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A revision of mechanistic modeling of mild steel corrosion in H_2S environments



Payman Sharifi Abdar, Mohiedin Bagheri Hariri, Aria Kahyarian*, Srdjan Nesic

Department of Chemical and Biomedical Engineering, Institute for Corrosion and Multiphase flow Technology, Ohio University, Athens, OH 45701, USA

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In this study, a predictive model for the corrosion rate and the polarization response of bare steel in aqueous hydrogen sulfide (H_2S) environments based on H_2S dissociation and its buffering effect was developed. In this model, the hydrogen ion reduction is the only cathodic reaction. The results confirmed that the increased limiting cathodic current densities and the characteristic "double wave" behavior in the cathodic current of this system could be explained by hydrogen sulfide dissociation in the vicinity of the metal surface. The effect of hydrogen sulfide on the rate of iron dissolution reactions, parallel to the acidic iron dissolution reaction. The developed model was shown to be able to reasonably represent the characteristic electrochemical behavior of this system. Furthermore, the predicted corrosion rates are shown to be in good agreement with the available experimental data in the literature over a wide range of conditions.

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1. Introduction

The deleterious effects of even a small amount of aqueous hydrogen sulfide $(H_2S)^1$ on the oil and gas transmission pipelines made from mild steel have been a driving force for numerous investigations over the past decades. However, the detailed mechanisms of H₂S corrosion of steel have been studied systematically only in more recent years [1–7]. In addition to the complexities arising from the homogeneous chemical reactions in the presence of H₂S, the formation of corrosion product layer made up of various iron sulfides with different physiochemical characteristics, have made the understanding of the mechanism of mild steel corrosion in aqueous H₂S environments a challenging objective. To make things more complicated, some iron sulfide crystal structures found in the corrosion product layer, i.e., pyrite, pyrrhotite, are semi-conductive [8]. It was suggested that the galvanic coupling between mild steel and iron sulfide layer could lead to severe localized corrosion [9–12]. Within this context, the modeling and the prediction of the corrosion rate in H₂S environment are crucial aspects of the pipeline design and the development of mitigation strategies in sour environments. The present study is an effort to incorporate the latest mechanistic understandings of mild steel

corrosion in the presence of H_2S into a comprehensive mechanistic model for corrosion rate prediction in such systems.

A number of corrosion rate predictive models for sour systems have been developed over the years. In 2009, Sun and Nesic proposed the first mathematical model to predict the corrosion rate of mild steel in H₂S-containing environments in the presence of the iron sulfide corrosion layer [2]. In this model, the authors assumed the protective iron sulfide layer with a known porosity and thickness is always present on the metal surface. The corrosion rate was, therefore, obtained by calculating the mass-transfer controlled corrosion current through the iron sulfide layer. This model could reasonably predict the corrosion rate in the conditions it was developed for; nonetheless, the lack of proper representation of electrochemical reaction kinetics, limited its validity range, particularly in marginally sour systems.

In a more recent study, Zheng et al. developed a mechanistic mathematical model for bare steel corrosion in H_2S containing solutions [13], where the electrochemical reactions were taken into account alongside the mass transfer processes. This study covers the influence of the experimental conditions such as pH, velocity, temperature, and partial pressure of H_2S up to 0.1 bar on the corrosion rate of mild steel during H_2S corrosion [13]. For cathodic current calculations, in addition to the hydrogen ion reduction reaction, the authors introduced an additional electrochemical reaction – direct reduction of H_2S – while the effect of the chemical dissociation of H_2S was not considered. This assumption was mainly based on the observation of two cathodic limiting currents

^{*} Corresponding author.

E-mail address: ak702711@ohio.edu (A. Kahyarian).

¹ These types of aqueous H_2S environments are commonly referred to as "sour" in contrast to aqueous CO_2 environments that are called "sweet".

in polarization data at certain conditions, associated with the hydrogen ion reduction and direct H_2S reduction. For the anodic region, it was argued that the HS⁻ intermediate species are dominating the iron dissolution mechanism, and the contribution of iron oxidation through the acidic dissolution mechanism was assumed negligible in the presence of H_2S . Later on, Zheng et al. modified their model to predict the corrosion rate of mild steel with a corrosion layer formed at the surface in the H_2S/CO_2 mixture [4,5]. In another study, Esmaeely et al. investigated the corrosion of mild steel at acidic solutions with pH_2S partial pressures extended up to 1 bar. The authors also used the same modeling approach as Zheng et al. to quantify their experimental data in this extended range of pH_2S [14,15].

In 2019, Nesic et al. laid out a detailed description of a comprehensive mechanistic model of mild steel corrosion in oil and gas transmission pipelines (MulticorpTM) [16]. This model accounted for the major corrosion environments, including sour corrosion, and also incorporated the effect of iron sulfides corrosion product layer. The contribution of the direct reduction of H₂S on the cathodic current was still assumed to be substantial. In addition, the rate of iron dissolution was simplified due to the lack of adequate understanding of anodic reaction in H₂S-containing solutions. The crystallization and growth of the iron sulfides layer were mechanistically calculated in this model. The authors offered a comparison of the model prediction with the selected experimental results from the existing database at the Institute for Corrosion and Multiphase flow Technology (ICMT), where a generally good agreement was found [16].

However, in a recent mechanistic study, Kahyarian and Nesic showed that the direct reduction of H₂S during the corrosion process is, in fact, insignificant [17]. The authors argued that the hydrogen ion reduction is the sole cathodic reaction in H₂S corrosion of mild steel. The contribution of H₂S to the corrosion process was shown to be through its chemical dissociation inside the boundary layer, leading to the observation of increased limiting currents and, in certain conditions, a secondary limiting current [17]. With this new development in mechanistic understanding of H₂S corrosion of mild steel, it can be argued that the existing models referred to above are now known to be based on an inaccurate mechanistic view of the system. The present study aims to provide an updated corrosion rate predictive model for the corrosion of mild steel in aqueous H₂S solutions based on the recent developments in mechanistic understandings of this system. In this attempt, the new model was developed based on hydrogen ion reaction as the sole cathodic reaction, while accounting for the buffering effect of H₂S. Moreover, the influence of the presence of H₂S on anodic iron dissolution reaction was introduced by adding a reaction pathway parallel to the acidic iron dissolution reaction. In the following sections, the details of the underlying physicochemical processes and the relevant mathematical relationships are laid out. Furthermore, the results of this model are compared with experimental polarization data and corrosion rate data found in the open literature.

