Mechanism and Modeling of Galvanic Corrosion Between Mild Steel and Iron Sulfides

in Acidic Solutions

A dissertation presented to

the faculty of

the Russ College of Engineering and Technology of Ohio University

In partial fulfillment

of the requirements for the degree

Doctor of Philosophy

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August 2023

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This dissertation titled

Mechanism and Modeling of Galvanic Corrosion Between Mild Steel and Iron Sulfides

in Acidic Solutions

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Abstract

SHARIFI ABDAR, PAYMAN, Ph.D., June 2023, Chemical and Biomolecular Engineering

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Director of Dissertation: Srdjan Nesic

Sour hydrocarbon reservoirs, containing H₂S gas, are receiving increasing attention due to the growing demand for energy. Although uniform corrosion is not a significant obstacle for oil and gas companies in sour environments, the major challenge in this field is prevention of localized corrosion that can cause failures in production infrastructure. Formation of different types of iron sulfides as corrosion products has been postulated to be a main culprit for localized attack, due to their wide-ranging physicochemical properties, such as their electrical conductivities. The galvanic coupling between iron sulfides layers and mild steel was shown to be the mechanism associated with the localized attacks in sour environments. However, the mechanism of galvanic coupling between mild steel and iron sulfides has not been understood due to the lack of systematic and parametric studies. The research described herein addresses the galvanic coupling between mild steel and iron sulfide polymorphs to investigate the involved mechanisms.

For the first step, the uniform corrosion of mild steel in aqueous H₂S solutions was critically reviewed, and the mechanism associated with this system including the involved chemical electrochemical reactions was fully described. Furthermore, the mathematical modeling of uniform corrosion rate of mild steel in H_2S environments was also comprehensively reviewed. In addition, some new approaches for the modeling of electrochemical reactions as well as corrosion rate were proposed, and the validity of the proposed models were verified through comparing with experimental data.

Next step of the current research focused on the galvanic corrosion between mild steel and iron sulfides using both experimental and modeling investigations. In the experimental section, a systematic study was performed in order to determine the contribution of the influential parameters on the galvanic corrosion between mild steel and iron sulfides. On that account, the effect of several important parameters including iron sulfide type, cathode to anode surface area ratio, and solution's conductivity was examined. Although the conductivity of solution did not show significant impact on the galvanic corrosion rate in the studied experimental conditions, the type of iron sulfide as well as the cathode to anode surface area ratio notably affected the galvanic coupling process. Specifically, the two types of iron sulfides used here, pyrite and pyrrhotite, were shown to produce different galvanic corrosion due to their different electrochemical behaviors. To further elucidate the mechanism of the impact of iron sulfide type, the cathodic behavior of pyrite and pyrrhotite was systematically studied using rotating disk electrode system. The results revealed that pyrrhotite has significantly higher cathodic current than pyrite. This difference originates from different cathodic reactions occurring at the surface of these iron sulfides. Therefore, the associated cathodic reactions were also proposed in this study.

The modeling section started with the proposed model for the cathodic current density of mild steel, pyrite, and pyrrhotite. The mathematical model was based on the proposed cathodic reactions as well as the constants found from experimental investigation. The proposed model was then verified by comparing it to the experimental data obtained in this study. In the final part of the current study, a mathematical model based on the polarization measurements was proposed for the prediction of galvanic corrosion rate between mild steel and iron sulfides. The model was compared with the experimental results at various experimental conditions, and very good agreement was found between experimental and modeling results.

To summarize, the current research was ale to reveal some mechanistic aspects of the galvanic coupling between mild steel and iron sulfides. The impact of the influential parameters and the electrochemical characteristic of iron sulfides were revealed. Also, the current research, for the first time, developed a mathematical model for the prediction of cathodic current on iron sulfides and the galvanic corrosion rate between mild steel and iron sulfides.

Dedication

То

my parents, Ahmad and Fahimeh, who unconditionally supported me during my life and during all stages of my long academic journey. my little brother, Mehran, who has always been there for me. my lovely Sima, who always accompanied me during the difficulties and joys.

Acknowledgments

I would like to thank everyone who offered assistance, time, and support throughout the different steps of this dissertation. First and foremost, I would like to express my sincere appreciation and gratitude to my advisor Professor Srdjan Nesic, who supported me during a very difficult period of my life, trusted me, and accepted me as his Ph.D student. I would like to thank him for his encouragement, support, mentorship, and belief during my Ph.D study at Ohio University. His critical view of my research, from the beginning to the end, and the immense scientific knowledge he brought into our discussions, lead me to improve my knowledge and gradually progress in my research. He gave me freedom in many aspects of my Ph.D life and supported my attendance at conferences and events that contributed to my professional growth.

I would also like to express my appreciation to my committee members, Dr. Marc Singer, Dr. Rebecca Barlag, Dr. Howard Dewald, and Dr. David Young for their interest in my work and willingness to be on my committee.

Additionally, I would like to express my gratefulness to two members of ICMT, Dr. David Young and Dr. Bruce Brown. Dr. David Young unconditionally helped me with writing this dissertation. His chemistry knowledge also assisted me throughout my research. Dr. Bruce Brown, as my project leader, always contributed his time and energy to my work. Without him, performing the experiments would not have been possible. Also, I want to thank him for his scientific comments, and his help with writing the reports and papers. I would also like to thank Dr. Marc Singer for his support and his valuable comments on my research during my Ph.D study. My accomplishments would not have been possible without the help and support of my lab mates and collaborators at the Institute for Corrosion and Multiphase Technology (ICMT). Additionally, I would like to thank the students and staff at ICMT for making me feel supported and providing much needed assistance with my experiments. I have been fortunate to work in a friendly and cooperative atmosphere.

Finally, I would like to thank my friends and family who supported me during my time here, without their emotional support this journey would not be as joyful as it was.

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Chapter 1: Introduction

In 2001, CC Technologies, for the Department of Transportation's Federal Highway Administration (FHWA), published a study [1] which estimated the cost of corrosion in the United States; this focused on infrastructure, utilities, production, transportation, manufacturing, and government. At that time, it was determined that the total direct annual cost of corrosion in the United States is approximately \$276 billion, which equals 3.1% of the nation's then Gross Domestic Product (GDP). From this total cost, \$7 billion was attributed to gas and liquid transportation pipelines, \$1.4 billion from corrosion in oil and gas production, and \$5 billion was estimated for gas distribution [1]. In addition, another study assessed that 25% percent of failures in the oil and gas industry are related to corrosion; CO_2 and H_2S corrosion cause half of these failures [2]. In the most recent study that was published by NACE (National Association of Corrosion Engineers) in 2016 [3], the global cost of corrosion was estimated to be around \$2.5 trillion, which is equivalent to 3.4% of the global GDP. More importantly, it was estimated that the use of current corrosion control practices can save between 15 and 35% of the cost of corrosion (between \$375 and \$875 billion annually) [3]. Therefore, control and reduction of corrosion to prevent such failures significantly enhances asset integrity while reducing maintenance costs, eliminating environmental damage, maintaining production, and preventing loss of human life; reputational damage and costs associated with litigation are also avoided.

Two of the most important modes of metal degradation in oil and gas industries are CO₂ and H₂S corrosion, known as sweet and sour corrosion, respectively. H₂S is a hazardous gas (according to OSHA [4], long-term exposure to 5 ppm H₂S endangers human health, *i.e.*, respiratory damage, and exposure to higher than 700 ppm can lead to immediate death) which is produced in geological reservoir due to the degradation of sedimentary organic matters by sulfate-reducing bacteria and thermochemical sulfate reduction [5]. The production of oil and gas from sour oilfields has been increased during recent years leading to the increase of attention to the mitigation strategies related to failures in sour environments. Corrosion of mild steel in sour media could occur as uniform and localized modes of attack. However, localized corrosion, also known as pitting corrosion, is a major contributor to failures in sour environments. In addition, localized corrosion generally causes 12% of all oilfield corrosion incidents, therefore, its impact on the economics of oil and gas production is indisputable [2].

Localized attack of mild steel in H₂S environments is very complicated as several factors play roles in this type of corrosion. Owing to this complexity, limited studies have focused on this topic and thus its mechanism is poorly understood. One of the major complexities arises from the nature of corrosion products formed on the surface of mild steel during the corrosion process. These corrosion products, which are known as iron sulfides, could include various types or polymorphs with different physicochemical, structural, and electrical properties. Some polymorphs, *i.e.*, mackinawite, were shown to be very protective for uniform corrosion by acting as a diffusion barrier and surface blockage for transportation of corrosive species to the surface of mild steel [6]–[8]. On the other hand, the presence of other iron sulfide polymorphs was significantly correlated

with the propagation of localized corrosion in laboratory settings as well as oilfield observations [9]–[12].

Galvanic coupling between iron sulfides and mild steel has been suggested to be the main mechanism leading to localized corrosion in H_2S environments. Galvanic corrosion takes place when an active metal (anode) is corroded due to the connection to a more noble metal (cathode). This phenomenon is important in H_2S corrosion as some polymorphs of iron sulfides are semiconductive, and therefore could act as a cathode with regard to mild steel. In addition, the high porosity of these corrosion products increases the cathodic surface area resulting in a more intense galvanic corrosion rate. Hence, in case of discontinuity or rupture of the iron sulfide layer, a galvanic cell with an anode (mild steel), a cathode (iron sulfide), and electrolyte is established which initiates localized corrosion [9]. Previous research at the Institute for Corrosion and Multiphase Technology (ICMT) showed that galvanic coupling between pyrite and mild steel caused severe pitting corrosion on the surface of steel [13]. However, the numbers of studies investigating galvanic corrosion between steel and iron sulfides are limited. Moreover, the effect of influential experimental parameters on this galvanic system has not as of yet been explored. Therefore, a systematic study focusing on the mechanistic understanding of galvanic corrosion between mild steel and iron sulfides is needed.

The objective of the present dissertation research is to advance the understanding of the aforementioned system in acidic environments. To that end, a new experimental setup was designed, and a systematic study was developed in order to investigate the impact of various environmental parameters on the galvanic corrosion between mild steel and iron sulfides. In parallel to the experimental investigations, a mathematical model was also developed in order to predict the rate of galvanic corrosion between mild steel and iron sulfides in various experimental conditions.

Chapter 2: Background and Literature Review

This section reviews the fundamentals of hydrogen sulfide (H₂S) corrosion of mild steel with the focus on localized corrosion in the presence of iron sulfides. First, the chemistry of various iron sulfides as well as their physicochemical and thermodynamic properties are reviewed. Given how they form as corrosion products, the effect of iron sulfides on the localized corrosion of mild steel in previous studies is then described. Finally, literature results on the galvanic corrosion between mild steel and iron sulfides are critically reviewed.

Fundamentals of Corrosion of Mild Steel in Hydrogen Sulfide (H₂S)

Corrosion due to carbon dioxide (CO₂) and hydrogen sulfide (H₂S) gases are the most frequent corrosion processes associated with production and transportation of oil and gas. The CO₂ corrosion (sweet corrosion) mechanism is generally well defined; however, complications arise in the presence of H₂S gas which makes H₂S corrosion (sour corrosion) a significant challenge for oil and gas industries. CO₂ is present in almost every single oil and gas field, while only some fields contain H₂S gas. Therefore, H₂S always exists in the presence of CO₂ gas. H₂S gas, like other acid gases such as CO₂, dissolves and partially dissociates in water producing an acidic aqueous solution. This will lead to corrosion of mild steel if it is in contact with such a media, as governed by the associated chemical, electrochemical and transport processes.

In corrosion of mild steel in H_2S environments, metallic iron is spontaneously converted to ferrous ions (Fe²⁺), resulting in precipitation of iron sulfide in certain conditions [14]. The overall reaction for this process can be expressed as Reaction (1).

$$Fe_{(S)} + H_2S_{(aq)} \xleftarrow{K_{H_2S}} FeS_{(S)} + H_{2(g)}$$
 Reaction (1)

Iron sulfide (FeS) is the main corrosion product in H₂S corrosion environments. Ferrous ion is introduced to the solution by the corrosion process and, depending on the reaction mechanism, either reacts with S^{2-} or HS⁻. Precipitation kinetics of iron sulfides has been investigated by several researchers, with various related solubility product expressions depending on the different reaction mechanisms involved. Morse, *et al.*, proposed a reaction mechanism based on [H⁺] and [HS⁻] [15], however, Berner, *et al.*, proposed a different reaction based on [S²⁻] [16]. In a comprehensive review paper by Sun, *et al.*, [H⁺] and [HS⁻] based expressions were postulated to be the most reliable method [17]. Reaction (2) describes precipitation of iron sulfide as the reverse of iron sulfide solubility in acid, in which the solubility product can be calculated using Equation (1).

$$Fe^{2+}_{(aq)} + HS^{-}_{(aq)} \rightleftharpoons FeS_{(s)} + H^{+}_{(aq)}$$
 Reaction (2)

$$K_{sp,FeS} = \frac{[Fe^{2+}][HS^{-}]}{[H^{+}]}$$
Equation (1)

Precipitation occurs when ion concentrations exceed values where the solubility product ($K_{sp,FeS}$) is surpassed, the solubility limit of iron sulfide has been exceeded.

Benning, *et al.*, reported Equation (2) for calculating the solubility limit of iron sulfide [18]. It should be mentioned that this solubility limit equation is for mackinawite as it is the first type of iron sulfide which precipitates. Ning, *et al.*, experimentally measured the solubility product of mackinawite to have $pK_{sp,FeS}$ of 3.6 ± 0.2 at 25 °C [19].

$$K_{sp,FeS} = 10^{\left(\frac{2848.779}{T} - 6.374 + \log(K_{a,1})\right)}$$
 Equation (2)

Saturation level is the concept which dictates magnitude of precipitation and film formation on the steel surface. Saturation level of mackinawite can be found using Equation (3). Benning, *et al.*, demonstrated that when supersaturation of mackinawite is high precipitation takes place rapidly and readily [18].

$$SS = \frac{\frac{[Fe^{2+}][HS^-]}{[H^+]}}{K_{sp,FeS}}$$
 Equation (3)

Chemistry of Iron Sulfides

As was mentioned in the previous section, iron sulfides are the corrosion products of mild steel corrosion in H₂S environments. Iron sulfides exist as stoichiometric, as well as non-stoichiometric, polymorphs and related phases. At least eight different phases have been identified mineralogically [20]. Table 1 summarizes these phases and their key characteristics. Many of these phases have been identified as corrosion products in H₂S environments, and it was shown that they differently influence the corrosion of mild steel due to their distinct physicochemical properties [9], [11], [21].

Table 1.

Different polymorphs of iron sulfides and their characteristics

Name	Composition	Structure	Properties
mackinawite	FeSm	tetragonal	metastable material that is the major constituent of the FeS precipitated from aqueous solutions
cubic FeS	FeSc	cubic	highly unstable phase
troilite	FeSt	hexagonal	stoichiometric end member of the Fe _{1-x} S group
pyrrhotite	Fe _{1-x} S	Monoclinic or hexagonal	nonstoichiometric stable group where $x < 0.2$, monoclinic form is approximately Fe ₇ S ₈ , hexagonal form is approximately Fe ₁₀ S ₁₁
smythite	Fe ₉ S _{11s}	hexagonal	metastable phase related to the $Fe_{1-x}S$ group
greigite	Fe ₃ S _{4g}	cubic	metastable Fe ^{II} Fe ^{III} sulfide; the thiospinel of iron
pyrite	FeS _{2p}	cubic	stable iron(II) disulfide, known as "fool's gold"
marcasite	FeS _{2m}	orthorhombic	metastable iron(II) disulfide

Mackinawite. Mackinawite, an iron(II) monosulfide, is the result of reaction between Fe^{2+} and S^{2-} in ambient conditions. Mackinawite has a 2D layered crystal structure, in which Fe atoms are linked in a tetrahedral coordination to equidistant sulfur atoms [20]. In earlier research, mackinawite has been referred to as amorphous iron sulfide, however, Rickard, *et al.*, showed that amorphous iron sulfide does not truly exist, and it is actually identical to nanocrystalline mackinawite [20], [22], [23]. Mackinawite is an unstable phase as both Fe^{2+} and S^{2-} present on the surface of the mackinawite are quickly oxidized in the presence of oxygen or other oxidizing agents [24]. For a long time, researchers believed that mackinawite is an iron-rich non-stoichiometric (Fe1+xS) compound, but Rickard, *et al.*, proved that mackinawite is stoichiometric FeS, suggesting that the previous studies were hindred from analytical artifacts due to the presence of other metals in their samples [20], [25].

Cubic FeS. Cubic FeS, which is isomorphous with the sphalerite (ZnS) characteristic crystal structure, is an unstable phase which has been reported to transform to either mackinawite or troilite/pyrrhotite at room temperature, in hours to days [20]. Thus, it has not been found in nature due to its short lifespan. Cubic FeS forms through the reaction of metallic Fe and S²⁻ in acidic solutions (pH 2-6) at temperatures below 92 °C [26]. De Medecis, *et al.*, demonstrated that cubic FeS is not produced in the presence of chloride or oxygen [27].

Pyrrhotite Group. Pyrrhotite is a group of non-stoichiometric iron sulfides formulated as $Fe_{1-x}S$. The pyrrhotite group constitutes the most common mode of occurrence of iron sulfides in the Earth. The two main crystal structures that have been observed for pyrrhotite are hexagonal with formula $Fe_{10}S_{11}$ and monoclinic with formula Fe_7S_8 , which is the more stable form at low temperatures according to Rickard and Luther [20]. Troilite is the stoichiometric end-member of the pyrrhotite group when x = 0 (FeS). Smythite (Fe₉S₁₁) is another member of this group with rhombohedral structure and is normally found with carbonates [20].

Greigite. Greigite (Fe₃S₄) is the iron sulfide analogue of magnetite (Fe₃O₄), possessing cubic structure with close packed array of S atoms linked by Fe atoms. Griegite is an inverse spinel, thus including both Fe^{2+} and Fe^{3+} in its structure [20], [22]. Greigite is an unstable intermediary phase between the initial phase of mackinawite and final phase of pyrite. Due to the similarity between the structure of greigite and mackinawite, it could be deduced that mackinawite transforms to greigite by rearrangement of Fe atoms caused by partial oxidation of Fe^{2+} to Fe^{3+} . It was suggested that the formation of greigite could be favored at low pH (*i.e.*, 3) and in the presence of oxygen [20].

Pyrite. Pyrite or iron(II) disulfide (FeS₂) is the most common iron sulfide on the Earth's surface since it is the most stable phase. Pyrite has a cubic structure essentially identical to halite (NaCl), with S_2^{2-} occupying Cl⁻lattice positions and Fe²⁺ in those of Na⁺ [20]. Rickard, *et al.*, believed that the solid-state transformation of mackinawite or greigite to pyrite is not probable. Instead, pyrite is formed through the reaction of iron(II) monosulfide with either H₂S or S, *i.e.*, elemental sulfur. Marcasite (FeS₂) is a dimorph of pyrite with orthorhombic structure [20], [22].

Conductivity of Iron Sulfides

Besides physicochemical properties, iron sulfides can have different electrical properties, specifically conductivity, which plays an important role in corrosion processes. The presence of a conductive layer on steel could significantly influence electrochemical reactions by providing a larger cathodic surface area or enhancing galvanic coupling between iron sulfides and steel. Mackinawite is electronically anisotropic, it is conductive in the direction of oriented layers in its crystal structure and insulating in the perpendicular direction [28]. Several data sets have been reported for the conductivity of pyrrhotite, troilite and pyrite [29], [30]. The conductivity of pyrite has been reported in the range of 0.02 to 562 (Ω .cm)⁻¹ and it's been reported to be p-type, ntype and sometimes n-p semiconductive [29]. Figure 1 shows the range of resistivities found for iron sulfides in comparison with other materials.



