{2+} is released to solution. In this scenario, with the same molar concentration for H₂S, corrosion rates in water should be equal to that in the gas phase or in other solvents. Furthermore, the corrosion rate should be not a function of potential, Fe^{2+} concentration should be zero at super-saturated solution for iron sulfide because no iron dissolves to the solution (or may be more than zero in under-saturated conditions or due to dissolution of iron sulfide).

For the iron dissolution and iron sulfide precipitation electrochemical mechanism, anodic and cathodic reactions can occur in two different locations. Fe^{2+} released to solution can react with bisulfide (HS⁻) or sulfide (S²⁻) ions to form iron sulfide. Therefore, corrosion rate in an aqueous electrolyte should be much higher than in the gas phase or in other solvents at room temperature. Corrosion rate will be a function of potential and ferrous ion concentration can increase with time during the corrosion process. Accordingly, the non-electrochemical and electrochemical mechanisms should be distinguishable due to solvent effects, observed changes in ferrous ion concentrations during tests and applied potential effects. This would tell us which mechanism is dominant. Bearing in mind the above differences, three sets of experiment were designed to:

- Investigate the effect of polar solvent on corrosion rate.
- Examine if electrochemical techniques can be applied to H₂S corrosion systems
- Investigate the ferrous ion concentration changes in super-saturated solution during tests.

A.2. Experimental Method

A.2. 1 Effect of Different Solvents on Corrosion Rate

The solubility of H₂S in different solvents is shown in Table 15

Table 15. The solubility of H ₂ S in different solvents			
Solvent	Mole fraction, N		
Water	0.0020		
Ethylene glycol	0.0128		
Ethanol	0.0177		
Methanol	0.0276		
Heptane	0.054		

Four different environments for mild steel corrosion were investigated:

• DI water purged with 100 ppm H_2S in N_2 (7 days)

- \circ 1 wt% NaCl with 100 ppm H₂S in N₂ (6 days)
- \circ Ethylene Glycol purged with 100 ppm H₂S in N2 (6 days)
- Heptane 3 psi partial pressure in 200 psi (7days)

A.2. 2 Examine if Electrochemical Techniques Can be Applied to H₂S Corrosion

Two methods were used. First, electrochemical techniques were applied to H_2S corrosion to measure the corrosion rate and verify with other non-electrochemical techniques, such as weight loss analysis, Fe^{2+} concentration measurement and quartz crystal microbalance (QCM). Second, different potentials were applied to check if H_2S corrosion can respond to applied potential.

A.2.3 Measure Fe^{2+} Concentration Changes during the Corrosion Process in Supersaturated Solution for Iron Sulfide.

According to introduction, the non-electrochemical and electrochemical mechanism should be distinguishable by observed changes in ferrous ion concentrations in the saturated bulk solution. If the ferrous ion concentration still increases in the saturated bulk solution for iron sulfide, the electrochemical mechanism can occur.

A.3. Experimental Set-up

A.3.1 Glass Cell

The experiment apparatus (glass cell) is shown in Figure 102. The reference electrode was Ag/AgCl (saturated KCl), counter electrode was platinum and the working electrode was a cylindrical X-65 carbon steel sample with ca. 5.4 cm2 surface area. Several carbon steel samples were hung from a nylon string into the glass cell at the same time the working electrode was inserted.



Figure 102. Glass-Cell for experiment

1. Reference Electrode 2. Luggin capillary 3. Platinum Counter Electrode 4. Temperature Probe 5. Bubbler 6. Working Electrode (X65 carbon steel) 7. pH meter 8. Rotator.

A.3.2 EQCM Device

The EQCM device is from Stanford Research Systems (QCM200), and is shown in Figure 103. It includes a controller, a crystal oscillator and crystal holder. The crystals used in this current study include platinum coated and iron coated quartz crystals. Instead of using a rotating cylinder electrode, the QCM holder is put into the glass cell set-up as the working electrode. The reference electrode is an Ag/AgCl electrode and a platinum wire served as the counter electrode.



Figure 103. QCM200 from SRS.

A.3 Results and Discussion

A.3.1 Effect of Different Solvents on Corrosion Rate

Weight loss results in different solvents are shown in Table 16. For DI water purged with 100 ppm H₂S/N₂, the weight increased by about 2 milligrams after the experiment and decreased about 39 milligrams after removal of the corrosion product film with Clarke solution. The corrosion rate calculated from this weight change corresponded to 0.03 mm/year. For 1 wt% NaCl with 100 ppm H₂S in N₂, the corrosion rate was about 0.04~0.06 mm/year. For ethylene glycol purged with 100 ppm H₂S, the corrosion rate was almost zero. For heptane the corrosion rate is almost zero as well. These results indicate that H₂S corrosion can easily happen in a water environment, which favors an electrochemical process.