2. Theoretical background

2.1. Water chemistry

The corrosion of mild steel in H_2S environments can be seen as a sequence of reactions starting with the dissolution of H_2S gas in water, according to Reaction (1). Aqueous H_2S , as a weak diprotic acid, partially dissociates to HS^- and H^+ ions, as shown via Reaction (2), followed by the dissociation of HS^- to H^+ and S^{2-} according to Reaction (3). In addition to reactions associated with H_2S , water as the solvent also partially dissociates according to Reaction (4). Reactions (1) through (4) result in the formation of an acidic, corrosive solution, buffered with undissociated aqueous H₂S.

$$H_2 S_{(g)} \rightleftharpoons H_2 S_{(aq)} \tag{1}$$

$$H_2S_{(aq)} \rightleftharpoons HS^-_{(aq)} + H^+_{(aq)}$$
⁽²⁾

$$HS^{-}_{(aq)} \rightleftharpoons S^{2-}_{(aq)} + H^{+}_{(aq)}$$
(3)

$$H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + H^+_{(aq)} \tag{4}$$

The solution speciation in the presence of H_2S can be obtained based on the chemical equilibria in the solution, as discussed in more detail elsewhere [17]. The concentration of aqueous H_2S can be described based on Henry's law, assuming an ideal solution and gas phase:

$$H_{H_2S} = \frac{C_{H_2S_{(aq)}}}{p_{H_2S_{(q)}}}$$
(5)

where H_{H_2S} (M.bar⁻¹) is the Henry constant of H_2S and can be calculated from Table 1. $C_{H_2S_{(aq)}}$ is the concentration of dissolved H_2S (M), and $p_{H_2S_{(g)}}$ (bar) is the partial pressure of H_2S gas. The chemical equilibria for H_2S dissociation, Reactions (2) and (3), can be expressed as Eqs. (6) and (7), respectively. Here the concentrations of all the species are shown as C_i (M). Also, K_{H_2S} and K_{HS^-} are the equilibrium constants of Reactions (2) and (3), respectively, as shown in Table 1.

$$K_{H_2S} = \frac{C_{HS^-(aq)}C_{H^+(aq)}}{C_{H_2S_{(aq)}}}$$
(6)

$$K_{HS^{-}} = \frac{C_{S^{2-}(aq)}C_{H^{+}(aq)}}{C_{HS^{-}(aq)}}$$
(7)

The chemical equilibria of water dissociation (Reaction (4)) can be expressed by Eq. (8) in which K_w is the equilibrium constant as noted in Table 1.

$$K_{W} = C_{H^{+}_{(aq)}} C_{OH^{-}_{(aq)}}$$
(8)

The solution speciation can be obtained by solving the chemical equilibria equations shown above, along with the electro-neutrality equation (Eq. (9)).

$$\sum_{i} z_i C_i = 0 \tag{9}$$

An example of one such calculation is shown in Fig. 1, where the concentrations of $H_2S_{(aq)}$, $HS^{-}_{(aq)}$, and $S^{2-}_{(aq)}$ are calculated in mildly acidic pH range at 30 °C for constant pH₂S of 0.1 and 1 bar.



Fig. 1. The pH dependence of H_2S/H_2O system speciation at 30 °C, for 1 bar H_2S (solid lines), and 0.1 bar H_2S (dashed lines).

Table 1

The equilibrium and kinetic rate constants for the reactions in H₂O/ H₂S system.

Parameter	Reference
* $H_{H_2S} = (10^{-3}\rho_W) \ 10^{-(b_1+b_2-T+b_3-T^2+b_4)} T^{+b_5\log(T))} (M.bar^{-1})$ by $= 6.343 \times 10^2 \ b_2 = 2.709 \times 10^{-1} \ b_2 = -1.113 \times 10^{-4}$	[18]
$b_1 = 0.343 \times 10^{-1}, b_2 = 2.763 \times 10^{-1}, b_3 = -1.113 \times 10^{-1}, b_4 = -1.6719 \times 10^4, b_5 = -2.619 \times 10^2$	
* $K_{H_2S} = (10^{-3}\rho_w) \ 10^{(c_1+c_2 T+c_3 T^2+C_4)} T^{+c_5 \ln(T))}$ (M)	[19]
$c_1 = 7.8243945 \times 10^2, \ c_2 = \ 3.61261 \times 10^{-1}, c_3 = \ -1.6722 \times 10^{-4},$	
$c_4 = -2.05657315 \times 10^4, c_5 = -1.42741722 \times 10^2$	
$K_{HS^-} = 10^{-17.4}$ (M)	[20]
${}^{*} K_{w} = (10^{-3} \rho_{w})^{2} \ 10^{(a1 + \frac{a2}{T} + \frac{a3}{T^{2}} + \frac{a4}{T^{3}} + (a5 + \frac{a6}{T} + \frac{a7}{T^{2}}) \log(10^{-3} \rho_{w}))} $ (M ²)	[21]
$a_1 = -4.098, a_2 = -3.2452 \times 10^3, a_3 = 2.2362 \times 10^5, a_4 = -3.984 \times 10^7$	
$a_5 = 1.3957 \times 10^1, a_6 = -1.2623 \times 10^3, a_7 = 8.5641 \times 10^5$	
$k_{b,H_2S} = 7.5 \times 10^{11} (M^{-1}.s^{-1})$	[17]
$k_{b,HS^-} = 1 \times 10^{11} $ (M ⁻¹ .s ⁻¹)	[17]
$k_{b,w} = 1.4 \times 10^{11}$ (M ⁻¹ .s ⁻¹)	[22,23]

* ρ_w is the density of water (kg.m⁻³).

2.2. Electrochemical reactions

 H_2S corrosion of mild steel, as an electrochemical process, occurs through anodic iron dissolution, Reaction (10) and cathodic hydrogen ion reduction, Reaction (11). The water reduction reaction may also occur at more negative potentials, Reaction (12). A brief review of the developments in mechanistic understanding of both cathodic and anodic reactions involved in mild steel corrosion in the presence of H_2S are discussed in the following sections.

$$Fe \ \Rightarrow \ Fe^{2+} + 2e^{-} \tag{10}$$

$$H^+_{(aq)} + e^- \rightleftharpoons \frac{1}{2} H_{2(g)} \tag{11}$$

$$H_2 O_{(l)} + e^- \Rightarrow \frac{1}{2} H_2_{(g)} + 0 H_{(aq)}^-$$
 (12)

2.2.1. Cathodic reactions

The mechanistic understanding of the cathodic reactions in the presence of H₂S has been evolving significantly over the years [17,24-27]. One of the earliest studies on the mechanism of mild steel corrosion in the presence of H₂S was published by Bolmer in 1965 [28]. In that study, based on the observed increased cathodic currents in the presence of H₂S, the author proposed that the cathodic current attributes to the direct reduction of H₂S in addition to that from hydrogen ion reduction [28]. Later, Wikjord et al. went further to argue that the direct reduction of H₂S is more probable than H^+ reduction due to its high polarizability and absorbability on the iron surface [29]. In another study, Morris et al. investigated the influence of H₂S addition on the carbon steel corrosion rate. It was noted that the cathodic limiting current was increased by the increase of H₂S concentration, while the cathodic current in the charge transfer controlled region remained almost unchanged. The authors interpreted this observation by assuming that H₂S is reduced during cathodic polarization [30]. Such observations and arguments have been frequent in the literature [1,26,27,31-33], albeit without explicit experimental evidence. A systematic experimental investigation of the mechanism of cathodic reactions in this system was only published in more recent years.