Figure 1. Resistivities of iron sulfides compared with metals and insulators. [31]

Thermodynamics of Iron Sulfides

In order to predict the iron sulfide type formed during the corrosion process, the stability of each polymorph in various experimental conditions should be firstly determined. Also, it is mostly the case that these polymorphs transform to each other depending on the condition and duration of the process involved. Both kinetics and thermodynamics of these polymorphs play roles in controlling the stability of each phase. From a thermodynamics point of view Pourbaix, or pH-potential, diagrams have been vastly used as the main predictive tool to establish the stability of corrosion products. Ning, *et al.*, [19] developed a comprehensive thermodynamic model for a H₂S-H₂O-Fe system for a wide range of experimental conditions. The model provided Pourbaix diagrams for systems with scenarios considering the most relevant types of iron sulfides: mackinawite, greigite, pyrrhotite, and pyrite. The effect of several influential parameters including temperature, pH₂S, and Fe²⁺ ion concentration were considered. Figure 2 shows an example of Pourbaix diagrams for four different systems at various temperatures [13], [19].



Figure 2. Pourbaix diagrams for H₂S-H₂O-Fe system showing step changes in temperature up to 250°C (T = 25°C to 250°C, $[H_2S]_{aq} = 9.4 \times 10^{-3}$ M, $[Fe^{2+}] = 10$ ppm, $[Fe^{3+}] = 10^{-6}$ M): A) mackinawite, B) mackinawite/greigite, C) mackinawite/greigite/pyrrhotite, D) mackinawite/greigite/pyrrhotite/pyrite. [13], [19]

The thermodynamic model was then validated by successfully predicting the corrosion products formed during multiple experiments. For this purpose, the iron sulfide layers formed during H₂S corrosion of mild steel at various conditions were analyzed by X-ray diffraction (XRD) and the results confirmed the type of polymorph predicted by the thermodynamic model [11], [13], [19].

Iron Sulfides as Corrosion Products of H₂S Corrosion of Steel

Mackinawite is the initial corrosion product of mild steel in H₂S environments. For a long time, researchers believed that amorphous iron sulfide is the initial corrosion product which rapidly converts to mackinawite, but it was found that amorphous iron sulfide is identical to mackinawite in a nanocrystalline form [15]. Due to its metastability, cubic FeS is not expected to be a long-term corrosion product in the field or in laboratory experiments [5], but it has been encountered in top-of-the-line corrosion environments, forming in condensed water, an aqueous condition free from NaCl [21]. A variety of pyrrhotites have been extensively reported as corrosion products of mild steel in H2S media [16], [17], [22]-[24]. Greigite is not a common corrosion product but has been observed in laboratory research. It seems that the presence of oxygen could enhance greigite formation [25]. It has been observed as a corrosion product in several laboratory and field experiments, especially at high H₂S partial pressures as well as at elevated temperatures [25], [26]. Pyrite is expected to be the long-term corrosion product of mild steel in H₂S environments given its thermodynamic stability. However, pyrrhotite can be another long-term corrosion product depending on field or experimental conditions. Marcasite and smythite are not common corrosion products, being found mostly in geological settings.

Transformation of Iron Sulfides

Several studies have investigated the transformation of iron sulfides at various experimental conditions. Wikjord, et al., [32] studied phase transitions associated with iron sulfide polymorphisms for pH<5, pH₂S up to 20bar and at 80-180°C. They concluded that the phase transition follows the sequence mackinawite \rightarrow cubic FeS \rightarrow troilite \rightarrow pyrrhotite \rightarrow pyrite [32]. Liu, *et al.*, showed that at high pH₂S and high temperature mackinawite transforms to troilite and then to pyrrhotite [33]. Taylor, et al., showed that at 1.8MPa pH₂S and 160 °C, the iron sulfide phase transitions were as follows: mackinawite \rightarrow greigite + pyrrhotite \rightarrow pyrite and troilite \rightarrow pyrrhotite \rightarrow pyrite [34]. Gao, et al., also observed the same transformation pattern by increasing either time exposure or partial pressure of H₂S or temperature. The pattern was as follows: mackinawite \rightarrow troilite + mackinawite \rightarrow pyrrhotite \rightarrow pyrite +(pyrrhotite) [10], [21], [35]. Therefore, it can be concluded that pyrite and pyrrhotite are the final corrosion products in H₂S environments. Figure 3A shows a well-known schematic relating to the transformations of different phases of iron sulfide which was proposed by Rickard in 1969 based on mineralogical and geological studies [36]. Note there are peculiarities therein, such as greigite transforming to pyrrhotite which was not seen in any corrosion experiments. Also, the conversion of pyrrhotite to pyrite was discussed in several studies. These peculiarities could be due to the difference between corrosion processes and geological phenomena. Therefore, a novel scheme specific to corrosion processes is needed. Based on the literature review section, this study proposes the diagram shown in Figure 3.B.



Figure 3. A) Iron sulfides interrelationship in aqueous solution by Rickard [30], B) Iron sulfides transformations in corrosion of mild steel proposed by this study.

Influence of Iron Sulfides on Localized Corrosion of Mild Steel

Localized corrosion has always been the major problem in sour media due to the complexity of corrosion products and their effect on pitting corrosion, which resulted in unpredictability of encountered phenomena. This has garnered broad attention of scientists in order to develop accurate corrosion models. Therefore, several studies have analyzed the localized corrosion of mild steel in H₂S media. Various experimental conditions have been used and the effect of different conditions on localized corrosion have been studied and discussed. Different types of iron sulfides can be formed, depending on the experimental conditions, which differently influence localized corrosion. In this section, the effects of experimental conditions as well as iron sulfide polymorphism on localized corrosion of mild steel are critically reviewed. ICMT researchers have performed several studies in this field, which are described first. Afterwards, studies from other researchers are discussed.

Much research at ICMT has focused on localized corrosion of mild steel in H₂S environments. In 2013, Brown investigated the effect of various parameters, *i.e.*, pH,

temperature and CO₂ partial pressure, on localized corrosion of mild steel in single-phase and multiphase flow systems [37]. An empirical model was created based on flow loop experiments in limited temperature, pressure and H₂S partial pressure ranges. Unfortunately, lack of XRD analysis in-house at the time prevented observing any phase changes of the iron sulfides present, such that the only documented phase was mackinawite. In addition, it was shown that when CO₂ is present in the system, carbonic acid could diffuse through the developed iron sulfide layer and form an iron carbonate layer below. The carbonic acid was also postulated to re-equilibrate due to pressure effects and form carbon dioxide gas, which would then fracture the mackinawite corrosion product layer from the inside [37], [38].

In another study Ning, *et al.*, [13] designed an experiment such that different polymorphs of iron sulfides were formed spontaneously during 11 days at 80 °C. The X65 steel specimens were removed and then analyzed after 4, 7, 9, and 11 days. Profilometry measurements in conjunction with XRD results demonstrated that localized attack occurred when corrosion products consisted of higher proportions of greigite and/or pyrite. This observation signaled a possible correlation between localized corrosion and the formation of greigite and/or pyrite. In order to prove this postulate, the author performed several under deposit experiments with pyrite particles. Based on the results, a three-step descriptive model was proposed for pitting corrosion in the presence of a layer containing a mixture of pyrite and mackinawite: 1. Steel is exposed to hydrogen sulfide and a protective mackinawite layer is formed; 2. Part of the mackinawite layer is transformed to pyrite when the environment favors this process. As the formed pyrite crystals are conductive, they connect mackinawite sheets together to provide a less resistive pathway for electrons to be transferred and consumed by cathodic reactions on the bulk solution side of the corrosion product; 3. Galvanic effects between the steel surface and pyrite crystals occur, which lead to the localized corrosion of steel [13].

Gao et al. [35] studied the effect of three parameters, namely partial pressure of H₂S, temperature and time exposure, on the corrosion products as well as localized corrosion of mild steel at elevated temperatures. The results for all three parameters follow the same trends in both iron sulfide formation and pitting corrosion as described by Ning. As an example, the results for different partial pressure of H₂S are shown in Figure 4. At 0.10 bar pH_2S , the main iron sulfide was identified as troilite (FeS) with a small amount of mackinawite (FeS). Elongated needle- and flower-like morphologies can be seen in the SEM images, which are characteristic of troilite crystals. At pH_2S of 0.5 bar, a dense layer of pyrrhotite crystals with a hexagonal flake-like morphology is clearly seen in SEM images. XRD data proves this result by showing that troilite was totally transformed to pyrrhotite. When the pH₂S was increased to 1.0 bar, some pyrite (FeS₂) appeared in addition to the pyrrhotite according to XRD analysis. SEM images at this condition show some cubic pyrite crystals on the surface of the pyrrhotite. Finally, further increase of H₂S partial pressure to 2 bar leads to formation of only pyrite. The specimen surface was completely covered by large cubic pyrite crystals as shown in *Figure 4*. According to Gao, et al., localized attack was only observed at 1 and 2 bar H₂S, with pitting ratios of 5.2 and 4.2, respectively. In the same manner, by increasing temperature
and exposure time, localized corrosion was seen when pyrite was detected in corrosion products [35]. This observation of localized corrosion is consistent with previous research, which indicated that the formation of pyrite caused localized corrosion.



Figure 4. Surface morphologies of A) troilite at $pH_2S=0.10$ bar, B) pyrrhotite at $pH_2S=0.50$ bar, C) pyrrhotite/pyrite at $pH_2S=1.0$ bar, D) pyrite at $pH_2S=2.0$ bar. [35]

Navabzadeh investigated the effect of the pyrrhotite layer on localized corrosion. All the experiments were done on a non-uniform preformed pyrrhotite layer on the X65 steel specimens. This preformed layer was then exposed to aqueous CO₂, H₂S and CO₂/H₂S electrolyte. It was concluded that the contact between a non-uniform semiconductive pyrrhotite layer and the steel surface in a corrosive media could lead to galvanically driven localized corrosion [39]. She performed under deposit experiments in order to establish whether there was any effect of pyrrhotite on localized corrosion. Her studies resulted in a general conclusion that, regardless of iron sulfide type, poor layer formation or disruption which leads to discontinuities in corrosion products initiates localized corrosion which is then propagated *via* galvanic coupling [9], [31].

In addition to work conducted by ICMT researchers, several studies have provided experimental results at different conditions which show the impact of iron sulfide on localized corrosion. Pessu, et al., studied the influence of pCO₂, pH₂S and temperature on localized corrosion of X65. It was observed that mackinawite is the only corrosion product after 168 hours at 30 °C at different pH₂S while at 80 °C pyrrhotite is also formed at higher pH_2S . It was concluded that the presence of a combined pyrrhotite and mackinawite layer at 80 °C could enhance pitting corrosion compared to the presence of only mackinawite at 30 °C [40], [41]. A series of flow loop tests were carried out by Omar, et al., at 30 and 80 °C for different CO₂/H₂S mixtures. Localized attack was observed only at the highest flow velocity when mackinawite was presented, possibly due to layer breakdown. Unfortunately, lack of corrosion product analysis prevents articulation of any definitive conclusions on the effect of different iron sulfides on localized corrosion [12]. Kvarekval and Svenningsen, performed flow loop experiments in a CO₂/H₂S environment at 60 °C. By using EDS analysis, they found pyrrhotite and mackinawite as corrosion products after 7 days of testing which correlated with 800 µm pit depth In another series of autoclave experiments, Kvarekval and Svenningsen, extensively investigated the effect of different parameters on localized corrosion of mild steel in H₂S media. Mackinawite was the major component of corrosion products at 25 °C. While all the parameters were constant, by increasing the temperature to 60 °C, a mixture of mackinawite, troilite and pyrrhotite was observed. Further increase of

temperature to 120 °C resulted in observation of pyrrhotite as the major component of corrosion products. With these respective increases in temperature, localized corrosion rates were measured as 4.8, 1.3 and 14.7 mm/y [42]. The results showed that the presence of pyrrhotite significantly enhances localized corrosion. A significant gap in this work is that analyses were performed only for the temperature effect, the effect of other parameters have not been analyzed. Ren, *et al.*, investigated the behavior of N80 steel in a quiescent electrolyte with CO₂ and H₂S at 100 °C. Severe pitting corrosion was observed when partial pressure of H₂S was 0.01 MPa and postulated to be due to the presence of loose and brittle coarse grains of mackinawite. On the contrary, pitting attack was slight when pH₂S was raised to 0.02 MPa as more compact fine grains of pyrrhotite formed as corrosion products [43].

Galvanic Coupling Between Iron Sulfides and Mild Steel

As the last section of the literature review, previous studies on the galvanic coupling between iron sulfides and mild steel is reviewed here. Galvanic coupling between iron sulfides and mild steel has been postulated to be an important mechanism leading to localized corrosion. A study performed by Ning demonstrated that galvanic coupling between pyrite and steel causes severe localized corrosion. Pyrite particles were placed on a steel surface in the following conditions: 25 °C, pH₂S 0.1 bar, 1 wt.% NaCl and pH 4.0. This resulted in severe localized corrosion as shown in Figure 5.A. In the same conditions, a 60 µm insulating plastic mesh was placed between the pyrite particles and steel surface. No localized attack was observed in this condition as seen in Figure 5.B. This experiment proved that the localized corrosion process has electrochemical characteristics [13].



Figure 5. SEM images of the steel after Galvanic coupling experiments with pyrite a) in the absence of mesh, b) in the presence of mesh (25 °C, pH₂S 0.1 bar, 1% NaCl and pH 4.0). [13]

Few researchers conducted experiments to measure galvanic current between iron sulfides and mild steel. Navabzadeh showed that corrosion rate for the X65-pyrrhotite couple is slightly higher than for the X65-pyrite couple in CO₂, H₂S and N₂ media. It was also concluded that the galvanic effect is amplified in H₂S media because the uniform corrosion rate in this environment is significantly decreased [31]. However, no surface analyses, as well as an insufficient number of experiments, were done in order to make definitive conclusions from these observations. Furthermore, she measured localized corrosion on a preformed pyrrhotite layer in two different solutions: deionized (DI) water and 1 wt.% NaCl. The results showed that the specimen exposed to a more conductive solution was attacked at a much higher rate (13.7 mm.yr⁻¹) than the specimen exposed to the less conductive solution (4.2 mm.yr⁻¹). These results confirm that conductivity could increase the localized corrosion due to galvanic coupling [31], [39]. In another study,

Tjelta and Kvarekval, showed that iron sulfides act as cathodic sites when coupled to X65 steel. They concluded that pyrite has the largest ability to polarize steel but pyrrhotite produces the largest galvanic coupling current, which is contradictory because one expects pyrite produces the largest current as it has the largest polarizing ability [44]. Also, Yepez, *et al.*, postulated that corrosion current is increased due to galvanic current between pyrite or pyrrhotite and steel, concluding that the electromotive force for the galvanic current is reduction of a disulfide to a sulfur deficient iron sulfide in the case of pyrite, and elimination of cation vacancies to transform pyrrhotite to the more stable iron sulfide [45]. However, their experimental setup was of rudimentary design, surface areas were not clearly defined, and no definitive proof was provided for their conclusions.

Chapter 3: Research Gaps, Hypotheses, and Objectives

Research Gaps

Although the aforementioned studies have shed some light on how iron sulfides can govern localized corrosion, the phenomena involved remain unclear and subject to speculation. Consequently, they need to be investigated more thoroughly. The above literature review demonstrated that the presence of pyrite repeatedly resulted in localized corrosion via galvanic coupling. However, it remains unclear whether it happens because of disruption in the corrosion product layer due to the transformation of other iron sulfides to pyrite or because of the specific physicochemical characteristics of pyrite. Furthermore, localized corrosion occurred in some cases in the presence of pyrrhotite. On the other hand, pyrrhotite was protective in other cases. Therefore, it is undetermined whether pyrrhotite protects the surface or leads to pitting attack; this is complicated by the fact that pyrrhotite is really a family of non-stoichiometric iron sulfides (Fe_{1-x}S). Mackinawite itself has, in some cases, caused localized corrosion which could be associated with layer disruption or, at least, lack of coherent surface coverage. As pyrrhotite and pyrite are both conductive and have similar physicochemical characteristics, it is expected that they behave similarly when coupled to mild steel. Thus, one research gap requiring investigation is the link between pyrite and pyrrhotite associated with localized corrosion of mild steel.

According to previously reported research, galvanic coupling significantly affects the corrosion rate of steel but most of the studies involved suffer from experimental and analytical deficiencies. The results of these studies are in some cases contradictory and confusing. Experimental setups are not well designed or reported, for example, the morphology and surface area of the iron sulfides are typically unspecified. Cathode to anode surface area ratio is a significant factor in galvanic corrosion, therefore, without knowing surface areas the results are not fully understandable. Also, there has not been a comprehensive research program which studies the impact of different experimental conditions, such as cathode to anode surface area ratio, conductivity, and pH.

Phase transformation of iron sulfides is an influential parameter in localized corrosion and should be investigated in all experiments in order to obtain a clear explanation of the influence of iron sulfides on corrosion mechanisms. Unfortunately, in previous galvanic coupling studies limited surface analyses were performed, to elucidate the iron sulfides present on the steel, after the experiments to verify the formation of corrosion products or identify phase transformations that could have occurred. Potentially, the difference between the corrosion effects of pyrite and pyrrhotite could be found by investigating the surface chemistry of iron sulfides during the experiments.

The main motivation for conducting this study is the lack of consistent data from systematic studies, as well as contradictory results provided by different researchers. Localized corrosion of mild steel in sour media has always attracted the attention of corrosion engineers and researchers as its prediction and control is a key challenge in the oil and gas industries. There have been numerous papers on laboratory experiments and field experiences in different conditions, but none are able to clearly explain the mechanism of localized corrosion by iron sulfides. Previous studies have only considered the influence of each parameter in a limited sense, leading to discrepancies in results. Iron sulfide transformations during the experiments also complicate interpretation of the results. Therefore, there have been various research hypotheses, and associated postulates, about the impact of iron sulfide polymorphism on localized corrosion of mild steel.

In this context, designing an experimental setup which produces reliable results, planning a systematic study, resolving the previous contradictory postulates, as well as elucidating mechanistic aspects involved in the galvanic corrosion between mild steel and iron sulfides, are the motivations for this study.

Hypotheses

Based on the understanding and the results found in the literature, multiple hypotheses can be postulated and then tested in the current study. The main hypothesis of this research is that the corrosion of mild steel is increased due to its coupling to iron sulfides. Based on this hypothesis, the effect of three influential parameters: iron sulfide type, cathode to anode surface area ratio, and solution conductivity, each one derived from a hypothesis listed below, are investigated.

- Pyrite and pyrrhotite should show galvanic corrosion rates of relatively the same magnitudes when coupled to steel as they have relatively similar physicochemical characteristics. They both have been found as corrosion products when localized corrosion occurred.
- 2. Increasing cathode to anode surface area ratio should increase the galvanic current due to the higher cathodic current.

 Increasing the solution conductivity (NaCl concentration) should increase the galvanic corrosion.

Objectives

The objective of this study is two-fold: 1. Systematic investigation of galvanic corrosion between mild steel and iron sulfides in various experimental conditions; 2. Development of a mechanistic model for prediction of galvanic corrosion between mild steel and iron sulfides.

Systematic investigation of galvanic corrosion between mild steel and iron sulfides in various experimental conditions: The experimental part aims firstly to assess the validity of hypotheses by examining the effect of influential experimental parameters on the galvanic corrosion between mild steel and iron sulfides, and secondly to characterize the electrochemical behavior of iron sulfides to improve the understanding of surface chemistry of iron sulfides which will be also used for the modeling section. Therefore, the two objectives of this part are as follows:

- 1. Factors in galvanic corrosion between mild steel and iron sulfides in acidic solutions
 - 1.1. Effect of iron sulfide type
 - 1.2. Effect of cathode to anode surface area ratio
 - 1.3. Effect of solution conductivity
- Electrochemical characterization of cathodic reactions on the surface of iron sulfides Development of mechanistic model for prediction of galvanic corrosion between mild steel and iron sulfides: The goal of the modeling section is first to provide a model for the electrochemical reactions occurring at the surface of mild steel and iron sulfides, and

secondly to develop a model for predicting the galvanic corrosion between mild steel and iron sulfides. Therefore, the two objectives of this part are as follows:

- 1. Modeling of electrochemical currents on mild steel and iron sulfides
- Modeling of galvanic corrosion between mild steel and iron sulfides in acidic solutions

Chapter 4: Uniform Corrosion of Mild Steel in H₂S Aqueous Solutions

The corrosion of mild steel in H₂S environments generally occurs in two main types: uniform, and localized. Although this study mainly deals with the situations associated with localized corrosion, understanding the mechanism and modeling of mild steel in H₂S aqueous solutions is crucial step for establishing the foundation of the tools will be used in localized corrosion. From a mechanistic point of view, the chemical and electrochemical reactions occurring at the surface of mild steel is identical in uniform and localized corrosion. Since most of the previous studies are focused on uniform corrosion which leaded to comprehensive understanding and modeling of this system, it is important to initially recognize the mechanism of corrosion processes in uniform corrosion and to examine the previous models developed in this area.