This is considered to be due to the action of water as a strongly polar protic solvent, facilitating the electrochemical reaction. Organic solvents can be classified as non-polar aprotic, dipolar aprotic and protic. The classification of a solvent as protic or aprotic is based on whether it has the ability to provide protons. Ethylene glycol is a protic solvent and Heptane is a non-polar aprotic solvent.

	Weight before experiment (g)	Weight change after experiment(g)	Weight change after Clarkes solution (g)	Corrosion rate (mm/y)
DI water purged with 100 ppm H_2S in N_2 (7 days)	9.4525	+0.0002	-0.0039	0.03
1 wt% NaCl with 100 ppm H ₂ S in N ₂	8.8435	-0.0002	-0.0053	0.04
(6 days)	9.3082	-0.0012	-0.0049	0.07
EthyleneGlycolpurgedwith100	8.7252	+0.0013	+0.0000	≈0
ppm H ₂ S in N2 (6 days)	9.2271	+0.0014	0.0001	≈0
Heptane 3 psi partial pressure in 200 psi (7days)	8.9381	+0.0008	-0.0006	≈0

Table 16. Weight loss results at four different solvent environments.

Solvent type plays a key role in corrosion processes due to salvation effects. In solvation, solvent molecules can form shells around dissolved ionic species to compensate for the columbic forces between oppositely charged ions in solution. The change to the nature of the solvent results in different solvation properties. Ethylene glycol and water are polar protic solvents, ferrous ion may exist in this type of solvent system. Heptane is a non-polar aprotic solvent, ferrous ion cannot exist. Also, Heptane cannot act as a reactant in hydrolysis, compared with how water can react with H₂S gas to form aqueous H₂S, or function as a protophilic solvent during dissociation of H₂S.

Corrosion reactions in organic solvents can be classified into two types: electrochemical and chemical. For electrochemical reaction, the reaction rate should be different when related to the different solvation and hydrolysis properties as well as solvent conductance. For the non-electrochemical reaction mechanism, the reaction rate should be the same in all the solvents with the same molar concentration of corrosion species.

A.3.2 Examine if Electrochemical Techniques Can be Applied to H₂S Corrosion

As discussed above, if a reaction is electrochemical then electrochemical techniques can be applied to obtain reaction rates and reaction rates themselves can be affected by the application of potential to an active surface.

Figure 104 compares the average corrosion rate obtained from weight-loss methods, Fe^{2+} measurements and an electrochemical technique (linear polarization resistance (LPR), using a B value 23mV) at two different pH values in the H₂S /N₂ environment. The corrosion rate measured by three different techniques including electrochemical techniques and non-electrochemical techniques showed good agreement. These experiments indicate that electrochemical techniques can be applied to the H₂S corrosion systems.



Figure 104. Comparison of corrosion rates obtained from weight-loss, Fe^{2+} measurement, and electrochemical measurements (Time-averaged) with different H₂S concentration and pH for 6 h.

Electrochemical quartz crystal microbalance (EQCM) is another effective method to measure the instantaneous corrosion rate from electrochemical and nonelectrochemical techniques at the same. Figure 105 shows the results of EQCM test in 100 ppm H₂S purged solution. At the pre-corrosion stage, mass decreases and corrosion rate is about 0.31 mm/year. After introducing 100 ppm H₂S, mass increases at first, and then decreases with time. The corrosion rate calculated from mass decrease is about 0.17 mm/year. The value is also in good agreement with corrosion rate measured form LPR (0.2 mm/year). This EQCM test also proves that the electrochemical techniques can be applied to H₂S corrosion systems.



Figure 105. Comparison of the instantaneous corrosion rate obtained from mass change of QCM and electrochemical(LPR): iron coated crystal, 1000 ppm H₂S/N₂, 1 wt% NaCl solution, 33 °C, total pressure=1 bar, pH 4.0, B Value 23 mV.

Moreover, different potentials were applied to H_2S corrosion system to check if the corrosion rate can respond to the applied potential. The experiments were performed by Yoon-Seok Choi[144]. The results did show that corrosion rate is controlled by the applied potential and indicate that H_2S corrosion process is based on electrochemical reactions.

A.3.3 Fe²⁺ Concentration Changes in Super-saturated Solution for Iron Sulfide

As the introduction stated, the non-electrochemical and electrochemical mechanism should be distinguishable by observed changes in ferrous ion concentrations in the super-saturated bulk solution. If the ferrous ion concentration still increases in the saturated bulk solution for iron sulfide, the electrochemical mechanism can occur.

Figure 106 show the water chemistry calculation at different pH. The solutions were always under-saturated at pH 3.0 and pH 4.0 for the 100ppm H₂S condition. Thus, iron sulfide can dissolve to make the iron concentration increase. The electrochemical

and non-electrochemical reaction mechanism cannot be disguise at this condition, because Fe^{2+} concentration increases could attribute to iron dissolution in the electrochemical reaction mechanism or iron sulfide dissolution in the nonelectrochemical mechanism. Therefore a test in a super-saturated solution for iron sulfide was designed at 2700ppm H₂S/N₂ and pH 6.0.