In 2013, Kittel et al. examined the effect of H_2S on the cathodic currents in acidic solutions on the surface of stainless steel. A secondary limiting current was observed at higher cathodic potential ranges (in pH of about 4), which was readily associated with the direct reduction of H_2S by the authors [25]. This mechanistic view was then used to develop a mathematical model for the kinetics of the cathodic reaction occurring in H_2S -containing environments. However, the secondary wave in the cathodic region was not thoroughly characterized, and the model could not accurately predict

the behavior of cathodic polarization at higher rotational speeds [24,25]. At about the same time, Zheng et al. published another systematic study on the mechanism of H₂S corrosion on the mild steel surface. The reported experimental cathodic polarization data were in general agreement with those obtained by Kittel et al. [25]. Zheng et al. also reported a similar "double wave" behavior in cathodic polarization curves. The authors demonstrated that the two limiting currents correspond to the mass transfer limitation of H^+ and H₂S from the bulk solution. By attributing these two waves to the reduction of H^+ and the direct reduction of H₂S, they developed a mechanistic model for H₂S corrosion of mild steel, while the chemical dissociation of H₂S inside the boundary layer was not accounted for [13].

Recently, Kahyarian and Nesic re-evaluated the significance of the contribution of the direct reduction of H₂S to cathodic currents [17]. It was shown that the mechanism of cathodic currents in the H₂S containing solutions is similar to those observed in the cases of CO₂ and carboxylic acids [17,34–37]. These weak acids, including H_2S , locally dissociate to buffer the surface H^+ concentration at the vicinity of the metal surface, thus increasing the limiting current, while the direct reduction of the weak acid itself (e.g., H_2S) is in fact insignificant. The unique behavior in the presence of H₂S was shown to be due to its relatively higher pKa (about 7), requiring the surface pH to be at substantially higher values (as compared to acetic acid and carbonic acid) before the dissociation reaction occurs to any appreciable extent. This mechanism behind the observed secondary limiting currents is referred to as the "buffering" effect of H₂S [17]. While less commonly cited, this behavior is not unique to aqueous H₂S. Similar double wave cathodic sweeps are also observed in the presence of bicarbonate ion with pKa of ~11, showing the general validity of this mechanistic view [38,39].

2.2.2. Anodic reactions

The aforementioned studies conducted in recent years elucidated the mechanism of cathodic reaction in aqueous H_2S environments to a large extent; however, very little is known about the exact mechanism of anodic iron dissolution in the presence of dissolved H_2S . The available experimental data are limited, and the mechanistic studies are rather immature [30,40–43]. The early research on the anodic dissolution of iron in the H_2S -containing solutions could be found in a study by lofa and Batrakov in 1965 [43]. lofa et al. observed that the presence of H_2S accelerated the rate of anodic dissolution, thereby shifting the corrosion potential to more negative values. They proposed that the hydrogen sulfide ions form a chemisorbed layer on the surface of the electrode, which acts as a surface catalyst, enhancing the kinetics of iron dissolution reaction [43]. This mechanism is analogous to the well-known "catalytic mechanism" of iron dissolution proposed by Heusler in which Fe²⁺ reacts with hydroxyl ion (OH⁻) to form a catalytic surface compound such as (FeOH)_{ads} [44]. In another study, Morris et al. reported that the increase of H₂S concentration in acidic solution within the pH range of 3-4 shifted the corrosion potential to more negative values. This phenomenon was attributed to the change of reversible potential of iron in the presence of H₂S. Apparently, the Tafel slope of anodic reaction and exchange current density remained unaffected by H₂S presence [30]. In 1980, Shoesmith et al. adopted the hypothesis proposed by Iofa, et al. in order to introduce a mechanism that involves the H₂S chemisorption (Reaction (13)), followed by an oxidation step involving a twoelectron transfer step (Reaction (14)). In this mechanism, depending on the experimental conditions, the produced (FeSH⁺)_{ads} could either convert to a corrosion products layer (Reaction (15), i.e., inhibition effect), or it can further hydrolyze to Fe^{2+} (Reaction (16)) [33].

$$Fe + H_2S + H_2O \rightarrow (FeSH^-)_{ads} + H_3O^+$$
(13)

$$(FeSH^{-})_{ads} \rightarrow (FeSH^{+})_{ads} + 2e^{-}$$
 (14)

$$(FeSH^+)_{ads} \rightarrow FeS_{1-x} + xSH^- + (1-x)H^+$$
(15)

$$(FeSH^+)_{ads} + H_3O^+ \to Fe^{2+} + H_2S + H_2O$$
 (16)

The acceleration effect that dissolved H₂S can have on iron dissolution was further investigated by Cheng et al. using AC electrochemical techniques. It was found that the anodic reaction of iron in H₂S containing acidic solutions is gradually promoted by increasing pH and H₂S concentration (especially when [H₂S]/[H₃O⁺] $< 10^{1.5}$), up to the point that it reaches a maximum and becomes independent of further pH and H₂S increase. This behavior was associated with the high surface coverage of H₂S. The EIS analysis by Cheng et al. gave added support to the model proposed by Shoesmith et al. for anodic dissolution mechanism of iron in H₂S environment, with the exception that Cheng et al. assumed a two-step reaction for anodic dissolution Reaction (14), each step including one-electron transfer [42]. Therefore, the first step of anodic dissolution in sour media was claimed to be the chemisorption of H₂S according to the Reaction (17) followed by several oxidation steps which finally converts (FeSH⁻)_{ads} to Fe²⁺ according to Reactions (18)-(20) [40,42]:

$$Fe + H_2S + H_2O \rightarrow (FeSH^-)_{ads} + H_3O^+$$

$$\tag{17}$$

$$(FeSH^-)_{ads} \rightarrow (FeSH)_{ads} + e^-$$
 (18)

$$(FeSH)_{ads} \rightarrow FeSH^+ + e^-$$
 (19)

$$FeSH^+ + H_3O^+ \to Fe^{2+} + H_2S + H_2O$$
 (20)

This study was accompanied by a series of publications by Ma et al. [40,41,45] through impedance spectroscopy analysis of the effect of H_2S on iron dissolution. The Nyquist plot at the corrosion potential showed two overlapping capacitive loops in highly acidic solutions (pH 0.75 and 2) with 0.4 mmol.L⁻¹ H_2S . The low-frequency loop was marked as the characteristic of H_2S adsorption on the surface of the iron. At higher overpotentials (with respect to corrosion potential), the capacitive loop at lower frequencies, ascribed to H_2S adsorption, gradually disappeared; instead, a low-frequency inductive loop emerged. Hence, Ma et al. concluded that the modified Shoesmith's model is valid at the lower anodic overpotentials where two capacitive loops were observed. However, the replacement of low-frequency capacitive loop by an inductive loop

at higher overpotentials indicates the dominance of Faradaic adsorption, as described by Bockris et al., was a result of Reactions (17) and (18) occurring as a single step described by Reaction (21) [33,40,41,46].

$$Fe + H_2S + H_2O \rightarrow (FeSH)_{ads} + H_3O^+ + e^-$$
 (21)

They also investigated the inhibiting effect of H_2S on iron dissolution and showed that the inhibition effect occurs because of the formation of the iron sulfide film, as shown by Reaction (15), when its formation is thermodynamically favorable (i.e., low H_2S concentration (< 0.04 mmol.L⁻¹), pH value in the range of 3–5, and immersion times longer than 2 h) [45].