For this purpose, this chapter includes a comprehensive literature review of the mechanisms proposed in previous studies as well as the previous models developed for corrosion rate prediction. Afterwards, the second part of this chapter involves new advancements in the modeling of corrosion rate of mild steel in H₂S aqueous solutions which was based on the latest mechanistic understanding of this system.

Chapter 4.A: Literature Review¹

The deleterious effects of even a small amount of aqueous hydrogen sulfide (H₂S) 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, and consequently several models have been proposed for the prediction of corrosion rates in H₂S aqueous solutions [14], [46]–[48]. This chapter provides a historical review on the corrosion of mild steel in H₂S environments. The first part begins with presenting the water chemistry of species in H₂S aqueous system which is fundamental for mechanistic and modeling sections. Then, a thorough review of the mechanisms reported in previous studies is presented in the second part. Ultimately, previous models for the prediction of electrochemical reactions as well as corrosion rates are reviewed in the last section.

¹ A version of this chapter was published as part of a journal publication: P. S. Abdar, M. B. Hariri, A. Kahyarian, and S. Nesic, "A revision of mechanistic modeling of mild steel corrosion in H₂S environments," Electrochimica Acta, vol. 382, p. 138231, Jun. 2021.

Water Chemistry of H₂S Corrosion System

The corrosion of mild steel in H₂S environments can be seen as a sequence of chemical reactions starting with the dissolution of H₂S gas in water, according to Reaction (3). Aqueous H₂S, as a weak diprotic acid, partially dissociates to HS⁻ and H⁺ ions, as shown via Reaction (4), followed by the dissociation of HS⁻ to H⁺ and S²⁻ according to Reaction (5). In addition to reactions associated with H₂S, water as the solvent also partially dissociates according to Reaction (6) result in the formation of an acidic, corrosive solution, buffered with undissociated aqueous H₂S.

 $H_2S_{(g)} \rightleftharpoons H_2S_{(aq)}$ Reaction (3)

$$H_2S_{(aq)} \rightleftharpoons HS^-_{(aq)} + H^+_{(aq)}$$
 Reaction (4)

$$HS^{-}_{(aq)} \rightleftharpoons S^{2-}_{(aq)} + H^{+}_{(aq)}$$
 Reaction (5)

$$H_2 O_{(l)} \rightleftharpoons OH^-_{(aq)} + H^+_{(aq)} \qquad \text{Reaction (6)}$$

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 [46]. The concentration of aqueous H_2S can be described based on Henry's law, assuming an ideal solution and gas phase:

$$H_{H_2S} = \frac{C_{H_2S_{(aq)}}}{p_{H_2S_{(g)}}}$$
Equation (4)

where H_{H_2S} (M.bar⁻¹) is the Henry constant of H₂S and can be calculated from Table 2. $C_{H_2S_{(aq)}}$ (M) is the concentration of dissolved H₂S, and $p_{H_2S_{(g)}}$ (bar) is the partial pressure of H₂S gas. The chemical equilibria for H₂S dissociation, Reaction (4) and Reaction (5), can be expressed as Equation (5) and Equation (6), 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 Reaction (4) and Reaction (5), respectively, as shown in Table 2.

$$K_{H_2S} = \frac{C_{HS^-(aq)}C_{H^+(aq)}}{C_{H_2S(aq)}}$$
Equation (5)
$$K_{HS^-} = \frac{C_{S^{2-}(aq)}C_{H^+(aq)}}{C_{HS^-(aq)}}$$
Equation (6)

The chemical equilibria of water dissociation (Reaction (6)) can be expressed by Equation (7) in which K_w is the equilibrium constant as noted in Table 2.

$$K_w = C_{H^+(aq)} C_{OH^-(aq)}$$
 Equation (7)

Table 2.

The equilibrium and kinetic rate constants for the reactions in H_2O/H_2S system.

Constant	Unit	Reference
$ {}^{*}H_{H_{2}S} = (10^{-3}\rho_{w}) \ 10^{-(a_{1}+a_{2}T+a_{3}T^{2}+a_{4}/_{T}+a_{5}\log(T))} $ $ a_{1} = \ 6.343 \times 10^{2}, a_{2} = \ 2.709 \times 10^{-1} $ $ a_{3} = \ -1.113 \times 10^{-4}, a_{4} = \ -1.6719 \times 10^{4} $ $ a_{5} = \ -2.619 \times 10^{2} $	(M.bar ⁻¹)	[49]
	(M)	[50]
$K_{HS^-} = 10^{-17.4} @ 25^{\circ}C$	(M)	[51]
	(M)	[52]
$k_{f,HS^-} = 7.5 \times 10^{-6.4}$	(s^{-1})	[46]
$k_{b,H_2S} = 7.5 \times 10^{11}$	$(M^{-1}.s^{-1})$	[46]
$k_{b,HS^-} = 1 \times 10^{11}$	$(M^{-1}.s^{-1})$	[46]
$k_{b,w} = 1.4 \times 10^{11}$	$(M^{-1}.s^{-1})$	[53], [54]
* ρ_w is the density of water in (kg. m ⁻³), and can be calculated using $\rho_w = 753$	8.596 + 1.87748 T ·	$-0.003562 T^2$

The solution speciation can be obtained by solving the chemical equilibria equations shown above, along with the electro-neutrality equation (Equation (8)).

$$\sum_{i} z_i C_i = 0$$
 Equation (8)

An example of one such calculation is shown in Figure 6, 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 bar and 1 bar.



Figure 6. 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).

Literature Review of Mechanism of Mild Steel Corrosion in H₂S Aqueous Solutions

The corrosion processes of mild steel in weak acids involves homogenous chemical reactions and electrochemical reactions. The former was already discussed during the water chemistry section, and the latter is discussed in this part. Therefore, as review of proposed electrochemical reactions, i.e., cathodic and anodic reactions, involved in H₂S corrosion of mild steel is critically examined here. Although mass transport phenomena can also be involved in the mechanistic understanding, it will be explained later coupled with the modeling literature review.

Electrochemical Reactions

H₂S corrosion of mild steel is an electrochemical process which involves anodic and cathodic reactions occurring at the surface of mild steel. Anodic dissolution of iron as shown in Reaction (7) is the only anodic reaction considered in this system. With regard to the cathodic reactions, different mechanistic understanding considered different series of cathodic reactions to occur at metal surface. However, the most recent mechanistic view considers only hydrogen ion reduction and water reduction reactions via Reaction (8) and Reaction (9), respectively.

- $Fe \rightleftharpoons Fe^{2+} + 2e^{-}$ Reaction (7)
- $2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$ Reaction (8)
- $2H_2O_{(l)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)} \qquad \text{Reaction (9)}$

Cathodic Reactions. During the past six decades, the mechanism of cathodic reactions in the presence of H_2S has been subjected to controversies leading to the evolution of the mechanistic understanding of this system. In 1965, as one of the first attempts to unravel the effect of H₂S on cathodic reactions on iron surface, Bolmer [55] observed that the cathodic current density was increased by the increase of H₂S concentration. This observation led the author to propose that the direct reduction of H_2S is the overall cathodic reaction which was limited by H_2S diffusion and hydrogen overvoltage. Apart from lack of information and multiple ambiguities about the experimental setup, the results showed that the diffusion-limited current density was not directly proportional to the concentration of H₂S. The author claimed that this deviation originated from stirring due to the evolving hydrogen bubbles at the surface of electrode. Furthermore, although pure charge transfer region was not recognizable in most cases, the author stated that the mechanism of hydrogen evolution changes with H₂S concentration which varies the Tafel slope of this region from 55 to 115 mV. It was suggested that at regions beyond the diffusion current, the reduction of HS⁻ or H₂O was responsible for increased cathodic current values [55].

The research in this area has been continued with higher extent in 1980s by several researchers. In a study dedicated to the investigation of corrosion products formation on the surface of steel in H₂S environment, Wikjord et al. stated that the direct reduction of dissolved H₂S is preferable due to its high polarizability and absorbability on the metal surface. However, the author did not provide more explanation about the statement as the focus of the study was on corrosion products [32]. Shoesmith et al. also considered the direct reduction of H_2S as the main cathodic reaction based on the previous studies [56]. Foroulis discussed the possibility of various cathodic reactions on the surface of iron in aqueous sulfidic solutions and stated that in acidic solutions, the main cathodic reaction is the reduction of H^+ with possible contributions of direct reduction of H_2S as well as reduction of H_2S to HS^- and then to S^{2-} [57].

In one of the key studies, Morris et al. [58] investigated the corrosion of carbon steel in acidic aqueous H_2S using rotating disk electrode setup. The authors noted that the cathodic limiting current density was increased by the increase of H₂S concentrations, while the cathodic Tafel slope remained unaffected due to the presence of H_2S ($b_c = 110$ -118 mV). Although it was also found that the addition of H₂S does not alter the exchange current density and reversible potential of cathodic reaction, the authors confirmed Bolmer's proposal by concluding that the increment of limiting current density stems from direct reduction of H_2S . Nevertheless, by examining the results of this study, one should recognize that the authors conclusion is in clear contradiction to their observations. In the absence of H_2S (i.e., acidic solution de-aerated with N_2), the only cathodic reaction is the reduction of H⁺. In contrast, when H₂S is present, considering the direct reduction reaction of H₂S should change both exchange current density and reversible potential as it adds a separate electrochemical reaction to the system. It is even probable that different Tafel slopes could be observed in this case. Whereas, noticing same values for these electrochemical parameters is more likely evidence for the uniqueness of cathodic reaction in absence as well as presence of H₂S [58].

In 1986, Ogundele and White [59] measured the polarization behavior of carbon steel in H₂S saturated water at various temperatures. One of the prominent features observed for the first time was the appearance of two linear Tafel regions, with slopes of 260 mV and 155 mV, for the cathodic current density. The authors followed Bolmer's claim by attributing the first Tafel slope to the direct reduction of H₂S. In a similar fashion, the second Tafel slope was related to the direct reduction of HS⁻ with the same mechanism even though the authors admitted that more experimental results are needed to prove it. Considering the first reaction as the rate determining step, the Tafel slope for both H₂S and HS⁻ reduction reactions was calculated to be 118 mV, which is different from the experimental observation. These discrepancies were not clearly addressed, although the effect of H_2S diffusion was raised as a possible reason. Huang and Shaw suggested the same mechanism and restated the same justification when the observed Tafel slope in their study, i.e., 270 mV, was largely deviated from theoretical 118 mV value [60]. The main flaw in these works is that the pure charge transfer region was not seen in polarization curve as they have measured the experiments in the static condition. Therefore, the proposed mechanism as well as the Tafel slopes could not be compared and thus verified by the experimental data [59], [60].

To put the above-mentioned theory in a nutshell, H_2S was hypothesized to increase the corrosion rate of steel by providing a new cathodic reaction, namely direct reduction of H_2S , in addition to H^+ reduction reaction. Regardless of the discrepancies observed in previous studies in order to validate this theory, it remained as the commonly accepted mechanism for the corrosion of steel in H_2S environments. However, in very recent years, this theory has been entirely re-evaluated and challenged by several studies leading to the introduction of a new theory, namely "buffering effect" mechanism. In short, buffering effect mechanism states that H₂S increases the corrosion rate of steel by partially dissociating and providing more H⁺ for the hydrogen reduction reaction, and indeed the direct reduction H₂S is insignificant. The dissociation of H₂S, as weak acid, at the vicinity of the metal surface has been totally ignored in previous works which was one of the reasons they could not accurately rationalize their experimental observations.

The importance of H₂S dissociation on the cathodic current was proposed for the first time by Kittel and Tribollet in a two-part study published in 2013 and 2014 [48], [61]. In this study, the authors first investigated the effect of H₂S on the cathodic currents in acidic solutions on the stainless-steel surface using rotating disk electrode (RDE) apparatus, and then provided a mathematical model based on their mechanism during the second paper. In presence of H_2S at pH 4, the cathodic polarization curve showed a second mass transfer limiting current at higher cathodic potential ranges in addition to the one for H^+ reduction reaction in the absence of H_2S . The second cathodic wave was simply attributed to the direct reduction of H₂S, although the authors stated that cathodic current in CO₂ and acetic acid solutions can be fully explained using only buffering effect (without direct reduction of these weak acids). The first mass-transfer limiting current (related to the H⁺ reduction) disappeared at pH 6 and the second mass-transfer limiting current was related to the direct reduction of H₂S contribution. The authors selected this less acidic media in order to characterize the direct reduction reaction of H₂S due to the elimination of H⁺ reduction reaction. However, the electrochemical characterizations at

pH 6 contradicts the direct reduction of H₂S hypothesis: the relation between rotational speed and mass-transfer limiting current deviates largely from Levich equation, the Tafel slope of 145 mV for the kinetic region suggested that the reaction is not pure charge transfer controlled. Despite this evidence, the authors believed that buffering effect is not sufficient to fully explain the cathodic current behavior as they could not justify the presence of the so-called "double-wave" behavior. Hence, the secondary wave was not completely characterized, and the mathematical model was not successfully predicting the cathodic currents at different rotational speeds. However, it should be noted that this study made a key contribution to the field as it introduced the concept of buffering effect in H₂S corrosion [48], [61]. At about the same time, Zheng *et al.* [47] published a systematic study on the H₂S corrosion of mild steel in extensive experimental conditions. The cathodic polarization curves showed the same "double-wave" behavior mostly in lower pH of 3 and 4. In a similar fashion, the two limiting currents were attributed to mass-transfer limiting current of H⁺ and H₂S reduction reactions but in this case the chemical dissociation of H_2S inside the boundary layer (buffering effect) was totally neglected [47]

In 2019, Kahyarian and Nesic [46] used theoretical analysis to reveal that buffering mechanism is entirely capable of describing the behavior of cathodic current in presence of H₂S, and the contribution of direct reduction of H₂S was shown to be inappreciable. In fact, it was elucidated that the mechanism of cathodic reactions is exactly the same as those formerly found for other weak acids, e.g., CO₂ and acetic acid. In other words, H₂S increases the cathodic current solely by providing additional hydrogen ions for hydrogen ion reduction reaction through dissociation process. The only question that arises here is: if only one cathodic reaction (hydrogen reduction reaction) takes place on the surface of electrode, why two mass-transfer limited currents ("doublewave") can be observed? This distinct characteristic stems from the relatively higher pK_a of H_2S (~7) compared to one of H_2CO_3 (~6.4) and acetic acid (~4.7), which requires higher pH at electrode surface to initiate dissociation reaction. In order to elucidate how the high pKa of H₂S brings about the double wave behavior of cathodic current, *Figure* 7 illustrates the concentration of species at the surface of electrode in conjunction with cathodic current density response in an acidic solution at pH 3 in presence of 0.1 bar H₂S. As it is seen, the surface pH as well as the concentrations of other species remain unchanged until the current reaches the first mass-transfer limiting current. Afterwards, the surface pH starts to increase due to the depletion of H^+ ions on the surface of electrode. At certain pH value, between 5 and 6, the dissociation of H₂S initiates as the equilibrium in Reaction (4) shifts to the right due to the depletion of H^+ ions. This process produces considerable amount of hydrogen ions on the surface of electrode leading to the increase in cathodic current density. The dissociation process continues until H₂S depletes, around pH 9, which resulted in the emergence of second mass-transfer limited current density. Noting that H₂S and HS⁻ concentration profiles intersect at pH 7, where pK_a of H_2S dissociation reaction lies. It is also worth mentioning that the selected condition does not favor the occurrence of the second dissociation step (Reaction (5)) due to its very high pK_a of around 17 [46], [51].



Figure 7. The relationship between the calculated surface pH and the surface concentration of H₂S and HS⁻, on the primary vertical axis, and the calculated current density, on the secondary vertical axis. Conditions: 25 °C, 2 m.s⁻¹ in a pipe with 0.012m ID, pH 3, pH₂S = 0.2 bar, and the potential range from -0.2 to -1.2 V vs. SHE. [46]

Anodic Reaction. Investigation on the mechanism of anodic dissolution has a long history dating back to the research around 1940s. Hitherto, most of the proposed mechanisms for the iron dissolution in acidic solutions have been based on the two wellknown mechanisms: "catalytic mechanism" proposed by Heusler [62], and "consecutive mechanism" proposed by Bockris and Kelly [63]–[65]. The "catalytic mechanism", shown through Reaction (10) - Reaction (12), assumed that the intermediate species (FeOH)_{ads} serves as a catalyst for Reaction (11). The Tafel slope of this mechanism was calculated to be around 30 mV, ($\alpha = \frac{1}{2}$), with the reaction order of two with respect to hydroxyl ion (OH⁻). However, the observed Tafel slope was 60 mV in transient condition by applying fast polarization technique in several experiments. In addition, assuming a two-electron transfer step is another drawback of this mechanism as simultaneous transfer of two electrons at the electrode surface has low probability [66].

$$Fe + OH^- \rightleftharpoons (FeOH)_{ads} + e^-$$
 Reaction (10)

$$Fe + OH^- + (FeOH)_{ads} \xrightarrow{RDS} (FeOH)_{ads} + (FeOH)^+ + 2e^-$$
 Reaction (11)

$$(FeOH)^+ + H^+ \rightleftharpoons Fe^{2+} + H_2O$$
 Reaction (12)

The "consecutive mechanism", which is shown through Reaction (13) - Reaction (16), was reported to be associated with Tafel slope of 40 mV, ($\alpha = \frac{2}{3}$). In addition, the reaction rate was reported to have first order dependence on hydroxyl ion (OH⁻) concentrations. This mechanism considers the electrode surface coverage due to the adsorption of water molecules, hydroxyl ions, and intermediate adsorbed species (FeOH)_{ads} [63], [64].

- $Fe + H_2 0 \rightleftharpoons Fe. H_2 O_{ads}$ Reaction (13)
- $Fe. H_2O_{ads} \rightleftharpoons (FeOH^-)_{ads} + H^+$ Reaction (14)
- $(FeOH^-)_{ads} \rightleftharpoons (FeOH)_{ads} + e^-$ Reaction (15)

 $(FeOH)_{ads} \xrightarrow{RDS} (FeOH)^+ + e^-$ Reaction (16)

 $(FeOH)^+ + H^+ \rightleftharpoons Fe^{2+} + H_2O$ Reaction (17)

According to the previous studies, it can be concluded that either mechanism could be valid depending on the microstructure of the surface as well as the experimental conditions such as the effect of the presence of anions such as halides which was not considered in these mechanisms [67]. It should be noted that these mechanisms have been proposed based on the experiments in the active dissolution region, however, the experimental results in wider range showed more complex behavior which are not consistent with these mechanisms. Lorenz and co-workers [68], [69] published several papers investigating the iron dissolution reaction in wider anodic range including transition and pre-passivation regions. They found that iron dissolution could occur through a combination of consecutive and catalytic mechanisms such that the consecutive mechanism controls the active dissolution range (low overpotential) and the catalytic mechanism controls the transition and the pre-passivation ranges (high overpotential) [68]–[71].

By the emergence of electrochemical impedance spectroscopy (EIS) as a powerful tool for exploring the reaction mechanism, starting from 1970s, this thriving technique has been used by couple of research groups, i.e., Keddam and co-workers, for investigation of the mechanism of iron dissolution reaction. In one of the most comprehensive studies, Keddam et al. [72], [73]investigated the iron dissolution mechanism in acidic solution in a wide range of pH (0-5), and proposed a mechanism involving three different paths, each one dominating at a certain overpotential. At low overpotential, the consecutive mechanism dominates the overall reactions while a self-catalytic mechanism with a ferrous intermediate (Fe(II)_{ads}) dominates at high

overpotential. A third self-catalytic path with a monovalent iron intermediate (Fe(I)_{ads}) also contributes to the impedance and current density of the overall reaction, although its contribution does not prevail in any region. Many other studies have used electrochemical impedance spectroscopy to find the iron dissolution mechanism during past years, however, use of various steady-state and transient techniques did not lead to a conclusive and unified mechanism until now [74]–[76].