The saturation calculations using two different mackinawite solubility constants are shown in Figure 107. If $K_{sp,mack}$ from Benning *et al.* [135] was used, the solution will become supersaturated when the Fe²⁺ concentration is over 0.4 ppm. If $K_{sp,mack}$ from Morse *et al.* [145], iron sulfide supersaturation occurs above an Fe²⁺ concentration of 0.76ppm. Figure 108 shows Fe²⁺ concentration still increased after the bulk solution became supersaturated with respect to mackinawite for either solubility constant calculation. This implies that the iron dissolution rate is greater than the ferrous ion precipitation rate, therefore the ferrous ion concentration is observed to increase. If only the 'direct' formation mechanism or the non-electrochemical reaction mechanism occurs then the ferrous ion concentration cannot increase. This indicates that the electrochemical reaction mechanism is dominant for H₂S corrosion.



Figure 106. Saturation of Mackinawite, 25°C, 0.97 bar N₂, 100 ppm H₂S, K_{sp,mack.} from Benning, *et al.*



Figure 107. Saturation of Mackinawite, 25°C, 0.97 bar N₂, 2700ppm H₂S, K_{sp,mack.} from Benning, *et al* and Morse, *et al*.



Figure 108. Fe^{2+} Concentration change at super-saturated condition, 25°C, 0.97 bar N₂, 2700 ppm H₂S, pH 6.0, static.

A.3 Summary

Results indicate that electrochemical mechanisms are more dominant for H_2S corrosion:

- Corrosion rate in water is highest for all the studied solvents, this is considered to be due to the action of water as a strongly polar protic solvent, facilitating the electrochemical reaction.
- All the electrochemical corrosion rate measurements are close to the weight loss values. The corrosion rate responds to an applied potential.
- Fe^{2+} concentrations were shown to become increasingly supersaturated with time.

Appendix B: Repeatability of Experiments

Some experiments in the current study were repeated. The potentiodynamic sweeps at different conditions in Figure 8 are repeated twice. The comparisons of repeated experiments are shown below respectively.

Potentiodynamic sweeps at pure N_2

The repeatability of the potentiodynamic sweep in pure N_2 gas purged solution is shown in Figure 109. The potentiodynamic sweep for the first time was taken in Figure 8



Figure 109. Repeatability of potentiodynamic sweeps in the N_2 gas purged solution, pH 4.0, 30°C, total pressure 1 bar, 1 wt% NaCl, 1000 rpm.

Potentiodynamic sweeps at 100 ppm(v) H_2S/N_2

Very good repeatability is obtained at this condition, as shown in Figure 110. The

curve obtained for the first time was used in Figure 8



Figure 110. Repeatability of potentiodynamic sweeps in the 100 ppm(v) H_2S/N_2 gas purged solution, pH 4.0, 30°C, total pressure 1 bar, 1 wt% NaCl, 1000 rpm.

Potentiodynamic sweeps at 1000 ppm(v) H₂S/N₂

The curve obtained for the second time was used in Figure 8



Figure 111. Repeatability of potentiodynamic sweeps in the 1000 ppm(v) H_2S/N_2 gas purged solution, pH 4.0, 30°C, total pressure 1 bar, 1 wt% NaCl, 1000 rpm.

Potentiodynamic sweeps at 1%(v) H₂S/N₂

The curve obtained for the second time was used in Figure 8



Figure 112. Repeatability of potentiodynamic sweeps in the 1%(v) H₂S/N₂ gas purged solution, pH 4.0, 30°C, total pressure 1 bar, 1 wt% NaCl, 1000 rpm.

Potentiodynamic sweeps at $10\%(v) H_2S/N_2$

The curve obtained for the second time was used in Figure 8


Figure 113. Repeatability of potentiodynamic sweeps in the 10%(v) H₂S/N₂ gas purged solution, pH 4.0, 30°C, total pressure 1 bar, 1 wt% NaCl, 1000 rpm.

Appendix C: Investigation of Electrochemical Reaction of Direct H₂S Reduction Using 316L Stainless Steel Electrode

C.1. Introduction

In the Chapter 4 and Chapter 5, an electrochemical model for short term exposure was developed in both H_2S/N_2 and H_2S/CO_2 systems. The direct reduction of H_2S as an additional cathodic reaction was introduced to our system. The charge transfer reaction kinetics parameters were obtained based carbon steel corrosion. However, the charge transfer region for the cathodic reaction is interfered by anodic dissolution of iron where it is dominant. The detail of electrochemical kinetics of H_2S is still needed further investigation. In the present study, stainless steel was used to avoid the interference of the anodic reaction of iron dissolution. The current work is to determine the electrochemical kinetic parameters of H_2S reduction and confirm the used in carbon steel corrosion.