Finally, in the study by Zheng et al., they assumed a similar mechanism as proposed by Bockris et al. [46] for iron dissolution in H_2S environments accounting HS^- instead of OH^- . The contribution of OH^- on the kinetics of anodic dissolution of iron in the presence of H_2S was ignored since it was considered negligible compared to that of HS^- . Hence, the exchange current density of iron dissolution was calculated based on the surface coverage by the HS^- species [13].

3. Mathematical modeling

The comprehensive mechanistic mathematical model developed in this study is similar to that presented in more detail in some of the earlier publications, which can be used as further Refs. [17,36]. The model is based on the mathematical solution of mass conservation equations (based on the Nernst-Plank equation) for the involved species inside the diffusion boundary layer, with the surface electrochemical reactions on one end and the bulk speciation on the other, serving as the boundary conditions. The model accounts for the mass transfer processes, including molecular diffusion, electromigration, the turbulent convection, as well as the simultaneously occurring homogeneous chemical reactions and heterogeneous electrochemical reactions.

3.1. The diffusion boundary layer

The rates of electrochemical reactions are evaluated based on the local concentrations of the species at the surface of the metal, which deviate from the bulk concentrations due to the heterogeneous nature of the electrochemical reactions. The mass conservation inside the boundary layer can be expressed by the well-known Nernst-Plank equation, as shown in Eq. (22) [47].

$$\frac{\partial C_i}{\partial t} = -\nabla N_i + R_i \tag{22}$$

In this equation, N_i is the flux of species *i*, represented as Eq. (23), and R_i describes the chemical reactions in which species *i* is either produced or consumed.

$$N_i = -z_i u_i F C_i \nabla \Phi - D_i \nabla C_i + \nu C_i \tag{23}$$

As it is seen in Eq. (23), the flux of species consists of three terms, which represent three mechanisms of mass transfer, namely electromigration, molecular diffusion, and convection. In the electromigration term, *F* is the Faraday's constant and ion *i* with the charge of z_i , and mobility of u_i ($m^2.V^{-1}.s^{-1}$) is driven by an electric field ($\nabla \varphi$) (V.m⁻¹). In the molecular diffusion term, species *i*, with the diffusion coefficient of D_i , is transferred as a result of the concentration gradient (∇C_i). Finally, the convective term accounts for the species *i* with a concentration C_i being carried by the flow with the velocity ν [47].

Noting that the convective term in Eq. (23) represents the velocity of the fluid inside the boundary layer, which can be explicitly known only in some laminar flow regimes such as that seen in the rotating disk electrode apparatus. However, in many

Table 2

Reference diffusion coefficients for different species at infinite dilution and 25 $^\circ\text{C}.$

Species	Diffusion coefficient / (m ² .s ⁻¹)	Reference
H_2S	1.93×10^{-9}	[52]
HS-	1.731×10^{-9}	[53]
S^{2-}	1.5×10^{-9}	[17]
OH-	5.273×10^{-9}	[53]
H^+	9.312×10^{-9}	[47]
Cl-	2.032×10^{-9}	[47,53]
Na^+	1.334×10^{-9}	[47]

cases, including the flow in pipelines as well as in laboratory setups such as rotating cylinder electrode (RCE), the turbulent flow regime is the common condition. In order to represent the effect of turbulent convection in the boundary layer, without resorting to complex computational fluid dynamics (CFD) calculations, one can adopt the eddy diffusivity concept to represent the turbulent convection effect [48]. Here the effect of turbulent convection is represented by a diffusion-like term with eddy diffusivity (D_t) that is a function of fluid properties, flow geometry, and the distance from the metal surface [48,49]. Eq. (23) can, therefore, be reorganized to give Eq. (24).

$$N_i = -z_i u_i F C_i \nabla \Phi - (D_i + D_t) \nabla C_i \tag{24}$$

In corrosion seen, for example, in fully developed pipe flow, only the flux N_i in the direction perpendicular to the metal surface is relevant, which reduces the mathematics Eqs. (22) and ((24)) to a one-dimensional problem, here in x direction. In addition, ion mobility (u_i) in the electromigration term can be replaced by D_i/RT according to Nernst-Einstein relation for ideal solutions. By applying these assumptions and introducing Eq. (24) in Eq. (22), they can be expressed in their final styles as Eqs. (25) and (26).

$$N_{i} = -(D_{i} + D_{t})\frac{\partial C_{i}}{\partial x} - \frac{z_{i}D_{i}FC_{i}}{RT}\frac{\partial \Phi}{\partial x}$$
(25)

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left((D_i + D_t) \frac{\partial C_i}{\partial x} \right) + \left(\frac{z_i D_i F}{RT} \right) \frac{\partial}{\partial x} \left(C_i \frac{\partial \Phi}{\partial x} \right) + R_i$$
(26)

The values of molecular diffusivity (D_i) in the equations above are listed in Table 2. In order to obtain the molecular diffusivity at different temperatures, the Stokes-Einstein relationship, as described in Table 3, can be used [47]. In addition, the eddy diffusivity (D_t) profile inside the diffusion boundary layer of a fully developed turbulent flow can be determined using the empirical Eq. (27) suggested by Arvanith [49]:

$$D_t = \nu \frac{0.0007x^{+3}}{\left[1 + 0.00405x^{+2}\right]^{1/2}}$$
(27)

where $v = \mu/\rho$ is kinematic viscosity (m².s⁻¹) of water and can be found using the equations in Table 3. The x^+ is the dimensionless distance from the wall obtained from Eq. (28). This equation is valid when $x^+ < 30$, and it is universal for all turbulent flow if appropriate dimensionless parameters are implemented.

$$x^{+} = \frac{x \left(\frac{\tau_{w}}{\rho}\right)^{0.5}}{\nu}$$
(28)

In the equation above, *x* is the distance from the wall (m), ρ is the density of water (kg.m⁻³) as defined in Table 3, and τ_w is the wall shear stress (Pa), which for single-phase pipe flow can be obtained from the Fanning friction factor, C_f :

$$\tau_w = \frac{1}{2}\rho C_f V^2 \tag{29}$$

where V is the average fluid velocity (m.s⁻¹). The Fanning friction factor is a function of the Reynolds number. It can be estimated,

for example, by the correlation of Swamee and Jain [50], which is expressed using the Darcy friction factor ($C_f = 4C_d$), represented by Eq. (30). This equation is an explicit version of the implicit Colebrook-White correlation [51].

$$C_d = 0.25 \left[\log \left(\frac{\frac{\mathcal{E}}{D_{eq}}}{3.7} + \frac{5.74}{\text{Re}^{0.9}} \right) \right]^{-2}$$
(30)

Here, ε accounts for the effect of surface roughness on the friction factor, and it is assumed to be zero in the present study (amounting to a hydraulically smooth surface). The Reynolds number is calculated by $Re=V.D_{eq}/v$ with D_{eq} being the equivalent characteristic diameter, which is equal to the pipe diameter.