Since the effect of anodic dissolution reaction in corrosion process is limited to the active dissolution and transition regions, it could be helpful to ending this section by proposing one of the most plausible mechanisms based found in the literature. In this mechanism, as illustrated in *Figure 8*, iron dissolution occurs through both consecutive and catalytic mechanisms in parallel with two different adsorbed species. This mechanism was verified in previous studies in various acidic solutions even when considering the effect of anions [77], [78].

$$Fe \xrightarrow{K_1} Fe(I)_{ads} \xrightarrow{K_2} Fe(II)_{sol}$$

$$K_{-3} \downarrow K_3 \qquad K_4$$

$$Fe(I)^* ads$$

 $Fe(I)^*ads + Fe \xrightarrow{K_4} Fe(II)sol + Fe(I)^*ads + 2e^-$

Figure 8. Mechanism of iron dissolution in active dissolution and transition regions [77], [78].

Effect of H₂S on Iron Dissolution Reaction. The aforementioned studies

conducted in recent years elucidated the mechanism of cathodic reaction in aqueous H2S

environments to a large extent; however, very little is known about the exact mechanism of anodic iron dissolution in the presence of dissolved H₂S. The available experimental data are limited, and the mechanistic studies are rather immature [58], [79]-[82]. The early research on the anodic dissolution of iron in the H₂S-containing solutions could be found in a study by Iofa et al. in 1965 [79]. Iofa et al. observed that the presence of H₂S 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 [79]. 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} [62]. In another study, Morris et al. reported that the increase of H_2S 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 H_2S . Apparently, the Tafel slope of anodic reaction and exchange current density remained unaffected by H₂S presence [58]. 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 (18)), followed by an oxidation step involving a twoelectron transfer step (Reaction (19)). In this mechanism, depending on the experimental conditions, the produced (FeSH⁺)_{ads} could either convert to a corrosion products layer (Reaction (20), i.e., inhibition effect), or it can further hydrolyze to Fe^{2+} (Reaction (21))) [56].

$$Fe + H_2S + H_2O \rightarrow (FeSH^-)_{ads} + H_3O^+ \qquad \text{Reaction (18)}$$

$$(FeSH^-)_{ads} \rightarrow (FeSH^+)_{ads} + 2e^- \qquad \text{Reaction (19)}$$

$$(FeSH^+)_{ads} \rightarrow FeS_{1-x} + xSH^- + (1-x)H^+ \qquad \text{Reaction (20)}$$

$$(FeSH^+)_{ads} + H_3O^+ \rightarrow Fe^{2+} + H_2S + H_2O \qquad \text{Reaction (21)}$$

The acceleration effect that dissolved H₂S can have on iron dissolution was further investigated by Cheng et al. [83] 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 $[H_2S]/[H_3O^+] < 10^{1.5}$), 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 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 (19), each step including one-electron transfer [83]. Therefore, the first step of anodic dissolution in sour media was claimed to be the chemisorption of H₂S according to the Reaction (22) followed by several oxidation steps which finally converts (FeSH⁻)_{ads} to Fe²⁺ according to Reaction (23) - Reaction (25) [80], [83]:

$Fe + H_2S + H_2O \rightarrow (FeSH^-)_{ads} + H_3O^+$	Reaction (22)
$(\text{FeSH}^-)_{\text{ads}} \rightarrow (FeSH)_{\text{ads}} + e^-$	Reaction (23)
$(FeSH)_{ads} \rightarrow FeSH^+ + e^-$	Reaction (24)
$FeSH^+ + H_3O^+ \rightarrow Fe^{2+} + H_2S + H_2O$	Reaction (25)

This study was accompanied by a series of publications by Ma et al. [80]-[82] through impedance spectroscopy analysis of the effect of H₂S 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 H₂S. The low-frequency loop was marked as the characteristic of H₂S adsorption on the surface of the iron. At higher overpotentials (with respect to corrosion potential), the capacitive loop at lower frequencies, ascribed to H₂S 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 Reaction (22) and Reaction (23) occurring as a single step described by Reaction (26) [56], [63], [80], [81].

$$Fe + H_2S + H_2O \rightarrow (FeSH)_{ads} + H_3O^+ + e^- \qquad \text{Reaction} (26)$$

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 (20), 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 2h) [82].

Finally, in the study by Zheng et al., they assumed a similar mechanism as proposed by Bockris et al. [84] 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 [47].

Literature Review of Modeling of Mild Steel Corrosion in H₂S Aqueous Solutions

Thus far, the electrochemical reactions involved in the corrosion of mild steel in H₂S environments were reviewed. This section focuses on a historical review on the mathematical models developed for corrosion of mild steel in sour systems. In addition, the concept of mass transfer which plays an important role in the modeling of corrosion rate specifically in oil and gas pipelines as well as various experimental systems, is described here.

The mathematical models for corrosion rate prediction of mild steel pipelines can be generally classified in three categories depending on the level of theoretical and mechanistic foundations implemented into the model. Empirical/semi-empirical models rely only on mathematical functions fitted to the experimental data. These mathematical functions are either arbitrarily chosen or based upon elementary theoretical principles. Elementary mechanistic models implement simplified theories of corrosion processes. Lastly, comprehensive mechanistic models are the most advanced type and rooted in the physicochemical fundamentals of corrosion processes [14], [67].

The empirical/semi-empirical models, such as the famous de Waard and Milliams model [85] were proposed historically prior to other types. These models have been only provided for CO₂ corrosion of steel and did not account for the effect of H₂S. The elementary mechanistic models have been also derived initially for CO₂ corrosion by the work of Gray et al., [86], [87]and the effect of the presence of H₂S has not been included until late '90s in a study published by Anderko et al. [88], [89]. Nonetheless, understanding the approach used by Gray et al. is necessary as it was used as the core of other elementary mechanistic models proposed later on for H₂S corrosion. Grey et al. considered iron dissolution reaction as the only anodic reaction, and hydrogen ion reduction reaction and direct reduction of carbonic acid as the cathodic reactions [86], [87]. Gray et al. proposed that the cathodic reaction includes two regions: charge transfer controlled, and mass transfer controlled. The same concept has been used as a basis for later studies and the model has been improved later on by the publication of Nesic et al. [90], [91]. The total cathodic current density can be calculated with a correlation, as shown by Equation (9), including mixed charge transfer controlled and mass transfer controlled regions.

$$\frac{1}{i_{tot}} = \frac{1}{i_{ct}} + \frac{1}{i_{lim}}$$
 Equation (9)

The current density associated with charge transfer can be found from so-called Tafel equation (Equation (10)), which is a simplified approximation of Butler-Volmer equation at high overpotentials.

$$i = i_0 \times 10^{-\frac{\eta}{b}}$$
 Equation (10)

where i_0 (A.m⁻²) is the exchange current density, *b* (V.dec⁻¹) is the Tafel slope, and η (V) is the overpotential, which equals to difference between the applied potential and the equilibrium potential of the associated reaction. Exchange current density can be calculated by Equation (11).

$$i_0 = i_0^{ref} \left(\frac{C_{H^+}}{C_{H^+}^{ref}}\right)^{0.5} \times e^{-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{T^{ref}})}$$
Equation (11)

where i_0^{ref} (A.m⁻²) is the reference exchange current density, C_{H^+} (M) concentration of H⁺ in bulk, $C_{H^+}^{ref}$ (M) is the reference bulk concentration, ΔH (J.mol⁻¹) is the enthalpy of activation, T (K) is the temperature, and T^{ref} is the reference temperature. All the values for the mentioned parameters and more details of calculations can be found elsewhere [91]. In addition, the Tafel slope is defined as Equation (12):

$$b = \frac{2.303RT}{\alpha nF}$$
 Equation (12)

where α is called charge transfer coefficient. It should be mentioned that the current density of the anodic iron dissolution reaction can also be calculated by a similar Tafel equation with different values for the related parameters. More details can be found in the related references [91].

The limiting current density in Equation (9) represents the contribution of mass transfer and depends on the geometry of the system. Equation (13) is the general form of describing current density based on the mass transfer of reactant species.

$$i_{lim} = nFk_m C_i^b$$
 Equation (13)

where k_m (m.s⁻¹) is called mass transfer coefficient and depends on the Sherwood number through Equation (14).

$$k_m = \operatorname{Sh} \frac{D_i}{L}$$
 Equation (14)

L (m) is the characteristic length of the specific geometry, and D_i (m².s⁻¹) is the diffusion coefficient of species. Numerous empirical correlations have been proposed for the calculation of Sherwood number pipeline as well as different experimental systems which can be found in related references [92]–[94].

The equations described above first reported for the corrosion of mild steel in CO_2 environments, but the same approach was later used for the case of H₂S corrosion. The effect of H₂S in elementary mechanistic models first appeared in 1999 by Anderko et al., [88], [89] grounded in the models developed earlier by Gray and Nesic, the effect of H₂S has been incorporated in both cathodic and anodic reactions. On that account, a cathodic current due to the direct reduction of H₂S and an anodic current proportional to the surface coverage of HS⁻ ions have been added to calculations. Surprisingly, the added cathodic current has been assumed totally under charge transfer control since H₂S has been considered to be always available on the electrode surface. This assumption seems irrational as previous experimental studies [55], [58] already proved that the presence of H₂S increases the cathodic limiting current.

One of the earliest mathematical models for corrosion rate prediction of mild steel in H₂S environments has been published in 2009 by Sun and Nesic [7]. Since the model was developed for mild steel corrosion in the presence of corrosion products layer, the authors assumed that the corrosion process are always under mass-transfer control. Hence, the electrochemical reactions including cathodic and anodic reactions have been totally neglected. Although this was the first attempt in modeling H_2S corrosion, the lack of the kinetic of electrochemical reactions did not allow for proper mechanistic representation of the corrosion processes. Later on, the elementary mechanistic modeling of H_2S corrosion reached its well-established form by a series of paper published by Zheng et al. [47], [95]. The first study emerged in 2014 for bare steel corrosion in pure H₂S environment considering the electrochemical reactions as well as mass transfer using a rotating cylinder electrode (RCE) apparatus. Three electrochemical reactions have been contributed into total cathodic reaction namely: hydrogen ion reduction reaction, direct reduction of H₂S, and water reduction reaction. The cathodic current density of two former reactions has been calculated using Equation (9), considering the reactions under mixed mass and charge transfer control while the water reduction reaction was totally under charge transfer control. As for anodic reaction, the current density was related to the surface coverage of OH^- through Bockris mechanism in the absence of aqueous H_2S , while it was related to the surface coverage of HS⁻ ion (the contribution of OH⁻ was totally neglected) in the presence of H₂S. The unavailable constants have been found based on their best-fit values to the experimental results. The simultaneous consideration of electrochemical reactions and mass transfer processes, for the first time, lead to the modeling of polarization curves in addition to the corrosion rates. The performance of model has been examined using the experimental results in various conditions covering
different pH values, velocity, temperature, and partial pressure of H_2S up to 0.1 bar, and good agreement has been achieved [47]. The sequel paper [95] has extended the scope to more realistic field conditions of sour corrosion by including a mixed CO₂/H₂S containing solutions. The presence of CO_2 has been considered by adding the reduction of H_2CO_3 in cathodic reactions using the values found previously for pure CO_2 corrosion study [90]. However, the exchange current has been decreased by a factor of 3 in presence of H_2S since the experimental results showed the retardation of H_2CO_3 reduction reaction when H₂S was present in the system. It should be noted that the factor 3 that was selected by the authors has no mechanistic basis and only used to fit the model to the experimental data. As it was discussed, the homogenous chemical reaction, i.e., buffering effect, has been totally disregarded in this study which could lead to the observed inconsistency. Here, encountering the main weakness of elementary mechanistic models which is their inability to incorporate homogenous chemical reactions since the species are assumed to be independent of each other in the mass transfer boundary layer. Zheng et al. also developed a model for mixed CO₂/H₂S corrosion in the presence of corrosion products layers[96]. In another study, Esmaeely et al. verified the model proposed by Zheng et al. for pure H₂S Corrosion of steel in absence of corrosion products for H₂S partial pressures up to 1 bar. The modeling results were in reasonable agreement with the experimental data for a broad range of experimental conditions: pH 3 to 5, temperature 30 and 80 °C, and rotating cylinder rotational speed of 100 and 1000 rpm [97].

In order to address the weaknesses observed in elementary mechanistic models, comprehensive mechanistic models have been developed based on the fundamental physicochemical laws. These models were able to predict concentration of species in mass transfer diffusion layer specifically at electrode surface by simultaneously implementing the Nernst-Planck equation and homogenous chemical reactions in the diffusion layer combined with heterogenous electrochemical reactions occurring at electrode surface. Therefore, mass conservation law for species *i* inside the mass transfer diffusion layer can be described as :

$$\frac{\partial C_i}{\partial t} = -\nabla N_i + R_i = D_i \frac{\partial^2 C_i}{\partial x^2} + \left(\frac{z_i D_i F}{RT}\right) \frac{\partial}{\partial x} \left(C_i \frac{\partial \Phi}{\partial x}\right) + v_x \frac{\partial C_i}{\partial x} + R_i \qquad \text{Equation (15)}$$

This equation considers the contribution of three types of transport phenomena involved in the system: diffusion, electromigration, and convection. The R_i term accounts for the rate of production or consumption of species *i* inside the mass transfer diffusion layer by homogenous chemical reactions. Different types of transport phenomena and the homogenous reaction term will be clarified in the next chapter.

This mechanistic approach has been appeared in simplistic way in CO₂ corrosion in early 1990 and then in more complete fashion in early 2000's through publications of Nesic et al. [91]. However, it was not implemented in H₂S corrosion until 2013 in papers published by Tribollet et al. for modeling of cathodic reactions on a stainless steel rotating disk electrode in aqueous H₂S solutions [61]. A simplified mass conservation equation has been used considering hydrogen reduction reaction as well as direct reduction of hydrogen sulfide occurring at the surface of electrode. The anodic current and corrosion rate predictions were not in the scope of this research, and the model was only used to predict the cathodic polarization curves. Although the simulated results were in good agreement with experimental data in some conditions, discrepancies were observed for various rotational speeds [61].

A comprehensive mechanistic model for corrosion rate prediction of mild steel in oil and gas transmission pipelines (MulticorpTM) has been laid out in 2019 by Nesic et al. [14]. This model considered the major corrosion environments, including H₂S environment in the absence as well as the presence of iron sulfides corrosion products. The model was developed based on the complete form of Equation (15) and accounted for the buffering ability of H₂S. The boundary condition at electrode surface still considered the direct reduction of H₂S, while iron dissolution reaction was assumed to follow Bockris mechanism. Finally, the performance of the model was assessed by comparing the predicted corrosion rates with the existing experimental database of the Institute for Corrosion and Multiphase Technology (ICMT), where a good agreement was obtained [14].

Finally, in the most recent study, Kahyarian and Nesic [46] implemented the comprehensive mechanistic model using the complete form of Nernst-Plank equation and showed that H₂S is contributing to the cathodic current only through buffering effect, and the contribution of the direct reduction of H₂S in the cathodic current was shown to be insignificant. The authors successfully predicted the cathodic current density of mild steel in a wide range of experimental conditions considering only the hydrogen evolution

reaction and buffering effect; however, this study was limited to cathodic reaction, and thus the corrosion rate prediction was not provided [46]. A more complete version of this with a prediction model for the corrosion rate of mild steel in H₂S aqueous solutions has been published by Sharifi et al. [98]. The next chapter contains the results of this paper with a new simplified approach proposed in this dissertation.

Chapter 4.B: New Modeling Approaches²

The current chapter is an effort to provide new approaches to the modeling of mild steel corrosion in the presence of H₂S based on the latest mechanistic understandings of this system. Within this context, the first section proposes a predictive model for the corrosion rate prediction of mild steel in H₂S aqueous solutions which is mechanistically constructed on the buffering effect mechanism and mathematically derived from Nernst-Plank equation. The second part presents several mathematical correlations for the prediction of cathodic region, specifically mass transfer limiting current which would be valuable for any studies dealing with corrosion rate prediction in acidic solutions.

 $^{^{2}}$ A version of this chapter was published as part of a journal publication: P. S. Abdar, M. B. Hariri, A. Kahyarian, and S. Nesic, "A revision of mechanistic modeling of mild steel corrosion in H₂S environments," Electrochimica Acta, vol. 382, p. 138231, Jun. 2021.

A Predictive Model for Polarization Response and Corrosion Rate Prediction of Mild Steel in Aqueous H₂S Solutions

This section provides a predictive model for the corrosion rate and the polarization response of bare steel in aqueous hydrogen sulfide (H₂S) environments based on H₂S dissociation and its buffering effect. Hence, hydrogen ion reduction is the only cathodic reaction. Also, for the anodic region, the effect of hydrogen sulfide on the rate of iron dissolution reaction was also taken into account by introducing a reaction sequence involving sulfide intermediates into the calculations, parallel to the acidic iron dissolution reaction. This concept has been introduced for the first time in this study. The model used Nernst-Plank equation as a representative of transport processes occurring in the system. However, this equation was simplified by introducing several assumptions which are physically relevant to the electrochemical system used here. This simplified version has the advantage of using simpler mathematical equations which facilitate as well as accelerate the numerical calculations needed for determining the results. At the same time, this simplified model does not affect the accuracy of the results since the applied assumptions were physically appropriate. In order to verify the validity of the developed model, it was compared to experimental data from open literatures in a wide range of environmental conditions.

Mathematical Model

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 references [46], [99]. 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, turbulent convection, as well as the simultaneously occurring homogeneous chemical reactions and heterogeneous electrochemical reactions.

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 Equation (16) [100].

$$\frac{\partial C_i}{\partial t} = -\nabla . N_i + R_i$$
 Equation (16)

In this equation, N_i is the flux of species *i*, represented as Equation (17), and R_i describes the chemical reactions in which species *i* is either produced or consumed.

$$N_i = -z_i u_i F C_i \nabla \Phi - D_i \nabla C_i + v C_i$$
 Equation (17)

As it is seen in Equation (17), 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 (m².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 v [100].

Noting that the convective term in Equation (17) 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 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 [101]. 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 [101], [102]. Equation (17) can, therefore, be reorganized to give Equation (18).

$$N_i = -z_i u_i F C_i \nabla \Phi - (D_i + D_t) \nabla C_i \qquad \text{Equation (18)}$$

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 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 Equation (16) in Equation (18), they can be expressed in their final styles as Equation (19) and Equation (20).

$$N_{i} = -(D_{i} + D_{t})\frac{\partial C_{i}}{\partial x} - \frac{z_{i}D_{i}FC_{i}}{RT}\frac{\partial \Phi}{\partial x}$$
Equation (19)
$$\frac{\partial C_{i}}{\partial t} = \frac{\partial}{\partial x}\left((D_{i} + D_{t})\frac{\partial C_{i}}{\partial x}\right) + \left(\frac{z_{i}D_{i}F}{RT}\right)\frac{\partial}{\partial x}\left(C_{i}\frac{\partial \Phi}{\partial x}\right) + R_{i}$$
Equation (20)

Now, some assumptions could be helpful in order to mathematically simply these equations. First, the equations can be assumed as steady state, therefore the timedependent term in the left side of Equation (20) equals to zero. This assumption is definitely valid and represents the real experimental conditions. The polarization measurements normally sweeps at such a slow scan rate that the electrochemical reactions remain in steady state condition. The second assumption is to disregard mass transport due to electromigration. This assumption has also logical validity as all the corrosion measurements in real situations were performed in solutions with supporting electrolyte, i.e., high ionic strength and conductivity, in order to eliminate the effect of migration of ions in electric field. That being said, the above equations can be rewritten in the simpler format as shown in Equation (21) and Equation (22), which are the final equations that are solved for the modeling of electrochemical currents as well as corrosion rates.

$$N_i = -(D_i + D_t)\frac{\partial C_i}{\partial x}$$
 Equation (21)

$$0 = \frac{\partial}{\partial x} \left((D_i + D_t) \frac{\partial C_i}{\partial x} \right) + R_i$$
 Equation (22)

The values of molecular diffusivity (D_i) for each species in the equations above are listed in **Table 3**.

Table 3.

Reference diffusion coefficients for different species at infinite dilution and 25 °C.