C.2 Experimental

C.2.1 Method

X65 carbon steel is used for the corrosion behavior study in the Chapter 4 and Chapter 5. The detail of electrochemical parameters for H_2S reduction was difficult to obtain as the charge transfer region for cathodic reactions overlaps with the region where the dominant reaction is the anodic dissolution of iron. Therefore, a passive stainless steel was used to avoid the interference from the iron dissolution reaction. Figure 114 below shows a reasonable agreement obtained between the cathodic sweeps on the two steels (SS 316L and X65) under the same conditions. Based on these results, a stainless steel can be considered to be similar to mild steel for cathodic reactions under these environmental conditions.



Figure 114. Comparison of the cathodic sweeps obtained on X65 and stainless steel (316L) at 30°C, pH 4.0, aqueous solution saturated with N_2 with 1 wt% NaCl, RCE rotating speed 1,000 rpm.

C.2.2 Equipment and Procedure

The experimental set-up and procedure is the same as the experiments in Chapter

4. The carbon steel RCE was replaced with stainless steel RCE. The test matrix is shown

in Table 17.

Description	Parameters
Material	SS 316L Rotating Cylinder Electrode
Solution	1 wt% NaCl Solution
Purged Gas (H ₂ S volume fraction in H ₂ S/N ₂)	0 -10%(v) (0 - 0.1 bar)
Rotating Speed	1000 rpm
Total Pressure	1 bar
Temperature	30°C
рН	3.0, 4.0, 5.0, 6.0
Measurement Methods	EIS, Potentiodynamic Sweeps

Table 17. Test matrix for investigating direct H₂S reduction using stainless steel electrode

C.3 Results and Discussion

C.3.1 Without H_2S

Hydrogen ion (H⁺) exist in the aqueous solution all the time, so the reduction of H⁺ occurs for every case. To differentiate H_2S reduction from the H⁺ reduction reaction, the electrochemical kinetics of H⁺ reduction were investigated first.

When pH is increased by 1 unit, the charge transfer current for H^+ reduction decreased approximately 3 times (calculated based the current density value at -0.5 V in the graph) and the limiting current decreased by a factor of 10. The Tafel slope is close to 120 mV/decade. These results agreed well with the finding of both Bockris, *et al.* [27] and Stern, *et al.* [39].



Figure 115. Comparison of the cathodic sweeps obtained on 316L stainless steel (316L) at various pH, 30°C, pH 4.0, 1 wt% NaCl aqueous solution saturated with N_2 , RCE rotating speed 1,000 rpm.

C.3.2 With H_2S

Figure 116, Figure 117 and Figure 118 show comparison of cathodic potentiodynamic sweeps at different pH₂S (0, 0.1bar) and different pH (pH 4.0 to pH 6.0). The increase of pH₂S can enhance the limiting current at pH 4.0, pH 5.0, and pH 6.0, but the charge current density was observed to increase with pH₂S increase only at pH 6.0. This is because the dominant cathodic reaction at pH 4.0 and pH 5.0 is H⁺ reduction. The Tafel slope for H₂S reduction is close to 120 mv/decade, which is little different from the 150 mV/decade reported in recent literature[108].



Figure 116. Comparison of the cathodic sweeps obtained on 316L stainless steel (316L) in the 1 wt% NaCl aqueous solution saturated with different gas concentration of H_2S/N_2 , 30°C, pH 4.0, , RCE rotating speed 1,000 rpm.



Figure 117. Comparison of the cathodic sweeps obtained on 316L stainless steel (316L) in the 1 wt% NaCl aqueous solution saturated with different gas concentration of H_2S/N_2 , 30°C, pH 5.0, RCE rotating speed 1,000 rpm.



Figure 118. Comparison of the cathodic sweeps obtained on 316L stainless steel (316L) in the 1 wt% NaCl aqueous solution saturated with different gas concentration of H_2S/N_2 , 30°C, pH 6.0, RCE rotating speed 1,000 rpm.

C.3 Model

The modelling process is the similar with the process in Chapter 4. The different is that anodic reaction is not considered.

Figure 119-Figure 122 show a comparison between experimental and predicted sweeps at different bulk pH, without H_2S (Figure 119) and with H_2S (Figure 120 to Figure 122). The model predicted sweeps show a good agreement with the experimental data at these conditions.



Figure 119. Comparison of experimental (solid lines) and predicted sweeps (dashed lines), at 30 $^{\circ}$ C, 1 bar total pressure, 1 wt% NaCl solution saturated with N₂, 316 Stainless Steel, RCE rotating speed 1,000 rpm.



Figure 120. Comparison of experimental (solid lines) and predicted sweeps (dashed lines), at pH 4.0, 30 °C, 1 bar total pressure, 1 wt% NaCl solution saturated with different gas concentration of H_2S/N_2 , 316 Stainless Steel, RCE rotating speed 1,000 rpm.



Figure 121. Comparison of experimental (solid lines) and predicted sweeps (dashed lines), at pH 5.0, 30 $^{\circ}$ C, 1 bar total pressure, 1 wt% NaCl solution saturated with different gas concentration of H₂S/N₂, 316 Stainless Steel, RCE rotating speed 1,000 rpm.