In Eq. (26) R_i term accounts for the homogenous chemical reactions leading to the production or consumption of each species in the diffusion boundary layer. A chemical reaction j can be shown as Reaction (31) with the reaction rate evaluated by Eq. (32), where k_{fj} , and k_{bj} are the kinetic rate constants of the "forward" and "backward" reactions, respectively. Reactions (2), (3), and (4), i.e., dissociation of H₂S, HS⁻, and water, respectively, are estimated with kinetic rate constants listed in Table 1.

$$\sum_{r=1}^{n_r} C_r \rightleftharpoons \sum_{p=1}^{n_p} C_p \tag{31}$$

$$R_{j} = k_{f,j} \prod_{r=1}^{n_{r}} C_{r} - k_{b,j} \prod_{p=1}^{n_{p}} C_{p}$$
(32)

The rate of reaction R_i , of each species *i*, involved in *j* chemical reactions can be determined using Eq. (33) with s_{ij} being the stoichiometric coefficient of species *i* in reaction *j*.

$$R_i = \sum_i R_i s_{i,j} \tag{33}$$

With all these equations being accounted for, the concentration of each species i in the diffusion boundary layer and at the metal surface can be obtained by solving Eq. (26); in fact, one of those equations is written for each species i and the set of coupled partial differential equations is then simultaneously solved. The only remaining unknown parameter in these equations is the solution potential featured in electromigration term that can be determined by the aid of the electro-neutrality Eq. (9) as an additional independent relationship.

3.2. Initial and boundary conditions

To fully specify the system of partial differential equations discussed in the previous section, appropriate initial and boundary conditions need to be defined. At time zero, one can assume that the well-mixed solution being in equilibrium, comes in contact with the metal surface. Hence, the initial concentrations of all the species inside the boundary layer are known values obtained by solving the chemical equilibria equations.

For the boundary conditions, at the outer edge of the boundary layer ($x = \delta$), the solution can be assumed to remain at equilibrium at all times, with the known and constant values just as is seen in the bulk solution. At the metal surface, the flux of non-electroactive (non-reacting) species is set to zero. The flux of the electro-active species *i* can be defined based on the rate of electrochemical reactions at the metal surface as Eq. (34), where s_i is the stoichiometric coefficient, and other terms have their common electrochemical meaning.

$$N_i|_{x=0} = -\frac{s_i i_i}{nF} \tag{34}$$

In the present model, H^+ reduction is assumed to be the only cathodic reaction, and the iron dissolution is the only anodic reaction. The contribution of water reduction to the cathodic current

Table 3Temperature dependence of physicochemical properties.

Parameter	Relationship	Reference
Diffusion coefficient	$D_i = D_{i,ref} \frac{T}{T_{ref}} \frac{\mu_{ref}}{\mu}$	[47]
Water density / (kg.m ⁻³)	$\rho_{\rm w} = 753.596 + 1.87748 \ T - 0.003562 \ T^2$	[54]
Water viscosity / (cP)	$\mu = \mu_{ref} 10^{(\frac{1.7799}{(T-273.15)+89.93})}$	[55]
	$T_{ref} = 293.15 \ K, \ \mu_{ref} = 1.002 \ cP$	

at the corrosion potential found in acidic solutions can be assumed insignificant and was ignored in the calculations. The metal surface boundary condition for the two electro-active species is then:

$$N_{H^+}|_{x=0} = -\frac{i_{C,H^+}}{F}$$
(35)

$$N_{Fe^{2+}}|_{x=0} = -\frac{i_{A,Fe^{2+}}}{2F}$$
(36)

The cathodic current density associated with H^+ reduction reaction can be described using the standard electrochemical kinetics [17]:

$$i_{C,H^+} = -n_{H^+} F k_{0,H^+} C_{H^+}^{S} {}^{m_{H^+}} \exp\left(\frac{-\alpha_{H^+} n_{H^+} F(E_{app})}{RT}\right)$$
(37)

where $n_{H^+} = 1$ is the number of electrons transferred, k_{0H^+} is the reaction rate constant, $C_{H^+}^S$ is the concentration of H^+ adjacent to the metal surface, m_{H^+} is the reaction order, E_{app} is the applied overpotential, α_{H^+} is the charge transfer coefficient, and *F*, *R*, and *T*, are Faraday's constant, gas constant, and temperature in K, respectively. The values of $k_{0,H^+} = 1.2 \times 10^{-8} \text{ (mol}^{0.5} \text{.m}^{-0.5} \text{.s}^{-1})$ and $m_{H^+} = 0.5$ were obtained based on the best fit of the model to experimental polarization data, which agree with those obtained in earlier publications.

The iron dissolution in acid solutions is a complex electrochemical reaction with numerous elementary steps and intermediate species. However, in the active dissolution range, where a ~40 mV.dec⁻¹ Tafel slope is observed, this reaction is commonly believed to follow the mechanism proposed by Bockris et al. [46]. The rate of iron dissolution in the active dissolution range and in acidic solutions can, therefore, be expressed as:

$$i_{A,OH^{-}} = n_{Fe^{2+}}Fk_{0,OH^{-}}C_{H^{+}}^{S} m_{H^{+}} \exp\left(\frac{\alpha_{j}FE_{app}}{RT}\right)$$
 (38)

where $n_{Fe^{2+}} = 2$ is the number of electrons transferred, k_{0,OH^-} is the reaction rate constant, and other parameters have their common electrochemical meanings.

As discussed earlier in the text, the presence of H_2S in the system has been observed to increase the rate of iron dissolution through a parallel set of electrochemical reactions with various sulfide intermediate species. Such behavior is consistently observed in the existing literature, while the exact governing mechanism and the interaction of sulfide intermediates with hydroxide intermediates are yet to be fully understood. A full discussion of the details of the iron dissolution mechanism in the presence of H_2S is beyond the scope of the present study. Regardless, in order to in some way represent the contribution of H_2S in iron dissolution, as a critical part of H_2S model for the corrosion of mild steel, the rate of this parallel reaction was expressed in the same form as that used for acidic solutions:

$$i_{A,HS^{-}} = n_{Fe^{2+}}Fk_{0,HS^{-}}C^{S}_{HS^{-}} m_{HS^{-}} \exp\left(\frac{\alpha_{j}FE_{app}}{RT}\right)$$
 (39)

where the parameters have a similar meaning as those in Eq. (38). Assuming $\alpha_j = 1$, the values of $k_{0,0H^-} = 10 \pmod{m^{-2}.s^{-1}}$, $m_{H^+} =$



Fig. 2. Simulated anodic polarization curve for various partial pressures of H_2S at 30 $^\circ C$ and pH 4 and 5.