Species	Diffusion coefficient / (m ² ·s ⁻¹)	Reference
H ₂ S	1.93×10^{-9}	[103]
HS ⁻	1.731×10^{-9}	[104]
S ²⁻	1.5×10^{-9}	[46]
OH^-	5.273×10^{-9}	[104]
H^+	9.312×10^{-9}	[100]
Cl ⁻	2.032×10^{-9}	[100], [104]
Na ⁺	1.334×10^{-9}	[100]

In order to obtain the molecular diffusivity at different temperatures, the Stokes-Einstein relationship, as described in Table 4, can be used [100]. Table 4.

 Parameter
 Relationship
 Reference

 Diffusion coefficient
 $D_i = D_{i,ref} \frac{T}{T_{ref}} \frac{\mu_{ref}}{\mu}$ [100]

 Water density / (kg.m⁻³)
 $\rho_w = 753.596 + 1.87748 T - 0.003562 T^2$ [91]

 Water viscosity / (cP)
 $\mu = \mu_{ref} 10^{\left(\frac{1.1709 \left(T_{ref} - T\right) - 0.001827 \left(T_{ref} - T\right)^2}{(T - 273.15) + 89.93}\right)}$ [105]

 $T_{ref} = 293.15 K, \mu_{ref} = 1.002 cP$ $T_{ref} = 293.15 K, \mu_{ref} = 1.002 cP$ [105]

Temperature dependence of physicochemical properties

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 Equation (23) suggested by Arvanith [102]:

$$D_t = v \frac{0.0007x^{+3}}{[1 + 0.00405x^{+2}]^{1/2}}$$
 Equation (23)

where $v = \mu/\rho$ is kinematic viscosity (m².s⁻¹) of water and can be found using the equations in Table 4. The x^+ is the dimensionless distance from the wall obtained from Equation (24). This equation is valid when $x^+ < 30$, and it is universal for all turbulent flow if appropriate dimensionless parameters are implemented.

$$x^{+} = \frac{x(\frac{\tau_{w}}{\rho})^{0.5}}{v}$$
 Equation (24)

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 4, 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 :

$$\tau_w = \frac{1}{2}\rho C_f V^2 \qquad \qquad \text{Equation (25)}$$

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 [106], which is expressed using the Darcy friction factor ($C_f = 4C_d$), represented by Equation (26). This equation is an explicit version of the implicit Colebrook-White correlation [107].

$$C_d = 0.25 \left[\log\left(\frac{\frac{\varepsilon}{D_{eq}}}{3.7} + \frac{5.74}{Re^{0.9}}\right) \right]^{-2}$$
 Equation (26)

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 Equation (22) 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 (27) with the reaction rate evaluated by Equation (27), where $k_{f,j}$, and $k_{b,j}$ are the kinetic rate constants of the "forward" and "backward" reactions, respectively. Reaction (4), Reaction (5), and Reaction (6), i.e., dissociation of H₂S, HS⁻, and water, respectively, are estimated with kinetic rate constants listed in Table 2.

$$\sum_{r=1}^{n_r} C_r \rightleftharpoons \sum_{p=1}^{n_p} C_p$$
Reaction (27)
$$R_j = k_{f,j} \prod_{r=1}^{n_r} C_r - k_{b,j} \prod_{p=1}^{n_p} C_p$$
Equation (27)

The rate of reaction R_i , of each species *i*, involved in *j* chemical reactions can be determined using Equation (28) with $s_{i,j}$ being the stoichiometric coefficient of species *i* in reaction *j*.

$$R_i = \sum_{j} R_i s_{i,j}$$
 Equation (28)

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

Equation (22); in fact, one of those equations is written for each species *i* and the set of coupled partial differential equations is then simultaneously solved.

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 Equation (29), where s_i is the stoichiometric coefficient, and other terms have their common electrochemical meaning.

$$N_i|_{x=0} = -\frac{S_i l_i}{nF}$$
 Equation (29)

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

$$N_{H^+}|_{x=0} = -\frac{\iota_{C,H^+}}{E}$$
 Equation (30)

 $N_{Fe^{2+}}|_{x=0} = -\frac{i_{A,Fe^{2+}}}{2F}$ Equation (31)

The cathodic current density associated with H^+ reduction reaction can be described using the standard electrochemical kinetics [46]:

$$i_{C,H^+} = -n_{H^+}Fk_{0,H^+}C_{H^+}^{S} \stackrel{m_{H^+}}{=} \exp\left(\frac{-\alpha_{H^+}n_{H^+}F(E_{app})}{RT}\right) \qquad \text{Equation (32)}$$

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 $k_{0,H^+} = 1.2 \times 10^{-8} \text{ (mol}^{0.5} \text{.m}^{-0.5} \text{.s}^{-1} \text{)}$ 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.

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 \sim 40 mV.dec⁻¹ Tafel slope is observed, this reaction is commonly believed to follow the mechanism proposed by Bockris et al. [63]. The rate of iron dissolution in the active dissolution range and in acidic solutions can, therefore, be expressed as:

$$i_{A,OH^{-}} = n_{Fe^{2+}}Fk_{0,OH^{-}}C_{H^{+}}^{S} {}^{m}{}_{H^{+}}exp\left(\frac{\alpha_{j}FE_{app}}{RT}\right)$$
 Equation (33)

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 H₂S 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 H₂S is beyond the scope of the present study. Regardless, in order to in some way represent the contribution of H₂S in iron dissolution, as a critical part of H₂S 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:

$$i_{A,HS^{-}} = n_{Fe^{2+}}Fk_{0,HS^{-}}C_{HS^{-}}^{S} {}^{m_{HS^{-}}}exp\left(\frac{\alpha_{j}FE_{app}}{RT}\right)$$
 Equation (34)

where the parameters have a similar meaning as those in Equation (33).

Assuming $\alpha_j = 1.5$, the values of $k_{0,OH^-} = 5 \times 10^4 \pmod{2.5^{-1}}$, $m_{H^+} = 1$, $k_{0,HS^-} = 2 \times 10^7 \pmod{0.5 \cdot m^{-0.5} \cdot s^{-1}}$, and $m_{HS^-} = 0.5$ 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 ($i_{A,Fe^{2+}}$) can be calculated as a superposition of two parallel reaction rates (i_{A,OH^-} and i_{A,HS^-}). As a result, Equation (31) can be rearranged as Equation (35):

$$N_{Fe^{2+}}|_{x=0} = -\frac{i_{A,OH^-} + i_{A,HS^-}}{2F}$$
 Equation (35)

Figure 9 represents an example of the simulation results for the iron dissolution at different partial pressures of H₂S and various pH. The considerable effect of H₂S presence on the kinetics of the anodic reaction is evident, specifically at higher partial pressures of H₂S. At higher partial pressures of H₂S, the rate of the anodic reaction accounting for the contribution of H₂S in iron dissolution, i.e., i_{A,HS^-} , increases thereby enhancing the total anodic current. Figure 9 shows that the increment of anodic current due to the presence of H₂S is higher in pH 4 compared to that at pH 5. This implies that the contribution of H₂S on the mechanism of anodic dissolution becomes more notable in more acidic environments due to the lower concentrations of OH⁻ in such conditions.



Figure 9. Simulated anodic polarization curve for various partial pressures of H₂S at 30°C and pH 4 and 5.

Numerical Solution. Finite different method (FDM) was used to solve a set of coupled and non-linear partial differential equations, as listed in **Table 5**. The solution algorithm is similar to that discussed in detail in earlier studies [46], [99]. 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. The explicit scheme of time integration is used using Euler approximation. Regarding the non-linearity of the system, the solution at each time step is obtained iteratively until the desired accuracy of $R^2 = 10^{-10}$ is achieved (R^2 is the sum of the squared normalized errors for all unknown concentrations being calculated in this model). MATLAB software was used for numerical coding and simulations.

Table 5.

Summary of equations used in the mathematical model

Electrode surface boundary	
$N_i _{x=0} = -\frac{s_{ij}i_j}{n_j F}$	for all electro-active species
$N_i _{x=0}=0$	for all non-electroactive species
Diffusion boundary layer	
$0 = \frac{\partial}{\partial x} \left((D_i + D_t) \frac{\partial C_i}{\partial x} \right) + R_i$	for all species
Bulk boundary conditions	
$C_i = C_i^b$	

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. [47], [97]. 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 ($pH_2S = 0 - 1$ 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 [94]) with that for straight flow pipe (proposed by Berger and Hau [92]), to get

$$v_{\text{pipe}} = 3.09 \text{Sc}^{0.03} v^{0.186} \Omega_{\text{RCE}}^{0.814} d_{\text{RCE}}^{0.43} d_{\text{PIPE}}^{0.163} \qquad \text{Equation (36)}$$

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.

Figure 10 shows a comparison between the model (black broken lines) and the experimental cathodic and anodic polarization branches at different H₂S concentrations and fixed pH of 4.



Figure 10. 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. [47], 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 H_2S). Generally, it is seen that the limiting current densities increase as the H_2S content increases, which agrees well with the expected buffering effect of H_2S in such systems. The increase of H_2S 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 [46]. It worth noting that a broad "linear" current density range is seen in some conditions, for example, for $pH_2S = 0.1$ bar in Figure 10. 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 Figure 10 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 Figure 10, 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 H_2S 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 H_2S 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 bar to 0.1 bar. This behavior was previously attributed to the direct H_2S reduction reaction [47], [48], [61]. 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 *Figure 11*. The increase in the anodic current with higher H_2S is also reported elsewhere [83], [81], [58], suggesting that H_2S or other sulfide species can introduce parallel anodic pathways to the iron dissolution reaction. However, at the conditions of Figure 10, 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.

Figure 11 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 bar and 1 bar.





Figure 11. 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. The data for $pH_2S = 0.1$ bar and $pH_2S = 1$ bar were taken from Zheng et al. [47] and Esmaeely et al. [97], respectively.

The observed cathodic polarization behavior is in general agreement with that shown in Figure 10. 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 distinctive 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 *Figure 11*.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 H_2S chemical dissociation and the H_2S mass transfer.

The change in anodic current with pH₂S is more substantial at the H₂S partial pressure of 1 bar shown in *Figure 11*, compared to that seen in Figure 10 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 well-known Bockris mechanism [63], 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 [63]. 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 [47], [97]. 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 Equation (37) and Equation (38)[99], [108].

$$I_{corr} = \frac{B}{R_p}$$
 Equation (37)

$$CR = 1.16 \frac{B}{R_p/A}$$
 Equation (38)

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 Equation (39)[99], [108]:

$$B = \frac{b'_a b'_c}{2.303(b'_a + b_{\prime c})}$$
Equation (39)

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 6 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 $b_a = 40$ mV.dec⁻¹, and $b_c = 120$ mV.dec⁻¹, the value of the corrected B = 13 mV, is about half of what is assumed in the original study.

Table 6.

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	2.39	[109]
3	0.81	0.1	23	13	10.4	5.89	4.19	[109]
3	0.81	1	23	17	8.8	6.65	5.57	[110]
4	0.81	0	23	17	1.6	1.21	1.24	[109]
4	0.81	0.0001	23	17	1.22	0.92	1.28	[109]
4	0.81	0.001	23	17	1.3	0.98	1.35	[109]
4	0.81	0.01	23	17	1.55	1.17	1.43	[109]
4	0.81	0.1	23	17	1.95	1.47	1.92	[109]
4	0.81	1	23	13	4.4	2.49	2.98	[110]
4	0.22	0.01	23	17	1.0	0.76	0.89	[109]
4	2.50	0.01	23	17	2.0	1.51	1.82	[109]
4	0.22	0.1	23	17	1.2	0.91	1.19	[109]
4	2.50	0.1	23	17	2.45	1.85	2.27	[109]
5	0.81	0.0001	23	17	0.3	0.23	0.29	[109]
5	0.81	0.1	23	17	1.15	0.87	1.24	[109]
5	0.81	1	23	13	3.1	1.76	1.82	[110]

Summary of corrosion rate data from the existing literature, and the correction for B.

The comparison of the predicted corrosion rates with that obtained experimentally at pH 4 for various pH₂S is shown in Figure 12. Generally, a good agreement is obtained for the corrosion rate variation as a function of pH₂S. This trend is due to the effect of H₂S on both the cathodic and anodic reactions. The presence of H₂S 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 pH₂S range are compared to those with no H₂S, a small decline in corrosion rate is reported, which was not predicted by the model. The difference can, to some extent, be associated 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 electro-active surface area on the electrode [47]. However, this effect is not significant in high pH₂S since the corrosion rate significantly increases due to the presence of high concentration of H_2S .



Figure 12. Comparison of corrosion rate prediction by the present model (red dashed line) with experimental data (blue 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 error bars represent the deviations from the average values in repeated experiments. The experimental data are taken from Esmaeely et al. [97], and Zheng et al. [47].

In Figure 13, 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. Figure 13 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 Figure 13. 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.



Figure 13. 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 error bars represent the deviations from the average values in repeated experiments. The experimental data are taken from Esmaeely et al. [97], and Zheng et al. [47].

Figure 14 compares the experimental versus predicted corrosion rate, indicating the influence of pH – another critical parameter in aqueous H_2S corrosion of mild steel. Figure 14 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 [14], [46]. Furthermore, in more acidic solutions such as pH 3, the influence of the contribution of H₂S to the anodic reaction rate is amplified due to the decrease of anodic current obtained via the Bockris mechanism. Figure 14 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.



Figure 14. 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 pH₂S at 30°C and 1000 rpm RCE (equivalent to 0.81 m.s⁻¹ in pipe flow with 0.012 m ID). The error bars represent the deviations from the average values in repeated experiments. The experimental data are taken from Esmaeely et al. [97], and Zheng et al. [47].

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 Figure 15. 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 Figure 15 is about 22.8%, showing the capability of the presented model to predict the corrosion rates in a wide range of conditions reasonably well.



Figure 15. 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. The error bars represent the deviations from the average values in repeated experiments. Data were taken from studies by Zheng et al. (Red) [47] and Esmaeely et al. (blue) [97].

Summary

- A mechanistic mathematical model based on the buffering ability of H₂S was developed to predict the corrosion rate of mild steel in aqueous H₂S solutions.
- 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 successfully predict the corrosion rates of mild steel in H₂S environments over a wide range of conditions: from pH 3 to pH 5, velocity from 0.22 to 2.5 m.s⁻¹, and H₂S partial pressures up to 1 bar. The average absolute deviation of the predicted corrosion rates from the experimental data remained around 20%.

A Mathematical Correlation for the Cathodic Limiting Current in H₂S Aqueous Solutions

It was shown in the previous section that the presence of H₂S, like other weak acids, increases the limiting current of cathodic reactions by producing more H⁺ ions through buffering effect. When H₂S does not exist, i.e., strong acid solutions, the mass transfer limiting current for the hydrogen ion reduction occurs due to the depletion of H⁺ at the surface of electrode. Several correlations have been proposed for the evaluation of mass transfer limiting current for different geometries, for example, Levich equation is a famous correlation for the limiting current density of rotating disk electrodes (RDE) [92], [93], [111]. All the proposed correlations, in terms of corrosion in acidic environments, are dealing with strong acid solutions when weak acids do not exist. However, in the presence of weak acids, when H⁺ is depleted at the surface of electrodes, the weak acids dissociates to produce more H⁺ at the surface of electrode and thus increasing the current density of mass transfer limiting current. Cathodic limiting current plays an important role in determining the corrosion rate. Increasing the cathodic limiting current by increasing the mass transfer, e.g., increasing flow velocity, could lead to higher corrosion rate in many cases. Also, in some real situations, the cathodic current is equal to the mass transfer limiting current since the cathodic reaction is totally determined by the limiting current.

In order to find the cathodic limiting current due to the buffering effect, the complete mass conservation equation (Equation (20)) in the mass transfer boundary layer should be solved. Since this equation has non-linear terms, it can not be solved
analytically. Therefore, the best method to solve this equation is numerical methods which was implemented in the previous section. The results confirmed that the implementation of numerical method in mass conservation equation could successfully predict the cathodic current including the mass transfer limiting current. However, numerical methods are laborious which require discretization of equations which includes complex mathematical process, and expertise in coding software.

This section proposes a single mathematical correlation for the evaluation of cathodic limiting current for the weak acids, specifically for aqueous H₂S solutions. Several simplifying assumptions are needed to treat the non-linear mass conservation equation in an analytical approach. But these assumptions will be shown to have minor impact on the accuracy of the correlation. Finally, the correlation will be validated by comparing to the experimental results as well as mechanistic model solved with numerical methods as verified in the previous section.

Derivation of the Mathematical Correlation

Let us first assume the general case for a weak acid (HA) with only one dissociation step as shown in Equation (40).

$$HA \rightleftharpoons H^+ + A^-$$
 Equation (40)

The kinetic constant of this reaction depends on the rate of forward (k_f) and backward (k_b) reactions, as described in Equation (41).

$$K = \frac{C_{H^+}C_{A^-}}{C_{HA}} = \frac{k_f}{k_b}$$
 Equation (41)

Here, the first simplifying assumption can be implemented. Hence, assume that the concentration of conjugate base (C_A -) is a constant value. This assumption is valid when C_A - is very high such that it does not change significantly during the dissociation process. Considering this assumption, C_A - is no longer to be solved in mass transfer boundary layer, and a modified equilibrium kinetic constant (K') can be formatted as Equation (42).

$$K' = \frac{C_{H^+}}{C_{HA}} = \frac{k_f}{k_b C_{A^-}} = \frac{k_f}{k'_b}$$
 Equation (42)

The second assumption is to neglect the effect of electromigration as a transport process. The same assumption has been used in the previous section, and its validity has been verified. Also, the change of concentration of species in the mass transfer boundary layer can be considered as steady state. Once again, this assumption has been previously verified. Therefore, the flux of species and the complete mass conservation equation can be written as Equation (43) and Equation (44), respectively.

$$N_i = -D_i \frac{\partial C_i}{\partial x} + V_x C_i$$
 Equation (43)

$$0 = \frac{\partial}{\partial x} \left(D_i \frac{\partial C_i}{\partial x} - V_x C_i \right) + R_i = D_i \frac{\partial^2 C_i}{\partial x^2} - V_x \frac{\partial C_i}{\partial x} + R_i$$
 Equation (44)

The term V_x determines the velocity profile in the mass transfer boundary layer, and it indicates the effect of flow in the Nernst-Plank equation which depends on the flow properties and the geometry of the system. As V_x depends on the distance from electrode, it adds more complexity to the algebraic equation. Here, it can be assumed that V_x only determines the thickness of mass transfer boundary layer which is shown by δ_m . With this assumption, this term can be removed from the equation, instead, the equation can be solved from the surface of electrode to δ_m . As the concentration of A⁻ is constant, the equations will be solved only for two other species. As a result, the system of equations is written as the following two equations.

$$D_{HA} \frac{\partial^2 C_{HA}}{\partial x^2} + R_{HA} = 0$$
 Equation (45)
$$D_{H^+} \frac{\partial^2 C_{H^+}}{\partial x^2} + R_{H^+} = 0$$
 Equation (46)

Replacing the kinetic constants into the reaction rate term, the final equations can be reformatted as Equation (47) and Equation (48).

$$\frac{\partial^2 C_{HA}}{\partial x^2} + \frac{k'_b}{D_{HA}} C_{H^+} - \frac{k_f}{D_{HA}} C_{HA} = 0 \qquad \text{Equation (47)}$$

$$\frac{\partial^2 C_{H^+}}{\partial x^2} + \frac{k_f}{D_{H^+}} C_{HA} - \frac{k'_b}{D_{H^+}} C_{H^+} = 0 \qquad \text{Equation (48)}$$

These two equations should be solved simultaneously to find the concentration profiles of HA and H⁺ species. However, boundary conditions are required to solve these coupled equations. At the boundary of mass transfer layer and the bulk of solutions, which is the thickness of mass transfer boundary layer δ_m , the concentration of species is identical to their bulk concentration. At the surface of electrode, the boundary condition is different for HA and H⁺. To implement the mass transfer limiting current, the concentration of H⁺ is zero at the surface, as H⁺ ion is assumed to be completely depleted at the surface. For the case of HA, since it does not react at the surface of electrode, its flux is zero at the surface of electrode. **Table 7** lists the equations and the boundary conditions solved to obtain the concentration profiles.