Figure 122. Comparison of experimental (solid lines) and predicted sweeps (dashed lines), at pH 6.0, 30 °C, 1 bar total pressure, 1 wt% NaCl solution saturated with different gas concentration of H_2S/N_2 , 316 Stainless Steel, RCE rotating speed 1,000 rpm.

C.4 Summary

Direct reduction of H_2S in an aqueous system has been proven. The reaction rate of direct H_2S reduction increases with the increase in H_2S concentration. The reaction order with H_2S concentration is obtained. The Tafel slope is close to 120 mV/decade at 30 °C.

A simple electrochemical model, accounting for mass transfer resistance and charger transfer resistance, was developed which shows very good agreement with experimental data and data from the literature.

Appendix D: Determination of Mass Transfer Coefficients for Turbulent Flows Induced by a Magnetic Stirrer

D.1. Introduction

Several correlations have been used to predict liquid mass transfer coefficients for the corrosion study. For example, Eisenberg, *et al.* have developed a correlation for the mass transfer coefficient in RCE:

$$Sh = 0.0791 \times Re^{0.7} \times Sc^{0.356} \tag{70}$$

The one in turbulent single phase pipe flow was calculated by straight pipe correlation of Berger and Hau *et al.* [131].

$$Sh = 0.0165 \times Re^{0.86} \times Sc^{0.33} \tag{108}$$

In the studying of the effect of iron sulfide layer growth on the corrosion process in Chapter 6, a magnetic stirrer at the bottom was used to simulated flow condition instead of Rotating Cylinder Electrode (RCE). Therefore, the mass transfer coefficients for turbulent flows induce by a magnetic stirrer need to be determined. A mixture of potassium ferro-ferricyanide in the bulk presence of sodium hydroxide is the best and most suitable electrolyte for mass transfer studies, but the ferricyanide is a poison and H⁺ is the most common species in the corrosion study. For this reason, a deaerated strong acid solution (pH 4.0) was select as the electrolyte for mass transfer studies. The following reactions will occur in this system:

$$2\mathrm{H}^{+}_{(\mathrm{aq})} + 2\mathrm{e}^{-} \to \mathrm{H}_{2(\mathrm{g})} \tag{28}$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + OH_{(aq)}^-$$
 (30)

D.2. Experimental set-up

A typical three-electrode electrochemical cell setup was used as Figure 123 shows. The reference electrode is the saturated Ag/AgCl electrode and the counter electrode is a platinum ring. A cylindrical 316L stainless RCE electrode was utilized as the working electrode (12 mm in diameter and 15 mm in height). The potentiodynamic sweep was conducted from below OCP at scan rate of 1 mV/s.



Figure 123. Scheme of the test cell, courtesy of Cody Shafer.

The test matrix is shown in Table 18. The flow was created by a magnetic stirrer at the bottom of the glass-cell with the controlled speed varied from 100 rpm to 600 rpm.

Consequently, changing the Re number. The temperature is changed from 30 °C to 80 °C, thus changing the Sc number.

Material	316L stainless steel	
Temperature	30 °C , 60 °C, 80 °C	
Total Pressure (N ₂)	1 bar	
Test Solution	Deaerated acid 1 wt.% NaCl solution	
	(pH 4.0)	
Controlled stirring rate	100, 200, 400, 600 rpm	
Electrochemical Technique	Potentiodynamic Sweep	
-		

Table 18. Test matrix for determination of mass transfer coefficients

D.3. Results and discussion

D.3.1 Potentiodynamic sweep at various stirring rate

Figure 124 shows results of potentiodynamic sweep for various controlled speed range from 100 rpm to 600 rpm stirring rate with pH 4.0 solutions at 30°C. The charge transfer current is insensitive to the change of the stirring rate. The mass transfer limit current increase as the stirring rate increased. Similar behavior was observed at the different temperature, 60 °C and 80 °C as shown in Figure 125 and Figure 126. The mass transfer limited current density, which is used to calculate the mass transfer coefficient, can be extracted from the potentiodynamic sweep as illustrated in Figure 124 (The red dash arrow lines are the limiting current density at different stirring speed).



Figure 124. Potentiodynamic sweep for various controlled speed at 30 °C at pH 4.0, 1 wt.% NaCl solution.