1, $k_{0,HS^-} = 2 \times 10^7 \pmod{0.5.\text{m}^{-0.5}.\text{s}^{-1}}$, and $m_{\text{HS}^-} = 0.5$ are obtained in this study based on the best fit of the model to existing experimental data, and appear to represent the observed behavior reasonably well. By considering this additional pathway for iron dissolution in the presence of H₂S, the rate of anodic reaction $(i_{A,\text{Fe}^{2+}})$ can be calculated as a superposition of two parallel reaction rates $(i_{A,OH^-} \text{ and } i_{A,HS^-})$. As a result, Eq. (36) can be rearranged as Eq. (40):

$$N_{Fe^{2+}}|_{x=0} = -\frac{i_{A,OH^{-}} + i_{A,HS^{-}}}{2F}$$
(40)

Fig. 2 represents an example of the simulation results for the iron dissolution at different partial pressures of H_2S and various pH. The considerable effect of H_2S presence on the kinetics of the anodic reaction is evident, specifically at higher partial pressures of H_2S . At higher partial pressures of H_2S , the rate of the anodic reaction accounting for the contribution of H_2S in iron dissolution, i.e., i_{A,HS^-} , increases thereby enhancing the total anodic current. Fig. 2 shows that the increment of anodic current due to the presence of H_2S is higher in pH 4 compared to that at pH 5. This implies that the contribution of H_2S on the mechanism of anodic dissolution becomes more notable in more acidic environments due to the lower concentrations of OH⁻ in such conditions.

3.3. Numerical solution

Finite different method (FDM) was used to solve a set of coupled and non-linear partial differential equations, as listed in Table 4. The solution algorithm is similar to that discussed in detail in earlier studies [17,36,38]. Taylor's series approximation is used to discretize the partial differential equation. In order to improve the calculation time, a non-uniform spatial grid with a fine mesh at the metal surface was applied [17]. The explicit scheme of time integration is used using Euler approximation. The Newman's "BAND" open-source code algorithm is used to obtain the solution using the LU decomposition approach [47]. Regarding the non-

Table 4

Summary of equations used in the comprehensive mathematical mode	I.
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Electrode surface boundary	
$N_i _{x=0} = -\frac{s_{ij}i_j}{n_j F}$ For electro-active species	for all electro-active species
$N_i _{x=0} = 0$ $\sum z_i C_i = 0$	electro-neutrality equation
Diffusion boundary layer	
$\frac{\frac{\partial L_i}{\partial t}}{\frac{\partial I}{\partial x}} = \frac{\frac{\partial}{\partial x}}{\left(\left(D_i + D_t\right)\frac{\partial L_i}{\partial x}\right) + \frac{Z_i D_i r}{RT}\frac{\partial}{\partial x}\left(C_i\frac{\partial \varphi}{\partial x}\right) + R_i}{\sum_i Z_i C_i = 0}$	for all species electro-neutrality equation
Bulk boundary and initial conditions	
$C_i = C_i^b$	
$\Phi = 0$	

linearity of the system, the solution at each time step is obtained iteratively until the desired accuracy of $R^2 = 10^{-12}$ is achieved (R^2 is the sum of the squared normalized errors for all unknown concentrations being calculated in this model).

4. Results and discussion

In order to confirm the validity of the mathematical model, the predicted results were compared with the experimental data reported in earlier studies by Zheng et al. and Esmaeely et al. [13,15]. These studies provided a systematic experimental investigation on the polarization behavior and corrosion rates of mild steel in H₂S containing acidic solution. A wide range of realistic experimental conditions (pH₂S = 0 - 1 bar, pH = 3 - 5, and flow velocity = 0.22 - 2.5 m.s⁻¹) were examined to validate the accuracy of the model.

The model presented in this study was developed for typical turbulent flow conditions commonly seen in pipes and other conduits. Since the RCE setup is typically used in the laboratory setting, the equivalent conditions were obtained by equating the mass transfer coefficient for RCE (obtained by using the Eisenberg equation [56]) with that for straight flow pipe (proposed by Berger and Hau [57]), to get

$$\nu_{pipe} = 3.09Sc^{0.03}\nu^{0.186}\Omega_{RCF}^{0.814}d_{RCF}^{0.43}d_{PIPF}^{0.163} \tag{41}$$

where v_{pipe} is the equivalent pipe flow velocity (m.s⁻¹), Ω_{RCE} is the angular velocity of RCE (rad.s⁻¹), *d* is the diameter (m), and *Sc* is the Schmidt number.

Fig. 3 shows a comparison between the model (black broken lines) and the experimental cathodic and anodic polarization branches at different H_2S concentrations and fixed pH of 4.



Fig. 3. Cathodic and anodic polarization curves at various partial pressures of H_2S at 30 °C, pH 4, and 1000 rpm RCE (equivalent to 0.81 m.s⁻¹ in pipe flow with 0.012 m ID). The solid lines show the experimental measurements from Zheng et al. [13], and the black dashed lines represent the prediction by model.

The model predictions are in reasonably good agreement with the experimental data for both anodic and cathodic branches. The accuracy of the model is generally better or comparable to the earlier models, even though it is using fewer parameters to predict the polarization behavior of the system. In the cathodic region, the model reproduces the occurrence of the "double-wave" behavior and the magnitude of the corresponding limiting current densities, without having to introduce the additional cathodic reaction (direct reduction of aqueous H₂S). Generally, it is seen that the limiting current densities increase as the H₂S content increases, which agrees well with the expected buffering effect of H₂S in such systems. The increase of H₂S concentration leads to an increased capacity of the solution to further buffer the H^+ concentration at the electrode surface when it is under the diffusion-controlled limiting current regime [17]. It worth noting that a broad "linear" current density range is seen in some conditions, for example, for $pH_2S = 0.1$ bar in Fig. 3. This appears to be similar to what is seen under pure charge transfer control when "linear" Tafel behavior is observed. However, the "linear" section of the cathodic curve seen for $pH_2S = 0.1$ bar in Fig. 3 is not Tafel behavior as the observed cathodic current densities in this potential range are under mass transfer limitation of H^+ . The reason that the cathodic current is able to increase beyond the mass transfer limitation of H^+ , which appears to be in a linear-like fashion, is due to the buffering ability of H₂S through kinetically controlled dissociation reaction. Specifically, for $pH_2S = 0.1$ bar in Fig. 3, the first limiting current associated with the mass transfer limitation for free hydrogen ions occurs at about 2 A.m⁻². At more negative potentials, the current densities increase from 2 A.m⁻² up to about 60 A.m⁻² as a result of the kinetically controlled dissociation of H₂S to give more H^+ , driven by the increasing surface pH. At about 60 A.m⁻², the second limiting current is reached and is associated with the maximum buffering capacity, i.e., when the rate of limit in H₂S dissociation is reached. This also explains why this linear current range is pH₂S dependent. Hence, a shift in the apparent exchange current density and the Tafel slopes is observed experimentally, e.g., by increasing pH₂S from 0.01 to 0.1 bar. This behavior was previously attributed to the direct H_2S reduction reaction [13,24,25]. In the present model, the same behavior is obtained even if the cathodic currents result only from the H^+ reduction while concurrently accounting for the H₂S dissociation at the metal surface. The comparison of the modeling results with the experimental data showed that all significant characteristics of the cathodic sweep are well predicted using this simplified mechanistic view.