Table 7.

Summary of equations and the boundary conditions

Electrode surface boundary
$$\left(\frac{\partial C_{HA}}{\partial x}\right)_{x=0} = 0$$

 $C_{H^+}=0$

Diffusion boundary layer $\frac{\partial^2 C_{HA}}{\partial x^2} + \frac{k'_b}{D_{HA}} C_{H^+} - \frac{k_f}{D_{HA}} C_{HA} = 0$ $\frac{\partial^2 C_{H^+}}{\partial x^2} + \frac{k_f}{D_{H^+}} C_{HA} - \frac{k'_b}{D_{H^+}} C_{H^+} = 0$ Bulk boundary conditions $C_{HA} = C_{HA}^b$ $C_{H^+} = C_{H^+}^b$

Solving these two coupled differential equations requires very complex mathematical process which describes completely in Appendix A. The concentration profile of HA and H⁺ species are found as described in Equation (49) and Equation (50), respectively.

$$\frac{C_{HA}}{C_{HA}^{b}} = \frac{x + \frac{D_{HA}}{D_{H^{+}} \frac{K'}{\delta_{r}}} \left[\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) - \frac{K'D_{H^{+}}}{D_{HA}} \frac{\sinh\left(\frac{x - \delta_{m}}{\delta_{r}}\right)}{\cosh\left(\frac{\delta_{m}}{\delta_{r}}\right)} \right]}{\delta_{m} + \frac{D_{HA}}{D_{H^{+}} \frac{K'}{\delta_{r}}} \tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}$$
Equation (49)

$$\frac{C_{H^+}}{C_{H^+}^b} = \frac{x + \frac{m_A}{D_{H^+} \frac{K'}{\delta_r}} \left[\tanh\left(\frac{-m}{\delta_r}\right) + \frac{m_A}{\cosh\left(\frac{\delta_m}{\delta_r}\right)} \right]}{\delta_m + \frac{D_{HA}}{D_{H^+} \frac{K'}{\delta_r}} \tanh\left(\frac{\delta_m}{\delta_r}\right)}$$
Equation (50)

The mass transfer limiting current is proportional to the flux of H^+ at the surface of electrode using Equation (51).

$$i_L = FD_{H^+} \left(\frac{dC_{H^+}}{dx}\right)_{x=0}$$
 Equation (51)

Taking the limit of the concentration profile at the surface of electrode and then implementing it into Equation (51), as presented in Appendix A, the final equation for the mass transfer limiting current density of hydrogen ion reduction reaction is given by Equation (52).

$$i_{L} = F \frac{D_{H} + C_{H}^{b} + D_{HA} C_{HA}^{b}}{\delta_{m} + \frac{D_{HA}}{D_{H} + \frac{K'}{\delta_{r}}} \tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}$$
Equation (52)

In addition, it is very important to consider that the thickness of mass transfer boundary layer (δ_m) should be calculated based on the weighted average diffusion coefficient (\overline{D}) of both species using Equation (53).

$$\overline{D} = \frac{D_{HA}C_{HA}^{b} + D_{H} + C_{H^{+}}^{b}}{C_{HA}^{b} + C_{H^{+}}^{b}}$$
Equation (53)

In Equation (52), δ_r is called chemical reaction layer thickness and can be evaluated by Equation (54).

$$\delta_r = \sqrt{\left(\frac{D_{HA}D_{H^+}}{k'_b D_{HA} + k_f D_{H^+}}\right)}$$
Equation (54)

The concept of chemical reaction layer has been explained in detail in several references [111]–[113]. The homogenous chemical reaction, i.e., dissociation of weak acid, is occurring in the mass transfer boundary layer, but it is in equilibrium in most parts of this region. In other words, the rate of forward reaction (dissociation of HA) is equal to the rate of backward reaction (recombination of H⁺ and A⁻). However, very close to the surface of electrode, in chemical reaction layer, the rate of forward reaction

(dissociation of HA) is significantly higher than the rate of backward reaction (recombination of H⁺ and A⁻), since H⁺ is depleted at the surface of electrode which shifts the chemical reaction to the left according to Le Chatelier's principle.

Verification of the Mathematical Correlation

In order to verify the mathematical correlation obtained for limiting current density as shown by Equation (52), the values calculated from this correlation was compared with the experimental results for aqueous hydrogen sulfide as well as acetic acid solutions. The correlation was also verified by comparing with the values obtained from numerical simulations discussed in the previous chapter. The correlation is based on the assumption that the weak acid has one dissociation step. This is not valid for the case of aqueous H₂S solutions as it is a diprotic weak acid. However, the second dissociation step has a pK_a value of about 17 [46], and thus it does not contribute to the buffering effect in the present experimental conditions. As a results, it can be assumed that H₂S is a weak acid with one dissociation step, and therefore Equation (52) is valid for this weak acid.

Figure 16 show the experimental cathodic polarization curves of mild steel in various partial pressure of H_2S at pH 4 which were taken from previous literatures [47], [97]. Also, it includes the values of cathodic limiting current density (dashed vertical lines) calculated using Equation (52). As can be observed, the calculated values match very well with the experimental results. A slight deviation can be seen for the case of 0.01 bar. Low concentration of H_2S in aqueous solutions results in low concentration of H_2S in aqueous so

of HS⁻ ions is not larger than the concentration of H⁺ ions which leads to the significant change of HS⁻ concentration in the diffusion boundary layer. This condition is in contradiction to the major assumption that the concentration of HS⁻ is constant. This inconsistency could be the reason for the difference seen between experimental and calculated values at 0.01 bar. However, it should be noted that despite this discrepancy, the prediction of cathodic limiting current density is still very reasonable which validates the performance of the mathematical correlation.



Figure 16. Comparison of cathodic limiting current density between experimental data and the values predicted by Equation (52) at various 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 solid lines show the experimental measurements from Zheng et al. [47], and the dashed lines represent the prediction by mathematical correlation.

The performance of the mathematical correlation at various pH was also examined as shown in Figure 17. Once again, the experimental cathodic polarizations are presented at different partial pressure of H_2S for pH values of 3, 4, and 5. In all cases, the calculated cathodic limiting current, density represented as vertical lines, are in very good agreement with the experimental value of cathodic limiting current density. These results confirms that Equation (52) can successfully predict the cathodic limiting currents and catch the buffering effect at different pH and concentrations of H_2S .





Figure 17. Comparison of cathodic limiting current density between experimental data and the values predicted by Equation (52) 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 dashed lines represents the results predicted by the mathematical correlation. The data for $pH_2S = 0.1$ bar and $pH_2S = 1$ bar were taken from Zheng et al. [47] and Esmaeely et al. [97], respectively.

Apart from the experimental data, the performance of the mathematical correlation was also compared with that of numerical simulations. The numerical simulation has already been verified in the previous section. The reason for this comparison is that the numerical simulation was based on the comprehensive mass conservation equation and did not consider the assumption used for the derivation of mathematical correlation. Therefore, if a simplified mathematical equation can predict the cathodic limiting current similar to what numerical simulation, with laborious mathematical and coding processes, can predict, it can be a worthful and efficient substitution for numerical simulation. On that account, the cathodic limiting current density was compared between numerical simulation and Equation (52) for various

experimental conditions, and the results are listed in Table 8.

Table 8.

pН	Equivalent linear velocity (m.s ⁻¹)	pH2S (bar)	Simulated cathodic limiting current density (A.m ⁻²)	Calculated cathodic limiting current density (A.m ⁻²)
3	0.81	0.0001	19.1	21.1
3	0.81	0.1	71.7	89.3
3	0.81	1	644.3	676.3
4	0.81	0	1.92	1.91
4	0.81	0.0001	1.99	1.85
4	0.81	0.001	2.41	2.72
4	0.81	0.01	7.43	8.93
4	0.81	0.1	64.7	67.6
4	0.81	1	638.4	620.7
4	0.22	0.01	2.84	2.47
4	2.50	0.01	18.1	19.3
4	0.22	0.1	22.3	25.5
4	2.50	0.1	161.3	166.2
5	0.81	0.0001	0.37	0.23
5	0.81	0.1	64.1	61.9
5	0.81	1	637.8	530.5

Comparison of cathodic limiting current densities between values obtained from numerical simulations and values calculated by Equation (52).

The current densities calculated by the mathematical equation match very well with the values obtained from numerical simulations. The effect of pH, concentration of aqueous H₂S (partial pressure of H₂S), and flow velocity was examined, and the equation was able to capture the effect of all variables. Thus, the capability of the mathematical equation is verified for the case of H₂S aqueous solutions. This equation was derived for the general case of any weak acid with one dissociation step. In order to verify the general applicability of Equation (52) for any weak acid, the cathodic limiting current was calculated for the case acetic acid and then compared with the experimental data from open literatures [114]. Figure 18 demonstrates the effect of pH and acetic acid concentration on the experimental cathodic polarization curves. It also includes the calculated cathodic limiting current (vertical dashed lines) obtained from the mathematical correlation.



Figure 18. Comparison of cathodic limiting current density between experimental data and the values predicted by Equation (52) for different concentrations of undissociated acetic acid for $pH_2S = 0.1$ at 30°C, and 2000 rpm RDE. A) pH 3, B) pH 4, C) pH 5. The vertical dashed lines represents the results predicted by the mathematical correlation. The data were taken from Kahyarian et al. [114].

Once again, the cathodic limiting current obtained from Equation (52) show very good accordance with the experimental data at various conditions. The mathematical equation can successfully predict the cathodic limiting current and is able to capture the contribution of buffering effect and the effect of pH and concentration of acetic acid. In conclusion, the derived correlation was shown to be a valuable substitute for the numerical simulations. It can also provide quick estimation of corrosion rate when mass transfer limiting current is dominant in the cathodic region. More verification on the effectiveness of the derived equation is provided in Appendix A. Furthermore, an equation was also derived for estimation of the entire cathodic polarization curve, which are provided in Appendix A.

Summary

- A mathematical correlation (Equation (52)) was derived for the cathodic limiting current density of weak acids which considers the contribution of homogenous chemical reaction, i.e., buffering effect.
- The equation was verified for the case of H₂S aqueous solutions by comparing with the experimental results at various experimental conditions. The equation

was also compared with the results obtained from numerical simulations in the previous section.

- The comparison showed that the equation can successfully predict the cathodic limiting current at different experimental conditions.
- The equation was also examined for the case of acetic acid. It was shown that it can effectively predict the cathodic limiting current of at different pH and concentrations of acetic acid.

Chapter 5: Galvanic Corrosion of Mild Steel in Presence of Iron Sulfides

After reviewing the mechanism of uniform corrosion of mild steel in H_2S environments, this chapter focuses on the localized corrosion. As it was described in the introduction, the localized corrosion of mild steel in H_2S environments takes place due to the galvanic coupling between mild steel and conductive iron sulfides, which are the corrosion products of corrosion process in sour media. Localized corrosion is a multifacet phenomenon and has such a complexity that can not be fully investigated in one research project, which is why many aspects of this topic are still unknown. The current research is an effort to shed light on one of the key aspects which is the galvanic coupling between mild steel and iron sulfides.

To obtain this aim, the current chapter includes both experimental and modeling chapters for galvanic corrosion between mild steel and iron sulfides in strong acid solutions. Each section itself is also divided into two sections. The experimental chapter includes: 1. factors in galvanic corrosion between mild steel and iron sulfides which examines the effect of different experimental parameters on galvanic coupling process, and 2. electrochemical characterization of iron sulfides which studies the cathodic reactions on the surface of selected iron sulfides. The outcome of the experimental section clarifies parts of the mechanism involved in localized corrosion and significantly improves the mechanistic understanding of this system. The modeling chapter propose a modeling approach to predict the experimental results obtained in the experimental chapter. The modeling chapter includes: 1. modeling of electrochemical reactions on iron sulfides which, for the first time, provide a model for prediction of cathodic current on the surface of selected iron sulfides, and 2. modeling of galvanic corrosion between mild steel and iron sulfides which, also for the first time, develops a predictive model for corrosion rate of mild steel when coupled to iron sulfides. The developed models are validated by comparing them to the experimental data obtained in this study. These models would be valuable tools for the future researchers in this topic.

Chapter 5.A: Experimental Investigations

The content of this chapter is related to the investigations of two different experimental sections. The first section covers a systematic study on the effect of the most influential parameters in the galvanic corrosion between mild steel and iron sulfides. No systematic study exists related to this topic. Identifying the impact of each parameter is crucial for the elucidation and understanding of the mechanism galvanic coupling between steel and iron sulfides. The second section aims to uncover the electrochemical characteristics of iron sulfides, specifically their cathodic behaviors. Electrochemical reactions on the surface of iron sulfides are well-defined in numerous studies as reviewed in the previous chapters, but the nature of cathodic reactions on the surface of iron sulfides remained unrevealed. The cathodic reactions of iron sulfides play an important role in the coupling between mild steel and iron sulfides since they act as cathodes in this system. The results of these two sections, when combined together, would advance the understanding of localized corrosion of mild steel in H₂S environments.

Factors in Galvanic Corrosion Between Mild Steel and Iron Sulfides³

The unpredictability of pitting corrosion in sour media is a complicated challenge in this area as several factors, such as the nature of the corrosion products and the contribution of galvanic coupling, play a role in this type of corrosion [11], [42], [115]. Iron sulfides, as the corrosion products is H₂S corrosion of steel, consist of various polymorphs (i.e., mackinawite, pyrite, pyrrhotite) with different physicochemical and electrical properties. The physicochemical and thermodynamic properties of iron sulfides were investigated by other researchers [19], [20], [22]. Although the formation of these iron sulfides was shown to protect steel surface from uniform corrosion in many cases, their conductive nature was directly associated with the presence of severe localized attacks [9]–[11], [21], [40], [41]. Galvanic coupling between iron sulfides and mild steel is thought to be the main mechanism leading to localized corrosion on steel surface in H₂S environments. In one of the premiere studies done in this area, Ning et al. [13] showed that galvanic coupling between pyrite and steel could cause severe localized corrosion by designing a set of experiments to separate the influence of galvanic coupling from the chemical effects on the localized corrosion of steel in H₂S environments. In these experiments, the presence of pyrite particles on API 5L X65 steel surface in 1 wt.% NaCl solution at pH 4, 25 °C, and 0.1 bar pH₂S for one week, resulted in severe localized attacks on the surface of steel. In order to investigate the chemical effects, a nylon mesh with a 60 µm pore size was placed between pyrite particles and the steel surface in the

³ A version of this paper was published as a conference paper: P. S. Abdar, B. Brown, and S. Nesic, "Factors in Galvanic Corrosion between Steel and Iron Sulfides in Acidic Solutions," AMPP Annual Conference, Mar. 2022.

exact same experimental conditions, and no localized attack was observed. This study revealed that the localized corrosion of steel in presence of iron sulfides has an electrochemical nature, and thus proposed the galvanic coupling as the mechanism of these localized attacks [13]. However, the proposed mechanism is just the first step for achieving the final goal which is the prediction of localized corrosion of steel in aqueous H₂S solution. Prior to developing a prediction model, experimental data for the galvanic corrosion of steel in presence of different iron sulfides as well as for the surface chemistry of iron sulfides are needed.

Literature Review

Hitherto, few studies have measured galvanic corrosion between iron sulfides and mild steel in order to examine the proposed mechanism and understand the effect of experimental parameters on it [31], [44], [45], [116]. In one of the first studies, Tjelta et al. [44] experimented the electrochemical behavior of iron sulfides including pyrite, pyrrhotite and troilite in various pH values in aqueous H₂S solutions. In addition, the galvanic current and potential were measured when these iron sulfides were coupled to API 5L X65 steel. The results revealed that all iron sulfides act as cathodes when coupled to steel, however, pyrite showed the largest ability to polarize the steel surface while pyrrhotite-steel couple produced the highest galvanic current. The result was contradictory as the material that polarize the steel most is expected to produce the highest galvanic current. The source of this discrepancy could emerge from the experimental procedure as the galvanic current measurements did not match very well with the cathodic polarization results when the authors compared them [44]. In another

research, Yepez et al. [45] studied the galvanic coupling between carbon steel C1018 and two iron sulfide samples: pyrite, and mixture of pyrrhotite and troilite. It was shown that corrosion current of steel was increased due to coupling to both samples when mixture of pyrrhotite and troilite sample produced slightly higher current [45]. Finally, in 2018 Navabzadeh investigated the galvanic coupling between API 5L X65 steel and two iron sulfides: pyrite, and pyrrhotite in various environments at pH 4. The results showed that steel-pyrrhotite couple generates slightly higher galvanic current compared with steelpyrite couple in N₂, CO₂, and H₂S sparged solutions. However, the experimental results suffered from a significant decline in galvanic current during the experiments which remained unanswered in this research [31].

Although these studies confirm that the corrosion rate of steel significantly increased due to the galvanic coupling with iron sulfides, they lack the proper experimental design for galvanic measurements as well as the evaluation of the effect of influential experimental parameters. Apart from the discrepancies that were mentioned earlier, the experimental designs of these studies are subjected to one major drawback: the surface areas of the electrodes were not defined. One of the decisive factors in galvanic coupling phenomena is the ratio of cathode to anode surface area. Specifically in the case of localized corrosion of steel in H₂S environments, the porosity of iron sulfides results in a very high surface area of cathode which intensifies the rate of cathodic current. Therefore, interpreting the results of galvanic measurements while ignoring the surface area of electrodes is not conclusive, and in some cases, it could even be misleading.

After reviewing the literature dedicated to galvanic coupling measurements, it would be beneficial to concisely review some of the studies which investigated the underdeposit corrosion of steel in presence of iron sulfides. For instance, Kvarekval et al. [117] studied the effect of FeS (mixture of pyrrhotite and troilite) deposits on the surface of UNS K03014 carbon steel in H_2S/CO_2 environments. The results showed that the presence of FeS deposits significantly increased the weight loss corrosion and created severe localized attacks. The localized penetration depth was increased 20 times in some cases. The same experiments were also performed in presence of sand deposits which showed very low rate of localized corrosion. Ning [13] investigated the corrosion of API 5L X65 mild steel under pyrite and sand deposits in H₂S and CO₂ environments. Severe localized corrosion was observed in presence of pyrite while no localized attack was observed in presence of sand particles. In addition, the effect of the size of pyrite particles on localized corrosion was examined and it was concluded that the smaller particles lead to deeper localized pits. The author stated that smaller particles provides larger cathodic area. This observation is evidence for the importance of cathode to anode surface area ratio. Lastly, the influence of presence pyrrhotite layer on mild steel surface in various NaCl concentrations in CO₂ and mixed H₂S/CO₂ environments was investigated by Navabzadeh et al. [9], [31] A significant observation was that the localized corrosion rate in 1 wt.% NaCl solutions was reported three times higher than the solution without NaCl. This result not only showed that the presence of pyrrhotite layer enhances localized corrosion of mild steel, but also substantiated the galvanic nature of localized attack due to its change with solution conductivity. In conclusion, all the under-deposit studies

mentioned here reaffirmed that the corrosion rate of mild steel is increased when coupled to iron sulfides.

The present section aims to investigate the effect of influential experimental parameters: type of iron sulfide, cathode to anode surface ratio, and salt concentration, on the galvanic corrosion of steel due to coupling to iron sulfides. Understanding the impact of these factors could lead to revealing the proper mechanism of galvanic corrosion of steel in sour environments. Pyrite and pyrrhotite were selected as these corrosion products have been mostly found when localized attack of mild steel was observed in presence of H₂S, according to previous studies [10], [11], [21]. Cathode to anode surface ratio is another important factor in this process as the high porosity of iron sulfides formed on the surface of steel could increase the surface area of iron sulfides (cathode) to one or two order of magnitudes higher than the steel (anode). This high ratio could significantly amplify the effect of galvanic coupling and intensify the localized attack. The experimental setup in this study is designed such that the surface area of electrodes are clearly determined. Salt concentration is also an influential factor since higher salt concentration increases galvanic current by facilitating the electron transfer in solution. It is worth noting that all the experiments will be performed in acidic solutions because the presence of H₂S, as another influential factor, was shown in the literature to significantly affect [46], [47], [98] both anodic and cathodic reactions on steel surface leading to a more complex system. Therefore, it is reasonable to eliminate the effect of H_2S in this stage in order to clearly understand the importance of other influential factors. However, the effect of marginal concentration of H_2S will be examined in the final stage.