Figure 125. Potentiodynamic sweep for various controlled speed at 60 °C at pH 4.0, 1 wt% NaCl solution



Figure 126. Potentiodynamic sweep for various controlled speed at 80 °C at pH 4.0, 1 wt% NaCl solution

D.3.2 Determination of Mass Transfer Correlation

The measured current density from the potentiodynamic sweep is equal to the mass transfer flux of the electrochemical active specie through the concentration boundary layer to the electrode surface. Based on Faraday's law, the average mass transfer flux (N) to the electrode is given by

$$N = \frac{\iota_{\rm lim}}{nF} \tag{139}$$

Where	$i_{\rm lim}$	The limiting current density (A/m^2)
	n	The number of mols of electrons involved in oxidizing/reducing a
		mol of active species (mol _e /mol)
	F	Faraday's constant, 96485 (C/mol _e)

Mass transfer coefficient can be expressed by the following equation.

$$N = k_m (C_b - C_s) \tag{140}$$

Where

surface (mol/m^3)

 k_m mass transfer coefficient ((m/s) C_b the concentration of electrochemical active species in the bulk solution (mol/m³) C_s the concentration of electrochemical active species at the steel

Hence, the mass transfer coefficient, $k_{\rm m}$ can be easily calculated if the values of $i_{\rm lim}$, $C_{\rm b}$ and $C_{\rm S}$ are known.

$$k_m = \frac{i_{\lim}}{nF(C_b - C_s)} \tag{141}$$

Among these three parameter, i_{lim} and C_b are easy to obtain, C_S cannot be measured easily. However, under the diffusion control, the value of C_S is virtually zero. The mass transfer coefficient can be obtained via this way.

Once the mass transfer coefficient can be obtained from experimental results of potential dynamic sweep and the bulk concentration of H⁺ ions, the Sherwood number, Reynolds number, and Schmidt number can also be calculated by respectively based on the experimental condition.

$$Sh = \frac{k_m L}{D_{H^+}} \tag{142}$$

$$Re = \frac{\rho uL}{\mu} \tag{143}$$

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$$Sc = \frac{\mu}{\rho D_{H^+}} \tag{144}$$

Where	$k_{\rm m}$	the mass transfer coefficient (m/s)	
	D_{H^+}	Diffusion coefficient of H^+ ion (m^2/s)	
	L	Characteristic length, here is the diameter of the stirring bar (m)	
	u	The peripheral velocity of the stir bar (m/s)	
	μ	The dynamic viscosity $(kg/(m \cdot s))$	
	ho	The density of water solution (kg/m^3)	

The calculated process of diffusion coefficient of H^+ ion, water density, water viscosity can be given in the section 4.4.2 (H^+ reduction). Accordingly, Sherwood number (*Sh*), Reynolds number (*Re*), and Schmidt number(*Sc*) can be obtained respectively from experimental results.

In other hand, the Sherwood number, Reynolds number, and Schmidt number usually have an empirical relationship:

$$Sh = aRe^b Sc^c \tag{145}$$

Taking the logarithm on both sides of Equation (145), it will transform to a linear equation:

$$logSh = log(a) + blog(Re) + clog(Sc)$$
(146)

Base on the experimental results, *Sh*, *Re* and *Sc* are known. A multiple linear regression method can be applied to get the constant value of a, b and c. Finally the mass

transfer correlation for turbulent flows induced by a magnetic stirrer is developed as follows:

$$Sh = 1.482Re^{0.551}Sc^{0.191} \tag{109}$$

D.3. Summary

An empirical mass transfer correlation for turbulent flows induced by a magnetic stirrer was developed. The mass transfer coefficient of different species in this type experimental set-up can be calculated based on this empirical correlation.

Appendix E: Additional Surface Analysis of Carbon Steel in Chapter 6

In Chapter 6, total new 4 tests were performed, as listed in Table 19. Additional surface analyses of samples are illustrated in this section.

Run	рН	Magnetic Stirring rate
1	4	600
2	4	60
3	5	600
4	5	60

*The other conditions are the same:1 wt% NaCl sol, 80 °C, 10% H_2S/N_2 , 1 bar total pressure

Run #1: pH 4.0, 600rpm stirring rate, 80 °C

After 1 day



Figure 127. EDS analysis on corrosion product after 1 day corrosion, showing the composition of Fe, S, C element. Conditions: pH 4, 600rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .



Figure 128. XRD analysis of surface corrosion products after 1 day corrosion, showing mostly $FeC_{3.}$ Conditions: pH 4.0, 600rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H₂S, balance N₂.

After 7 day



Figure 129. EDS analysis on corrosion product after 7 days corrosion, showing the composition of Fe, S, C, and O element. Conditions: pH 4.0, 600rpm stirring rate, 1 wt% NaCl solution, 80 °C, 0.054 bar H_2S , balance N_2 .



Figure 130. XRD analysis of surface corrosion products after 7 days corrosion, showing iron carbide, Mackinawite, Troilite. Conditions: pH 4.0, 600rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .

After 1 day



Figure 131. EDS analysis on corrosion product after 1 day corrosion, showing the composition of Fe, S, C, and O elements. Conditions: pH 5.0, 600rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .



Figure 132. XRD analysis of surface corrosion products after 1 day corrosion, showing mackinawite. Conditions: pH 5.0, 600rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .

After 7 days



Figure 133. EDS analysis on corrosion product after 7 days corrosion, showing the composition of Fe, S, C, and O elements. Conditions: pH 5.0, 600rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .



Figure 134. XRD analysis of surface corrosion products after 7 days corrosion, showing iron carbide and mackinawite. Conditions: pH 5.0, 600rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .

Total day Quantization (Day Matrix Correction: ZAF Element Ut% At% CK 2.97 9.97 OK 1.58 3.95 FeK 61.69 44.13

after 6 days

Figure 135. EDS analysis on corrosion product after 6 days corrosion, showing the composition of Fe, S, C, and O elements. Conditions: pH 4.0, 60rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .



Figure 136. XRD analysis of surface corrosion products after 6 days corrosion, showing iron carbide, mackinawite and pyrrhotite. Conditions: pH 4.0, 60rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .

after 6 days



Figure 137. EDS analysis on corrosion product after 6 days corrosion, showing the composition of Fe, S, C, and O elements. Conditions: pH 5.0, 60rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .



Figure 138. XRD analysis of surface corrosion products after 6 days corrosion, showing mackinawite. Conditions: pH 5.0, 60rpm stirring rate, 80 °C, 1 wt% NaCl solution, 0.054 bar H_2S , balance N_2 .

Appendix F: The Mathematical Derivations for the Model in Chapter 7

The mathematical derivation for the electrochemical corrosion model in section 7.3.2 without corrosion product layer is shown here.

For minor species (10 species and 10 equations):

$$(F1) \frac{\partial c_{H_{-,s}}}{\partial t} = 0 = -\frac{i_{H_{+}}}{F} + k_{m_{-}H_{+}}(c_{H_{+,s}} - c_{H_{+,s}}) + \Delta x \bullet (k_{t_{-}H2S}c_{H_{2,S},s} - k_{b_{-}H2S}c_{H_{2,s},s} + k_{t_{-}HS}c_{H_{2,s},s} - k_{b_{-}HS}c_{H_{1,s},s}c_{S^{2,-},s} + k_{t_{-}Wa}c_{HAc,s} - k_{b_{-}HAc}c_{HA,c_,s} - k_{b_{-}HAc}c_{H_{1,s},s}c_{Ac_,s})$$

$$(F2) \frac{\partial c_{O_{-,s}}}{\partial t} = 0 = \frac{i_{H2D}}{F} + k_{m_{-}OH}(c_{OH_{-,b}} - C_{OH_{-,s}}) + \Delta x \bullet (k_{t_{-}Wa} - k_{b_{-}Wa}c_{H_{-,s}}c_{H_{-,s}})$$

$$(F3) \frac{\partial c_{H2,s,s}}{\partial t} = 0 = -\frac{i_{H2S}}{F} + k_{m_{-}H2S}(c_{H2S,-b} - c_{H2S,-s}) + \Delta x \bullet (k_{t_{-}H2S}c_{H_{2,S},s} + k_{b_{-}H2S}c_{H_{-,s}}c_{H_{-,s}})$$

$$(F4) \frac{\partial c_{HS^{-,s}}}{\partial t} = 0 = \frac{i_{H2S}}{F} + k_{m_{-}H2S}(c_{H2S,-b} - c_{H2S,-s}) + \Delta x \bullet (k_{t_{-}H2S}c_{H_{2,S},s} - k_{b_{-}H2S}c_{H_{-,s}}c_{H_{-,s}}c_{H_{-,s}})$$

$$(F4) \frac{\partial c_{HS^{-,s}}}{\partial t} = 0 = \frac{i_{H2S}}{F} + k_{m_{-}HS}(c_{HS^{-,b}} - c_{HS^{-,s}}) + \Delta x \bullet (k_{t_{-}H2S}c_{H_{2,S},s} - k_{b_{-}H2S}c_{H_{-,s}}c_{H_{-$$

Here, "s" represents surface, means the species concentration in the steel surface water layer. "b" represents bulk, means the species concentration in the bulk solution. k_{m_j} is the mass transfer coefficient of each specie. i_j is the current density of each electrochemical reaction

For major species (2 species, 2 equations):

$$(F11)\frac{\partial c_{Na^{+}_{-}s}}{\partial t} = 0 = k_{m_{-}Na^{+}}(c_{Na^{+}_{-}b} - C_{Na^{+}_{-}s}) + k_{m_{-}Na^{+}}\frac{F}{RT}c_{Na^{+}_{-}b}\Delta\Phi$$

$$(F12)\frac{\partial c_{Cl^{-}_{-}s}}{\partial t} = 0 = k_{m_{-}Cl^{-}}(c_{Cl^{-}_{-}b} - C_{Cl^{-}_{-}s}) - k_{m_{-}Cl^{-}}\frac{F}{RT}c_{Cl^{-}_{-}b}\Delta\Phi$$

Electroneutrality equation:

$$(F13)c_{H^{+}_s} + c_{Fe^{2+}_s} + c_{Na^{+}_s} = c_{OH^{-}_s} + c_{HS^{-}_s} + c_{S^{2-}_s} + c_{HCO3^{-}_s} + c_{CO3^{2-}_s} + c_{CI^{-}_s}$$

There are 13 equations and 13 unknowns.