In the anodic sweep at pH 4, the effect of H_2S on the rate of iron dissolution is minor up to $pH_2S = 0.1$ bar (seen both in model predictions and experimental data). However, a more prominent effect is observed as the pH_2S increased further up to 1 bar, as shown below in Fig. 4. The increase in the anodic current with higher H_2S is also reported elsewhere [30,41,42], suggesting that H_2S or other sulfide species can introduce parallel anodic path-



Fig. 4. Cathodic and anodic polarization curves for $PH_2S = 0.1$ bar and $PH_2S = 1$ bar at 30 °C, and 1000 rpm RCE (equivalent to 0.81 m.s⁻¹ in pipe flow with 0.012 m ID). A) pH 3, B) pH 4, C) pH 5. The solid lines show the experimental measurements, and the black dashed and dotted lines represents the results predicted by the present model. For $PH_2S = 1$ bar, the error bars represent the minimum and maximum measured values in at least 4 repeated experiments[15]. The data for $PH_2S = 0.1$ bar and $PH_2S = 1$ bar were taken from Zheng et al. [13] and Esmaeely et al. [15], respectively.

ways to the iron dissolution reaction. However, at the conditions of Fig. 3, it appears that the contribution of sulfide species remains minor, and the iron dissolution with hydroxide intermediates, as seen in acidic solutions, remains the dominating mechanism.

Fig. 4 compares the predicted results with the experimental data at the pH range from 3 to 5 for two different H₂S partial pressures of 0.1 and 1 bar. The observed cathodic polarization behavior is in general agreement with that shown in Fig. 3. The presence of double wave, two limiting currents associated with H^+ mass transfer and the buffering effect of H₂S, is seen at pH 3. This distinc-

tive behavior gradually fades away as the pH increases due to the smaller magnitudes of H^+ reduction. Considering that the free H^+ limiting current density (first limiting current) decreases from ~ 20 A.m⁻² at pH 3 to ~ 2 A.m⁻² at pH 4, the limiting current associated with free H^+ reduction at pH 5 is expected to be ~ 0.2 A.m⁻². With such a small value, at the conditions of Fig. 4.C, the free H^+ mass transfer limitation occurs at potentials above open circuit potential and, therefore, cannot be observed. The observed limiting current is then due to the combined effect of both H₂S chemical dissociation and the H₂S mass transfer.

The change in anodic current with pH₂S is more substantial at the H_2S partial pressure of 1 bar shown in Fig. 4, compared to that seen in Fig. 3 for lower H₂S partial pressures. As it was discussed in the previous section, the presence of H₂S is believed to provide a parallel reaction pathway for anodic dissolution reaction. At a fixed pH₂S, such impact is more prominent in the lower pH range due to a slower rate of the iron dissolution via the wellknown Bockris mechanism [46], and a more dominating contribution of sulfide intermediate species through Reactions (17-20) is seen. Overall, the anodic polarization curves obtained by the model agrees reasonably well with the experimental data. At pH 5, the apparent Tafel slope of the anodic reaction slightly differs from that seen in the lower pH range and the calculated results. That could be due to the change in the iron dissolution mechanism as noted in the literature [46]. Additionally, as highlighted earlier, at pH 5 the H^+ limiting current occurs above the open circuit potential. Therefore, the surface pH in this potential range deviates from the bulk values, and it is, to some extent, potential dependent. Such conditions could also lead to the observed deviations from the expected anodic Tafel slopes.

The strength of a given mathematical model is defined by its success in predicting the effects of a wide range of systematically varied parameters. To further evaluate the performance of the mechanistic model developed in this study, the predicted corrosion rate data is compared to those obtained in earlier studies [13–15]. The available experimental data were collected using linear polarization resistance (LPR) measurements, while accounting for the effect of the solution resistance. The experimentally obtained polarization resistance was then used to calculate the corrosion current and the corrosion rate by using Eqs. (42) and (43) [36,58].

$$I_{corr} = \frac{B}{R_p}$$
(42)

$$CR = 1.16 \frac{B}{R_p/A} \tag{43}$$

where I_{corr} and CR are respectively the corrosion current (A) and the corrosion rate in mm.yr⁻¹, *B* is in V, R_p is polarization resistant (ohm), and *A* is the surface area of the electrode (m²).

In the studies by Zheng et al. and Esmaeely et al., the authors used a fixed value of B = 23 mV for all experimental conditions. The value of B, especially where the corrosion potential is under the influence of mass transfer, cannot be assumed constant under different environmental conditions. That could lead to an inaccurate interpretation of the polarization resistance data. The value of B can be estimated with reasonable accuracy by extending the Stern-Geary equations to use the apparent Tafel slopes in place of the Tafel slopes under charge transfer controlled regime. The Stern-Geary equation can be viewed as a simple mathematical linearization of two exponential equations to rationalize if the cathodic and anodic curves at the vicinity of the corrosion potential can be reasonably expressed in an exponential form with some apparent Tafel slopes (irrespective of the underlying reaction mechanism), the value of B can be approximated via Eq. (44) [36,58]:

$$B = \frac{b'_{a}b'_{c}}{2.303(b'+b'_{c})} \tag{44}$$

Table 5

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рН	Equivalent linear velocity (m.s ⁻¹)	pH ₂ S (bar)	Assumed B value (mV)	Corrected B value (mV)	Reported corrosion rate (mm.yr ⁻¹)	Corrosion rate corrected for B value (mm.yr ⁻¹)	Predicted corrosion rate (mm.yr ⁻¹)	Ref.
3	0.81	0.0001	23	13	4.30	2.44	2.02	[13]
3	0.81	0.1	23	13	10.4	5.89	4.10	[13]
3	0.81	1	23	17	8.8	6.65	5.36	[15]
4	0.81	0	23	17	1.6	1.21	1.13	[13]
4	0.81	0.0001	23	17	1.22	0.92	1.20	[13]
4	0.81	0.001	23	17	1.3	0.98	1.30	[13]
4	0.81	0.01	23	17	1.55	1.17	1.49	[13]
4	0.81	0.1	23	17	1.95	1.47	1.79	[13]
4	0.81	1	23	13	4.4	2.49	2.55	[15]
4	0.22	0.01	23	17	1.0	0.76	0.81	[13]
4	2.50	0.01	23	17	2.0	1.51	1.75	[13]
4	0.22	0.1	23	17	1.2	0.91	1.13	[13]
4	2.50	0.1	23	17	2.45	1.85	2.21	[13]
5	0.81	0.0001	23	17	0.3	0.23	0.26	[13]
5	0.81	0.1	23	17	1.15	0.87	1.17	[13]
5	0.81	1	23	13	3.1	1.76	1.75	[15]



Fig. 5. Comparison of corrosion rate prediction by the present model (dashed line) with experimental data (bar chart) at different partial pressures of H₂S at 30 °C, pH 4, and 1000 rpm RCE (equivalent to 0.81 m.s⁻¹ in pipe flow with 0.012 m ID). The experimental data are taken from Esmaeely et al. [15], and Zheng et al. [13].

where b'_a and b'_c represent the apparent Tafel slopes of anodic and cathodic reactions, respectively.