Materials and Experimental Setup

A specific experimental setup was designed for this study in order to fulfill the objectives of galvanic coupling measurements and avoid the gaps observed in previous studies. API 5L X65 was selected as steel specimen with the composition shown in Table 9, and pyrite and pyrrhotite were selected as iron sulfides specimens.

Table 9.

Cr	Cu	Mn	Mo	С	Co	Ni	Si	Ti	As
0.15	0.14	1.51	0.16	0.05	0.012	0.38	0.25	0.01	0.015
Р	S	Al	Sn	Sb	V	Zr	Nb	Fe	
0.004	0.001	0.033	0.035	0.012	0.04	0.004	0.03	balance	

Chemical composition of API 5L X65 carbon steel (in wt.%)

Mineral pyrite and pyrrhotite were purchased from Ward's Science. For purity analysis, these rock-like minerals were powdered by pestle and mortar, then characterized by XRD measurement using XRD Rigaku Ultima IV with Cu K α (1.54 Å) radiation as shown in Figure 19. Very high purity was observed for pyrite sample when compared to the reference pattern ICDD# 00-0042-1340 [118]. The purity of pyrrhotite sample was also verified according to the reference pattern ICSD# 01-079-5969 [119], however, minor impurities were presented.



Figure 19. XRD analysis of mineral iron sulfide samples. A) pyrite, B) pyrrhotite

As it was mentioned, the surface areas of the samples were carefully designed in order to obtain the desired cathode to anode surface ratios. Since the formation of porous corrosion products could significantly increase the cathode surface area in real situations, the experiments were designed in a fashion that the cathode:anode surface area ratio started from 1:1, and then increased to the exact values of 8.2:1 and 91.1:1. The goal was to change the area ratio by around one and two orders of magnitude in order to detect the noticeable impact of this factor. From now on, in order to simply the illustrations, the ratios will be shown as 1:1, 8:1, and 91:1. The size of specimens was selected based on the capacity of manufacturing the materials. On that account, API 5L X65 steel and mineral iron sulfides specimens with two different surface areas, $(0.196 \text{ and } 0.0177 \text{ cm}^2)$ for steel and $(0.196 \text{ and } 1.613 \text{ cm}^2)$ for iron sulfides, were cut to the right shape. Afterward, these specimens were attached to a wire using silver conductive paste, and then were embodied in epoxy. These two electrodes were placed on a designed stainlesssteel holder with a fixed distance of two centimeters apart as shown in Figure 20. The two electrodes are insulated from each other while connected externally through a zeroresistance ammeter (ZRA). A platinum mesh counter electrode (titanium mesh coated with platinum) was placed in the middle of these two electrodes. Also, an Ag/AgCl (saturated KCl) reference electrode (RE) was kept between the Pt counter electrode (CE) and the working electrode (WE). The electrodes are facing each other in this design so that the current flow would be uniform. Also, the electrodes were kept in 2 cm distance to each other to minimize the solution resistance. The experiments were performed in an unstirred condition to minimize the effect of flow. The whole electrochemical setup was placed in a 2-L glass cell at 30°C and 1 bar atmospheric pressure as seen in Figure 20 for all the experimental measurements.



 gas outlet (2) Ag/AgCl reference electrode, (3) sparge inlet, (4) pH probe, (5) platinum counter electrode, (6) 2-liter glass cell, (7) iron sulfide electrode, (8) mild steel electrode, (9) stir bar, (10) electrode stand, (11) heat plate with stirrer. Image is courtesy of Cody Shafer



Figure 20. Overview of the experimental setup (left), and image of the electrochemical cell (right)

Prior to each experiment, the 2-L glass cell was filled with 1 wt.% NaCl solution and de-aerated with nitrogen for at least an hour. All electrodes were polished with 400 and 600 grit silicon carbide abrasive papers, then washed with isopropyl alcohol and finally dried with N₂ gas. For the galvanic coupling measurements, mild steel electrode was coupled to iron sulfide electrode (externally through potentiostat) for 2 hours during which galvanic current and galvanic potential were measured using zero resistance ammeter (ZRA) method. 2-hour test duration was chosen so that the measurements reach stability and also corrosion products could not form on the surface of steel. In order to observe the behavior of steel electrode during galvanic measurements, the open circuit potential (OCP) and the corrosion rate of uncoupled steel, using linear polarization resistance (LPR) method, were measured. For this purpose, the steel electrode was uncoupled from iron sulfide electrode every 30 minutes during the galvanic measurements and re-coupled after OCP and LPR measurements. In addition, potentiodynamic polarization sweeps with the scan rate of 0.5 mV.s⁻¹ were performed on both electrodes at the end of the two-hour galvanic measurements. Solution resistance was also measured using electrochemical impedance spectroscopy (EIS) and compensated for the experimental results. All electrochemical measurements were performed using a Gamry potentiostat Reference 600. The pH of solution was kept at 5.0, using HCl and NaOH, in order to mimic the pH of real conditions of oil and gas pipelines, however, the pH was constantly tracked during measurements using Oakton pH probe, and pH drift during the galvanic measurements was less than 0.1 which showed minimal impact on the results. Finally, the effect of conductivity was investigated using three different salt concentrations. To achieve this goal, the concentration of 1 wt.% NaCl solution was increased and decreased by an order of magnitude to 0.1 wt.% and 10 wt.% NaCl. Totally, the effect of three experimental parameters: iron sulfide type, cathode to anode surface area ratio, and conductivity was examined. **Table 10** show the test matrix of all experiments with the relevant experimental conditions.

Table 10.

Parameter	Conditions		
Material	X65, Pyrite	X65, Pyrrhotite	
Steel size	5 mm D (0.196 cm ²) 1.5 mm D (0.0177 cm ²)		
Iron sulfide size	5 mm D (0.196 cm ²) 1.27 cm ×1.27 cm (1.613 cm ²)		
Cathode/Anode ratio	1, 8, 90		
Temperature	30 °C		
Electrolyte	0.1 wt.%, 1 wt.%, 10 wt.% NaCl		
Sparge gas	N ₂		
Total pressure	1 bar		
pН	5.0 ± 0.1		
Exposure time	2 hours		
Electrochemical techniques	OCP, EIS, LPR, ZRA, Potentiodynamic sweep		

Test matrix for the galvanic corrosion measurements.

Results and Discussions

Fundamentals of Galvanic Corrosion Calculation from Polarization

Measurements. Prior to presenting the results of galvanic coupling measurements, it is of importance to review the fundamental nature of galvanic current between two dissimilar metals and also the procedure of calculating, or to put it more accurately, graphically estimating the coupled galvanic current from polarization measurements. The necessity of this section arises from the fact that an incorrect concept of nature of galvanic current has been observed continuously in various studies, the concept that the galvanic current is simply found as the intersection of cathodic polarization curve of cathode (i.e., metal with higher open circuit potential) and anodic polarization curve of anode (i.e., metal with lower open circuit potential). As it will be discussed, this estimation might be true with specific assumptions in some cases, but it is certainly not the universal and proper method of galvanic current calculation.

Let us assume first that an active metal, e.g., iron in this case, is immersed in an electrolyte. The condition is such that the metal is corroding in this electrolyte at its corrosion potential. The corrosion process consists of anodic and cathodic reactions which are occurring at the same location (surface of electrode). As an anodic reaction, iron metal is oxidized to iron ion, according to Reaction (7), and producing electrons which are consumed via cathodic reactions. The cathodic reactions in this example are the hydrogen evolution due to reduction of hydrogen ion (Reaction (8)) as well as the reduction of water (Reaction (9)). Figure 21.B qualitatively represents the corrosion current, corrosion potential, anodic and cathodic polarization curves for this electrode.



Figure 21. A) Representation of mild steel-iron sulfide couple and the related reactions, and B) a qualitative example of polarization curves of anode and cathode, and their related current in a galvanic couple (blue lines represents the currents related to mild steel, the red lines represents the currents related to iron sulfide, and the dashed black lines are total currents.

Now let us assume that the iron electrode is connected to a more noble electrode as shown in Figure 21.A. Open circuit potential, the anodic and cathodic polarization curves of this noble electrode are also qualitatively represented in Figure 21.B. When these two dissimilar metals are connected to each other, the less noble metal acts as anode or is corroded, while the more noble one acts as cathode or is protected. Therefore, anodic and cathodic reactions are not occurring at the same electrode, in contrast to the previous example. The electrons produced via anodic dissolution reaction due to the connection to the cathode is flowing through the external wire and consumed at the surface of cathode. The current due to this external connection is called galvanic current [120], [121]. However, it should be emphasized that the corrosion occurring on the surface of iron originates from two phenomena: the corrosion due to the galvanic coupling, and the corrosion due to the cathodic reaction on the surface of iron as shown

in Figure 21. Therefore, while iron serves as the anode for the external cathode, it serves as the anode for the cathodic reaction occurs at itself. The same conclusion could be derived for the more noble electrode; it is the cathode for the galvanic couple and at the same time for the anodic reaction occurs at itself. As a result, when the two dissimilar metals are galvanically connected to each other, the cathodic current of the couple is the summation of all cathodic currents occurring on the surface of both electrodes. The anodic current of couple can be found in similar fashion. The total anodic current and cathodic current of the couple are represented in Figure 21.B with black dashed lines. The potential at which the anodic current intersects the cathodic current, in other words the potential that both electrodes are rested at, is called coupled or galvanic potential. However, the current at the intersection point does not indicate the galvanic current, it in fact stands for the point that the total cathodic current equals the total anodic current [121], [122]. Accordingly, at this point the summation of cathodic current at anode and cathode is equal to the summation of anodic current at anode and cathode, as described by Equation (55).

$$i_{c,coupled}^{A} + i_{c,coupled}^{C} = i_{a,coupled}^{A} + i_{a,coupled}^{C}$$
 Equation (55)

In the above equation, $i_{c,coupled}^{A}$ and $i_{a,coupled}^{A}$ are the cathodic and anodic current of anode (i.e., iron) at coupled potential, respectively. Similarly, $i_{c,coupled}^{C}$ and $i_{a,coupled}^{C}$ indicate the cathodic and anodic current of cathode at coupled potential, respectively. A question that arises at the moment is, which of these current values represent the galvanic current? In fact, none of these current values is exactly the galvanic current. The term $i_{a,coupled}^{A}$ stands for the total anodic current of iron electrode at coupled potential which encompasses the anodic current due to external coupling, or galvanic current, as well as the anodic current due to cathodic reaction occurs at iron electrode. The latter current is equivalent to the cathodic current at iron electrode $i_{c,coupled}^{A}$ since the anodic current of corrosion process at iron electrode is the same as its cathodic current. As a result, the galvanic current is the difference between the total anodic current and the cathodic current at the surface of anode as illustrated by Equation (56) [120], [121].

$$i_{galvanic} = i^{A}_{a,coupled} - i^{A}_{c,coupled}$$
 Equation (56)

A similar conclusion can be derived for the external cathode as shown by Equation (57). It should be emphasized that the corrosion current of iron in galvanic coupling is identical to the total anodic current $i_{a,coupled}^{A}$ including all the corrosion processes occurring at its surface. Therefore, in order to calculate the corrosion rate of iron, the term $i_{a,coupled}^{A}$ should be used, not the galvanic current [121]. The inaccurate use of galvanic current instead of total anodic current for calculating corrosion rate has been also seen frequently in literature.

57)

$$i_{galvanic} = i_{c,coupled}^{C} - i_{a,coupled}^{C}$$
 Equation (

As a final note, let us re-examine the fact that many studies consider the intersection of cathode's cathodic curve and anode's anodic curve as the coupled potential and galvanic current. Based on the preceding discussions and by observing Figure 21 as a general case of galvanic coupling, it is evident that this point represents neither coupled potential nor galvanic current. However, the intersection point could be estimated as galvanic current for specific cases with certain assumptions. Considering Equation (55) the cathode's cathodic current $i_{c,coupled}^{C}$ could be equal to the anode's anodic current $i_{a,coupled}^{A}$ if the two other terms are ignored; in other words: 1. the anodic current of cathode should be negligible compared with the anodic current of anode, and 2. the cathodic current of anode should be negligible compared with the cathodic current of cathode. In this situation, Equation (55) can be simplified to Equation (58) as below.

$$i_{c,coupled}^{C} = i_{a,coupled}^{A}$$
 Equation (58)

Several other estimations are also probable depending on the magnitude of each current in various experimental conditions. Some of these cases will be illustrated in the next section.

Effect of Experimental Factors on Galvanic Corrosion Between Steel and Iron Sulfides

Effect of Iron Sulfide Type. As it was already mentioned, pyrite and pyrrhotite have been selected as iron sulfide types. This section investigates how these iron sulfides behaves differently when coupled to X65 steel electrode. First, the results of polarization measurements will be presented for these iron sulfides in order to predict the galvanic current and potential. The origin of the difference between the electrochemical response of pyrite and pyrrhotite will be discussed in more detail. Afterwards, the results of galvanic coupling measurements will be presented and compared with the prediction obtained from polarization data.

Electrochemical Polarization Curves for Iron Sulfides. Figure 22 displays the cathodic and anodic polarization measurements for X65 steel and iron sulfides at 1 wt.% NaCl and cathode to anode surface area ratio of 1. It is worth mentioning that the axis ranges of Figure 22.A and Figure 22.B are similar so that the results could be comparable. As it can be clearly seen, the cathodic current of pyrrhotite is much greater than pyrite in the same experimental condition, which could lead to the higher rate of galvanic current. For each case, the total cathodic current (black dotted lines) was calculated by adding the cathodic current of steel to that of pyrrhotite or pyrite. Noting that the anodic current of the iron sulfides has been disregarded since their values are much lower than anodic current of steel. Based on this assumption, the total anodic current (black dotted lines) is identical to the anodic current of steel. Hence, Equation (

57) can be rewritten as Equation (59) in which the galvanic current equals the cathode current of iron sulfides at coupled potential.

$$i_{galvanic} = i_{c,coupled}^{C}$$
 Equation (59)

In case of pyrrhotite shown in Figure 22, the total cathodic current is approximately equivalent to the cathodic current of pyrrhotite as its current is up to two orders of magnitude higher than the cathodic current of steel. Accordingly, by neglecting the cathodic current of steel, Equation (58) could be valid and the intersection of cathodic current of pyrrhotite with anodic current of steel can be estimated as galvanic current and coupled potential. For each iron sulfide, the galvanic current and coupled potential have been graphically approximated. As illustrated on Figure 22, the coupled potentials are -0.736 and -0.639 V vs Ag/AgCl, and the galvanic currents are around 6.1×10^{-7} and 2.4×10^{-5} A for pyrite and pyrrhotite, respectively.


Figure 22. Potentiodynamic polarizations on A) steel-pyrite couple, and B) steelpyrrhotite couple at 30 °C, 1 wt.% NaCl, pH 5, and cathode:anode surface area ratio of 1:1 (black dashed lines = total cathodic currents, and blue dotted line = calculated cathodic current on steel).

As it was seen, pyrrhotite showed very different cathodic behavior compared with pyrite which resulted in around two orders of magnitude higher galvanic current rate. The origin of this distinction emerges from their different physicochemical characteristics which cause different electrochemical reactions occurring on the surface of iron sulfides. Although investigation of electrochemical characteristics of iron sulfides is the main focus of next chapter, the probable electrochemical reactions introduced in literature will be concisely described to assist the understanding of galvanic interactions between steel and iron sulfides.

Pyrite with the chemical formula of FeS_2 is stoichiometric iron sulfide and the most thermodynamically stable phase [20]. In contrast, pyrrhotite is a group of nonstoichiometric iron sulfides formulated as $Fe_{1-x}S$ [20]. Therefore, it is expected that pyrite has lower reactivity compared to pyrrhotite due to its high stability. Very few studies focused on the cathodic reactions occurring on the iron sulfides specifically in acidic solutions. The only systematic research was done by Esmaeely et al. which also showed that the cathodic current on the surface of pyrrhotite is higher than that obtained on the surface of pyrite specifically where hydrogen evolution is not dominant (i.e., high overpotential, pH 5) [123]. Previous studies suggested various cathodic reactions taking place on the surface of iron sulfides. The most important reactions are discussed here, but a detailed review of the proposed reactions and validity of each will be examined in the next chapter. In the case of pyrite, the main proposed cathodic reactions are the reduction of pyrite to troilite [124], [125] and the reduction of polysulfides formed on surface of pyrite [126], [127], as shown by Reaction (28) and Reaction (29), respectively.

$$FeS_2 + 2H^+ + 2e^- \rightleftharpoons FeS + H_2S$$

$$S_{n(s)}^{2-} + 2(n-1)e^- \rightarrow nS^{2-}$$
Reaction (29)

Similar reactions were also proposed in the case of pyrrhotite. The reduction of pyrrhotite can occur in two different ways: solid-state reduction of pyrrhotite to troilite [128], and reductive dissolution of pyrrhotite [129], [130], as represented by Reaction (30) and Reaction (31), respectively. The reduction of polysulfides (Reaction (29)) was also proposed for pyrrhotite [126], [129].

$$FeS_2 + 2H^+ + 2e^- \rightleftharpoons FeS + H_2S$$
Reaction (30)
$$S_{n(s)}^{2-} + 2(n-1)e^- \rightarrow nS^{2-}$$
Reaction (31)

Therefore, the higher cathodic current of pyrrhotite can be related to the lower stability of this polymorph compared with pyrite and also to formation of more polysulfides at the surface of pyrrhotite since it is more prone to oxidation in various corrosive environments [126], [131].

Galvanic Coupling Measurements for Steel-Pyrite and Steel-Pyrrhotite couples. According to the experimental procedure described earlier, the coupled potential and the galvanic current were measured for steel-pyrite and steel-pyrrhotite couples using ZRA method, and the results are plotted in Figure 23.A and Figure 23.B, respectively. The blue line represents the corrosion potential (Figure 23.A) and corrosion current (Figure 23.B) of uncoupled steel which was measured every 30 minutes as shown by points. It is worth noting that the spikes observed every 30 minutes in the data was due to the disconnection and reconnection of the electrodes at these times for measuring the potential and corrosion current of uncoupled steel. When reconnecting the electrodes, the spikes appeared due to the sudden polarization of the mild steel at the beginning of the coupling. In addition, the results shown in these graphs are for one of the repetitions in each condition. Since the results were highly reproducible, and also for the sake of more clarity in the graphs, only one repetition was shown here. The effect of replications will be shown with error bars for the corrosion rate data. As observed in Figure 23, the increase in mild steel potential when coupled to pyrite was less than 10 mV, while it was around 100 mV when coupled to pyrrhotite which its ability to significantly polarize steel. The coupled potential found from galvanic measurements (-0.733 V for pyrite and -





Figure 23. A) potential, B) current of steel when coupled to pyrrhotite and pyrite at 30 °C, 1 wt.% NaCl, pH 5, cathode:anode surface area ratio of 1:1 (ZRA method).

In addition, the galvanic current of steel-pyrrhotite couple was notably higher than the galvanic current of steel-pyrite couple which was less than the corrosion current of uncoupled steel. The same conclusion was derived from polarization data since the cathodic current was higher on pyrrhotite electrode originated from the different nature of pyrite and pyrrhotite as discussed above. The values of galvanic current measured during galvanic coupling experiments (3.90×10^{-7} A for pyrite and 2.56×10^{-5} A for pyrrhotite) agree well with the values drawn graphically from polarization measurements considering that the values calculated for galvanic measurements are the average values during the two hours experiments (also the average value of two repeats). On that account, the results validate the reliability of the galvanic coupling measurements.

Lastly, the corrosion rates of uncoupled steel, coupled steel-pyrite, and coupled steel-pyrrhotite were determined for the above-mentioned experiments and are presented

in Figure 24. The data are the average of two replications with error bars showing the deviation from the average value.



Figure 24. Calculated corrosion rates of uncoupled and coupled X65 mild steel at 30 °C, 1 wt.% NaCl, pH 5, cathode:anode surface area ratio of 1:1.

The corrosion rates were calculated using Equation (60) in which M_{Fe} is molecular weight of iron 55.845, ρ_{Fe} is density of iron equal to 7874 Kg.m⁻³, *n* is equivalent number of 2 for iron, and F is faraday constant 96485 s.A.mol⁻¹.