The equations for the minor species are independent from the equations for the major species and the electroneutrality equation. The first step should be to solve the equations for the concentrations of the minor species (10 equations and 10 unknows).

The numerical technique introduced in Chapter 7 is used here.

For the sulfide species (H₂S, HS⁻, and S²⁻), three mass conservation equations become one mass conservation equation for total sulfide species and two more chemical equilibria equations. Equation (F3), (F4), (F5) become

$$(F3')0 = k_{m_{H2S}}(c_{H2S_{b}} - c_{H2S_{s}}) + k_{m_{HS}}(c_{HS^{-}_{b}} - c_{HS^{-}_{s}}) + k_{m_{S}^{2-}}(c_{S2^{-}_{b}} - c_{S^{2-}_{s}})$$

$$(F4')c_{H+_{s}} * c_{HS^{-}_{s}} = K_{hs} * c_{H_{2}S_{s}}$$

$$(F5')c_{H+_{s}} * c_{S^{2-}_{s}} = K_{bs} * c_{H+_{s}}$$

For carbon species (aqueous CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-}), Equation (F6), (F7), (F8), (F9) become

$$(F6)0 = k_{m_{cO_{2}}} (c_{CO_{2}_{b}} - c_{CO_{2}_{s}}) - k_{f_{b}} c_{CO_{2}_{s}} + k_{b_{b}} c_{H_{2}CO_{3}_{s}}$$

$$(F7')k_{m_{c}} + k_{2}CO_{3}} (c_{H_{2}CO_{3}_{b}} - c_{H_{2}CO_{3}_{s}}) + k_{m_{c}} + k_{CO_{3}^{-}} (c_{HCO_{3}^{-}_{b}} - c_{HCO_{3}^{-}_{s}}) + k_{m_{c}} - c_{CO_{3}^{2^{-}}_{s}})$$

$$+ k_{m_{c}} - c_{CO_{2}_{b}} - c_{CO_{2}_{s}}) = 0$$

$$(F8')c_{H^{+}_{s}} * c_{HCO_{3}^{-}_{s}} = K_{ca} c_{H_{2}CO_{3}_{s}}$$

$$(F9')c_{H^{+}_{s}} * c_{CO_{3}^{2^{-}}_{s}} = K_{bi} c_{HCO_{3}^{-}_{s}}$$

For H⁺ and OH⁻ species, 2 mass conservation equations become 2 new equations

$$(F1')0 = -(i_{H^+} + i_{H_2S} + i_{H_2O} + i_{H_2CO_3})/F + k_{m_-H^+} \left(c_{H^+_-b} - c_{H^+_-s}\right) + k_{m_-H_2S} \left(c_{H_2S_-b} - c_{H_2S_-s}\right) - k_{m_-S^{2-}}(c_{S^{2-}_-b} - c_{S^{2-}_-s}) - k_{m_-CO_3^{2-}_-b} + k_{m$$

For Fe²⁺ species, the mass conservation equation does not change.

Therefore, 10 mass conservation equations for the minor species will become 10 news equations as follows:

$$(F1')0 = -(i_{H'} + i_{H_2S} + i_{H_2O} + i_{H_2CO3})/F + k_{m_{-H'}} (c_{H'_{-b}} - c_{H'_{-s}}) + k_{m_{-H_2S}} (c_{H_{2S_{-b}}} - c_{H_2S_{-s}}) - k_{m_{-S}^{2-}} (c_{S^{2-}_{-b}} - c_{S^{2-}_{-s}}) - k_{m_{-S}^{2-}} (c_{S^{2-}_{-b}} - c_{H_2S_{-s}}) + k_{m_{-CO_2}} (c_{CO_2^{-b}} - c_{CO_2^{-b}}) + k_{m_{-CO_2}} (c_{CO_2^{-b}} - c_{CO_2^{-b}}) + k_{m_{-CO_2}} (c_{CO_2^{-b}} - c_{CO_2^{-b}}) + k_{m_{-CO_2}} (c_{CO_2^{-b}} - c_{CO_2^{-s}}) + k_{m_{-CO_2^{-s}}} (c_{CO_2^{-s}} - c_{CO_2^{-s}})$$

The bisection method is used to seek the solution. First, a $c_{H^+_{-s}}$ value is guessed. The Equations from (F2') to (F10) will become linear equations and it is easy to get the concentration of other species. Then the solutions from (F2') to (F10) are substituted to Equation (F1') to see if the solutions satisfy the equation. If not, a new $c_{H^+_{-s}}$ value will be guessed using the bisection method. The process is performed iteratively until a $c_{H^+_{-s}}$ value can satisfy all the equations.

After the concentration of the minor species are obtained. The concentration for major species (c_{Na^+} , and c_{Cl^-}) and potential gradient ($\Delta \Phi$) can calculated easily from Equations (F11) to (F13)



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