The apparent Tafel slopes can be obtained from the polarization data corresponding to each condition. Table 5 summarizes the corrosion rate data from the existing literature and the corresponding corrosion rates as obtained by implementing the correction for the *B* value calculated based on the polarization data for each condition. In certain conditions, the difference in the *B* value obtained this way can be up to two-fold, particularly where both cathodic and anodic currents are under charge transfer control. For instance, where $b_a = 40 \text{ mV.dec}^{-1}$, and $b_c = 120 \text{ mV.dec}^{-1}$, the value of the corrected B = 13 mV, is about half of what is assumed in the original study.

The comparison of the predicted corrosion rates with that obtained experimentally at pH 4 for various pH_2S is shown in Fig. 5. Generally, a good agreement is obtained for the corrosion rate variation as a function of pH_2S . This trend is due to the effect of H_2S on both the cathodic and anodic reactions (see Figs. 3 and 4). The presence of H_2S increases the cathodic limiting current through the buffering effect mechanism and the anodic current by additional contribution of a parallel anodic reaction. When results obtained in the lower pH_2S range are compared to those with no H_2S , a small decline in corrosion rate is reported, which was not predicted by the model. The difference can, to some extent, be asso-



Fig. 6. Comparison of corrosion rate prediction by the present model (lines) with experimental data (points) for different pH_2S at various flow velocities of 0.22, 0.81, and 2.5 m.s⁻¹ in pipe flow with 0.012 m ID (equivalent to 200, 1000, and 4000 rpm in experimental conditions), 30 °C, and pH 4. The experimental data was taken from Esmaeely et al. [15], and Zheng et al. [13].

ciated with the typical experimental errors in such measurements as seen from the error bars. In addition, a minor retardation effect from adding small concentrations of H_2S to the solution could emanate from the likely adsorption of sulfides intermediates on the surface of the steel, leading to a slight decrease of the electroactive surface area on the electrode [13]. However, this effect is not significant in high p H_2S since the corrosion rate significantly increases due to the presence of high concentration of H_2S .

In Fig. 6, the influence of flow velocity on aqueous H₂S corrosion of mild steel is shown. The model predictions are compared with the experimental data at different solution velocities for different partial pressures of H₂S. Fig. 6 reveals an increasing trend in corrosion rate with increasing flow velocities, suggesting that the corrosion process at pH 4 and H₂S partial pressures up to 0.1 bar remains under mass transfer influence at the conditions considered here. The model was able to successfully capture the corrosion rate variation as a function of flow velocity over a relatively wide range of environmental conditions. When all other experimental parameters are held constant, increasing the flow rate accelerates the mass transfer limiting current of H⁺ reduction in the cathodic region leading to an increase in corrosion rate as depicted in Fig. 6. The predicted corrosion rates are generally slightly higher than the experimental one; however, they are, in most cases, located within the range of experimental error.



Fig. 7. Comparison of the corrosion rate prediction by the present model with experimental data (bar charts) for pH values, 3, 4 and 5, and for various pH_2S at 30 °C and 1000 rpm RCE (equivalent to 0.81 m.s⁻¹ in pipe flow with 0.012 m ID). The experimental data was taken from Esmaeely et al. [15], and Zheng et al. [13].

Fig. 7 compares the experimental versus predicted corrosion rate, indicating the influence of pH - another critical parameter in aqueous H₂S corrosion of mild steel. Fig. 7 shows a steady decline in corrosion rates as the solution pH is increased. A higher concentration of H^+ , as the main cathodic reacting species in the sour systems, results in a higher rate of H⁺reduction, thereby promoting the overall rate of steel corrosion in H₂S containing environments [16,17]. Furthermore, in more acidic solutions such as pH 3, the influence of the contribution of H_2S to the anodic reaction rate is amplified due to the decrease of anodic current obtained via the Bockris mechanism. Fig. 7 confirms that the predicted results are in good agreement with the experimental data, although slight deviations can be observed at pH 3. These deviations could be due to the higher experimental errors marked by the large error bars in such experimental conditions. In addition, the effect of sulfide intermediates on the rate of iron dissolution reaction becomes more dominant at pH 3, which adds further complexity to the kinetics of the underlying electrochemical reactions. However, the model could successfully capture both the remarkable drop in the corrosion rate when changing the pH from 3 to 4 and the slight downward trend of corrosion rate when shifting pH from 4 to 5.

The comparison of the predicted corrosion rates with the experimental corrosion rate data over the whole range of varied parameters (pH 3 to pH5, pH₂S from 0 to 1 bar, and flow velocity from 0.22 to 2.5 m.s⁻¹) is shown in the parity plot in Fig. 8. All the predicted data points fall well within a 50% error range when compared to the experimentally measured data. The average absolute deviation for the data reported in Fig. 8 is about 19.7%, showing the capability of the presented model to predict the corrosion rates in a wide range of conditions reasonably well.

5. Conclusions

A mechanistic mathematical model based on the buffering ability of H_2S was developed to predict the corrosion rate of mild steel in aqueous H_2S solutions. The main findings are:

- The "double-wave" behavior of the polarization curve in the cathodic region stemming from the dissociation of H₂S inside the diffusion boundary layer was successfully captured by the model.
- The contribution of H₂S on iron dissolution modeled by providing a parallel reaction pathway resulted in a reasonable representation of the anodic current.
- The comparison of the experimental data with the results from the present model showed that this mechanistic model could



Fig. 8. Comparison of the experimental corrosion rates with predicted corrosion rates by the present model for wide ranges of experimental parameters. $3 \le pH \le 5$, $0 \le pH_2S \le 1$ bar, $0.22 \le$ velocity ≤ 2.5 m.s⁻¹. Dotted lines and dashed lines represent 50% and one-fold deviations, respectively. Experimental data was taken from studies by Zheng et al. (Red) [13] and Esmaeely et al. (blue) [15]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

successfully predict the corrosion rates of mild steel in H_2S environments over a wide range of conditions: from pH 3 to pH 5, velocity from 0.22 to 2.5 m.s⁻¹, and H_2S partial pressures up to 1 bar. The average absolute deviation of the predicted corrosion rates from the experimental data remained below 20%.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit authorship contribution statement

Payman Sharifi Abdar: Conceptualization, Data curtion, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Mohiedin Bagheri Hariri:** Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Aria Kah-yarian:** Conceptualization, Methodology, Software, Formal analysis, Writing – review & editing. **Srdjan Nesic:** Supervision, Formal analysis, Writing – review & editing.

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