Corrosion Rate (CR) =
$$\frac{i_{corr}M_{Fe}}{\rho_{Fe}nF}$$
 Equation (60)

Noting that i_{corr} is the total corrosion current density of steel ($i_{a,coupled}^{A}$ in Figure 21) including the corrosion of steel due to external connection to iron sulfide cathode and also due to cathodic reaction occurring on itself. The most accurate way to evaluate the total corrosion current is direct graphical estimation of $i_{a,coupled}^{A}$ from polarization

measurements. However, in cases when Equation (59) applies (i.e., Steel-pyrrhotite couple), the galvanic current value found from galvanic coupling measurements can be used. Even in case of pyrite, the galvanic current value can be implemented in Equation (56) to indirectly estimate the total corrosion current, even though graphical estimation of $t_{C,coupled}^{A}$ is still required. As was seen and will be shown later in a more complete format, the experimental results from both methods agree very well, but for the sake of consistency, all the corrosion rate calculations were based on the current values from galvanic measurements. Therefore, according to Figure 24, it can be summarized that the corrosion rate of steel does not significantly increase due to the coupling to pyrite, while it increases by about an order of magnitude when coupled to pyrrhotite.

Effect of Cathode to Anode Surface Area Ratio. The importance of cathode to anode surface area ratio during galvanic corrosion between two dissimilar metals has been subjected to many research papers [132]–[134] because in most real situations, the surface area of cathode differs from that of anode. In fact, the major issue is observed when the cathode surface area is much larger than the anode which resulting in severe localized corrosion of anode. It was previously shown that the galvanic current of various materials including carbon steel, when coupled to a more noble metal, is significantly amplified by increasing the cathode to anode surface area ratio [132]–[136]. In corrosion of mild steel in H₂S environments, the porosity of iron sulfide corrosion products formed during the corrosion process caused their larger surface area compared with mild steel. The effect of larger cathode surface area in this study was investigated by changing the surface areas of steel and iron sulfides in order to increase the cathode to anode surface area ratio by approximately one and two orders of magnitude. Figure 25 compares the

coupled potentials of steel-pyrite and steel-pyrrhotite couples for different cathode to anode surface ratios, while all other experimental parameters remained unchanged.



Figure 25. The effect of cathode:anode surface ratio on the galvanic potential of steel when coupled to A) pyrite, and B) pyrrhotite at 30 °C, 1 wt.% NaCl, and pH 5. The solid blue line shows the open circuit potential of uncoupled steel (ZRA method).

The coupled potential for both cases shifted to more positive value with respect to the cathode to anode surface area ratio showing that iron sulfides with the larger surface area could enhance the polarization of mild steel by forcing it to stabilize at overpotential farther from its corrosion potential (~ -0.740 V vs Ag/AgCl). The same observation was found when steel was galvanically coupled to different materials [133], [136]. Furthermore, the coupled potentials for all cathode:anode surface area ratio for steel-pyrrhotite couple are more positive than steel-pyrite couple which highlights the higher ability of pyrrhotite to polarizing mild steel. Galvanic current density was also compared for different cathode to anode surface area ratios and plotted in Figure 26. It should be noted that galvanic current density was represented for these cases instead of galvanic current as steel sample with different surface area was for obtaining the cathode:anode area ratio of 91:1.



Figure 26. The effect of cathode:anode surface ratio on the galvanic current of steel when coupled to A) pyrite, and B) pyrrhotite at 30 °C, 1 wt.% NaCl, and pH 5. The solid blue line shows the corrosion current of uncoupled steel (ZRA method).

The results in Figure 26 show that the current density was increased around one and two orders of magnitude by increasing the cathode to anode surface area ratio from one to 8 and 91. The increase in current density was due to the increase of cathodic current associated with the larger cathodic surface area. Taking into consideration that the current density is used for corrosion rate calculations, the enhancement of galvanic current attributed to larger cathode is rational. According to Hack [120], the effect of different surface areas of cathode or anode can be viewed by appreciating that the current is the multiplication of current density with surface area. Thus, larger surface area shifts the polarization curve of the material to the right, in other words to the higher current.

Similar to the previous section, corrosion rates were estimated from galvanic measurements for various cathode:anode surface area ratios. Remembering that the corrosion rates shown in Figure 27 are calculated based on the total corrosion current density $(i_{C,coupled}^{A})$ as discussed earlier. Noticing the logarithmic scale, the corrosion rate of both steel-pyrite and steel-pyrrhotite couples are nearly one and two orders of

magnitudes higher for cathode:anode area ratios of 8:1 and 91:1, respectively, when compared to the corrosion rate of 1:1 cathode to anode are ratio. The intensification of cathode current of larger cathode, as explained above, is the cause of increase in corrosion rate. Still, the corrosion rates of steel-pyrrhotite couple is much higher than steel-pyrite couple in all cathode:anode area ratios thanks to its higher cathodic activity.



Figure 27. The effect of cathode:anode surface area ratio on corrosion rates of uncoupled and coupled X65 mild steel at 30 °C, 1 wt.% NaCl, pH 5

Effect of Conductivity. The influence of changing conductivity via changing NaCl concentration was another experimental factor that was investigated. In theory, degree of conductivity could determine the solution's capacity to pass ions. Improving the conductivity of solution in a galvanic couple enables the solution to pass more ions between anode and cathode, thereby enhancing the reactions occurring on both electrodes. Thus, it is expected that increasing NaCl concentration could lead to a higher galvanic current. The NaCl concentration was changed from 0.1 to 10 wt.% (from 0.017 to 1.71 M) in this study. The effort was to vary the NaCl concentration by one and two orders of magnitude, same as what was done for cathode:anode area ratio, such that the effect of this factor would be influential. The conductivity of the solutions are 0.15, 1.6, and 12.6 S.m⁻¹ for 0.1, 1, and 10 wt.%, respectively, showing that the conductivity is also increased by approximately the same order of magnitude [137]. The specific design of the electrochemical setup with small distance between cathode and anode could minimize the effect of ohmic resistance drop.

Figure 28 compares the galvanic current for both steel-pyrite and steel-pyrrhotite couples for solution with various NaCl concentrations for cathode:anode surface area ratio of 1:1 . The corrosion current of uncoupled steel is shown as well similar to previous figures, but it is worth mentioning that only the corrosion current for 1 wt.% NaCl solution is shown. As it will be argued, the corrosion current of uncoupled steel itself is also changing with solution conductivity; however, this change is minimal compared to the galvanic current for couples. Therefore, only corrosion current for 1 wt.% NaCl solution is shown to simplify the figure.



Figure 28. The effect of salt concentration on the galvanic current of steel when coupled to A) pyrite, and B) pyrrhotite at 30 °C, pH 5, and cathode:anode surface area ratio of 1:1. The solid blue line shows the corrosion current of uncoupled steel (ZRA method).

Also, the coupled potential figures for various NaCl concentrations are not shown here for the sake of redundancy, but the values are presented in the summarized table. For steel-pyrrhotite couple, the galvanic current increased from 1.07×10^{-5} A to 2.56×10^{-5} A when NaCl concentration changed from 0.1 wt.% to 1 wt.%. However, further increase of NaCl concentration to 10 wt.% showed only a minor effect on galvanic current. On the other hand, the change of NaCl concentration did not clearly impact the galvanic current of steel-pyrite couple. As it is seen, the results do not meet the expectation that higher conductivity always enhances galvanic corrosion. This finding can be explained from two standpoints; one is the role of conductivity on transporting the ions during galvanic coupling, and second the effect of chloride concentration on the electrochemical reaction rate occurring on the surface of electrodes through changing the solution chemistry.

Let us initially select the steel-pyrrhotite couple to clarify the results from the first standpoint. In general, the higher the conductivity, the more the ions are transported. This also allows for higher electron transfer resulting in higher rates of electrochemical reaction. Accordingly, when NaCl concentration increases from 0.1 to 1 wt.% in steelpyrrhotite couple, higher conductivity leads to higher galvanic current. But, in some situations increasing ion transportation does not increase the rate of electrochemical reaction because it is limited by the kinetic of reaction. That being said, the reaction rate (i.e., current) at a specific experimental condition reached its highest value, and it can not increase regardless of increase in conductivity. In these situations, conductivity is no longer a rate limiting factor and the reaction is kinetically limited. The galvanic current of steel-pyrrhotite couple showed no improvement when NaCl concentration changed from 1 wt.% to 10 wt.%. The ion transportation provided by 1 wt.% NaCl already sufficed for transferring the highest current produced by steel-pyrrhotite couple. Likewise, the galvanic current for steel-pyrite couple did not alter by increasing NaCl concentration even from 0.1 wt.% to 1 wt.%. The galvanic current of steel-pyrite couple is nearly one order of magnitude lower than that of steel-pyrrhotite which indicates its lower electrochemical reaction rate as described earlier. Thus, it could be deduced that only 0.1 wt.% NaCl was able to transfer the maximum current produced. To further substantiate this theory, the influence of NaCl concentration on the galvanic current for cathode:anode area ratio of 8:1 was examined, as plotted in Figure 29, when greater current can be produced.



Figure 29. The effect of salt concentration on the galvanic current of steel when coupled to A) pyrite, and B) pyrrhotite at 30 °C, pH 5, and cathode:anode surface area ratio of 8:1. The solid blue line shows the corrosion current of uncoupled steel (ZRA method).

The impact of changing NaCl concentration from 0.1 wt.% to 1 wt.% on galvanic current of steel-pyrite couple can be recognized here in contrast to what was seen for cathode:anode area ratio of 1:1. This observation reaffirm that higher conductivity could increase the galvanic current when the reaction is capable of generating higher current and is not kinetically limited. Once more, the galvanic current of 10 wt.% NaCl is similar or even lower than that of 1 wt.% NaCl for both couples. The limitation of reaction kinetic was shown to be the reason why current could not further increase at higher conductivity, but the cause for declining the current at very high NaCl concentration will be expounded in the following.

The alternative interpretation comes from the fact that chloride concentration was extensively shown to influence the electrochemical reaction rate specifically iron dissolution reaction [138]–[140]. Madani Sani investigated the effect of a wide range of NaCl concentration (from 0 to 20 wt.% NaCl) on corrosion rate as well as electrochemical reactions of steel in weak acid solution (i.e., aqueous CO₂ solution) and

found that chloride ion concentration changes the electrochemical reaction rate of both cathodic and anodic reactions on the surface of steel due to the change of exchange current density of these reactions. In particular, the rate of iron dissolution reaction increased by increase of NaCl concentration up to 3 wt.% and then dramatically decreased at higher NaCl concentration [140]. Similar trend for influence of NaCl on iron dissolution reaction was observed in other studies, for instance, papers by Fang et al. and Liu et al. [138], [141]. Iron dissolution reaction occurs through adsorbtion of OH⁻ ion via either well-known Bockris mechanism or catalytic mechanism proposed by Heusler [63], [98]. It was suggested that Cl⁻ ion can also adsorb on the surface of iron and catalytically enhance the iron dissolution reaction through a similar pathway parallel to OH⁻ adsorbtion [138], [142], [143]. However, it was shown that the effect of OH^{-} on iron dissolution rate is stronger than Cl⁻ ions [140], [144]. Therefore, very high concentration of Cl⁻ ion could significantly inhibit the adsorbtion of OH⁻ ion, decreasing its surface coverage on iron surface, and consequently reducing the electrochemical reaction rate [144]. In addition, it was suggested that the retardation of iron dissolution rate could have its roots in the retardation of water activity at high NaCl concentrations which was demonstrated previously by Madani Sani et al. [140], [145].

Standish et al. measured the influence of chloride concentration on the galvanic coupling between carbon steel and copper and observed the same trend as presented in current study [133]. The galvanic current improved by increasing NaCl concentration from 0.001 M up to 0.1 M, then decreased by further increase of NaCl concentration to 3.0 M. The cause was revealed by potentiodynamic polarization curves which showed the

retardation of both carbon steel anodic reaction rate as well as copper cathodic reaction rate [133]. This result is in complete agreement with the results of the current study and the earlier discussions on the effect of chloride concentration on iron dissolution reaction.

Lastly, corrosion rates were also calculated for various NaCl concentrations for cathode:anode area ratios of 1:1 and 8:1, as demonstrated in Figure 30. The increase of NaCl concentration from 0.1 wt.% to 1 wt.% resulted in a notable increase in corrosion rate for steel-pyrrhotite couple, however, the change of corrosion rate was not significant when NaCl concentration increased to 10 wt.%. For steel-pyrite couple, the corrosion rate was not affected by NaCl concentration for cathode:anode area ratio of 1:1 since very low current was produced at this condition and low conductivity of 0.1 wt.% NaCl was capable of transporting this current. However, higher corrosion rate for 1 wt.% NaCl compared with 0.1 wt.% NaCl can be observed when cathode:anode area ratio was 8:1. It is worth mentioning that the impact of NaCl concentration is not identical to the impact of cathode:anode area ratio by one and two orders of magnitude does not increase the galvanic corrosion by the same order.



Figure 30. The effect of salt concentration on corrosion rates of uncoupled and coupled steel at 30 $^{\circ}$ C, pH 5 for A) cathode:anode surface area ratio of 1:1, and B) cathode:anode surface area ratio of 8:1.

A summary of the results at various experimental conditions is provided in **Table 11**. It should be mentioned that all the values reported in this table is the average of two replications for the reproduced conditions, and the exact value for the single repetition conditions.

Table 11.

Galvanic couple	NaCl Conc. (wt.%)	Cathode:Anode Surface Area Ratio	Galvanic Current Density (A.m ⁻²)	Coupled Potential (mV vs. Ag/AgCl)	Total Current Density (A.m ⁻²)	Total Galvanic Corrosion Rate (mm.yr ⁻¹)
	0.1	-	-	-	0.041	0.048
Steel	1	-	-	-	0.041	0.047
	10	-	-	-	0.043	0.050
	0.1	1	0.022	-0.719	0.042	0.049
Steel-	0.1	8.2	0.438	-0.656	0.438	0.508
	1	1	0.020	-0.733	0.048	0.056
pyrite		8.2	0.640	-0.662	0.641	0.742
		91.1	6.161	-0.588	6.161	7.150
	10	1	0.017	-0.728	0.043	0.050
		8.2	0.890	-0.645	0.890	1.033
	0.1	1	0.545	-0.630	0.545	0.633
Steel- Pyrrhotite	0.1	8.2	3.178	-0.514	3.178	3.688
	1	1	1.306	-0.646	1.306	1.519
		8.2	6.107	-0.580	6.107	7.087
		91.1	57.62	-0.491	57.62	66.88
	10	1	1.634	-0.630	1.634	1.896
	10	8.2	5.868	-0.580	5.868	6.811

Summary of the experimental results at various conditions

Comparison of Galvanic Corrosion Rates between ZRA and Polarization

Measurements. Thus far, the galvanic corrosion results presented and discussed were produced by galvanic coupling or ZRA measurements. The validity of these ZRA experiments and the accuracy of the produced data can be substantiated by comparing it to graphical estimation of corrosion rate from polarization measurements. Needless to say, minor deviations could be expected since the polarization method is a graphical one with some errors and also the polarization measurements were done at the end of two hour experiments, while the galvanic results were the average of the two hours duration. Anyhow, the values obtained from the two methods should be in a reasonable range which reveals the reliability of the results. That being said, the corrosion currents were graphically estimated from polarization measurements for all the experimental conditions. The values for conditions with two replications were averaged. The graphical method for estimation corrosion current from polarizations curves were already discussed earlier and represented in Figure 22. The comparison of galvanic corrosion rates between ZRA and polarizations measurements for different cathode:anode ratios for pyrite as well as pyrrhotite is demonstrated in Figure 31.



Figure 31. Comparison of galvanic corrosion rate between ZRA and polarization measurements for different cathode:anode surface area ratios at 30 °C, pH 5 for A) pyrite, and B) pyrrhotite.

The corrosion rates obtained from the two methods match very well. It should be noted that for the case of pyrite with cathode:anode surface area ratio of 1:1, the total current can only be found graphically as the cathodic current of steel can not be ignored. In this case, the total corrosion current from ZRA method was calculated based on the difference between galvanic current found from ZRA measurements and from graphical estimation of polarization curves. The results for different NaCl concentrations for cathode:anode surface ratio of 1:1 and 8:1 are also presented in Figure 32 and Figure 33, respectively.



Figure 32. Comparison of galvanic corrosion rate between ZRA and polarization measurements for different NaCl concentrations for cathode:anode ratio of 1:1 at 30 °C, pH 5 for A) pyrite, and B) pyrrhotite.



Figure 33. Comparison of galvanic corrosion rate between ZRA and polarization measurements for different NaCl concentrations for cathode:anode ratio of 8:1 at 30 °C, pH 5 for A) pyrite, and B) pyrrhotite.

The results very good agreement between ZRA and polarization method, which confirms the experimental approaches used in this study as well as the obtained experimental data. In addition, the small size of error bars in the replicated experiments signify the repeatability of the experiments. Therefore, obtaining very high accuracy and reproducibility in the results validates the experimental approaches used for this study. Table 12 summarizes the galvanic potential as well as the galvanic corrosion rate data for two methods in all experimental conditions.

Table 12.

		Cathode: Anode Surface Area Ratio	ZRA N	Aethod	Polarization Method	
Galvanic couple	NaCl Conc. (wt.%)		Coupled Potential (mV vs. Ag/AgCl)	Galvanic Corrosion Rate (mm.yr ⁻¹)	Coupled Potential (mV vs. Ag/AgCl)	Galvanic Corrosion Rate (mm.yr ⁻¹)
	0.1	1	-0.719	0.049	-0.715	0.053
		8.2	-0.656	0.508	-0.650	0.408
	1	1	-0.733	0.056	-0.729	0.069
Steel-pyrite		8.2	-0.662	0.742	-0.690	0.568
		91.1	-0.588	7.150	-0.582	5.574
		1	-0.728	0.050	-0.727	0.062
		8.2	-0.645	1.033	-0.625	1.125
	0.1	1	-0.630	0.633	-0.615	0.651
	0.1	8.2	-0.514	3.688	-0.530	2.961
G 1	1	1	-0.646	1.519	-0.635	1.214
Steel- Pyrrhotite		8.2	-0.580	7.087	-0.579	7.402
i yiiilottic		91.1	-0.491	66.88	-0.475	72.13
	10	1	-0.630	1.896	-0.625	1.658
		8.2	-0.580	6.811	-0.585	10.06

Summary of the experimental results for ZRA and polarization measurements at various experimental conditions.

Effect of pH. For final consideration, the effect of two other factors, pH and H₂S, was investigated briefly to further elucidate the mechanism of galvanic corrosion between steel and iron sulfides. Decreasing pH could increase the concentration of H⁺ ions and provides more acidic solutions, thus it can enhance the corrosion rate due to more severe corrosive environments. Since all the experiments shown up until now were performed at pH 5, few experiments were selected to be performed at pH 4. The list of selected experiments performed in this section is shown in Table 13.

Table 13.

Parameter	Conditions		
Material	X65, Pyrite	X65, Pyrrhotite	
Steel size	$5 \text{ mm D} (0.196 \text{ cm}^2)$		
Iron sulfide size	5 mm D (0.196 cm^2)	
Cathode/Anode ratio		1	
Temperature	30 °C		
Electrolyte	1 wt.% NaCl		
Sparge gas	N ₂		
Total pressure	1 bar		
pH	$4.0, 5.0 \pm 0.1$		
Exposure time	2 hours		
Electrochemical techniques	OCP, EIS, LPR, ZRA, Potentiodynamic sweep		

Test matrix for the experiments performed to investigate the effect of pH on galvanic corrosion between mild steel and iron sulfides.

Figure 34 compares the corrosion rate of different galvanic couples between pH 4 and pH 5, when cathode:anode surface area ratio is 1:1.



Figure 34. Comparison of galvanic corrosion rate between pH 4 and pH 5 for different galvanic couples for cathode:anode ratio of 1:1 at 30 °C.

It is expected to observe that the corrosion rate of uncoupled steel is increased at lower pH, as more acidic solution, or in other words more concentration of H⁺ ion increases the rate of hydrogen ion reduction reaction, thereby increases the cathodic reaction, and ultimately increases the corrosion rate. The same conclusion can be deduced by observing the results of steel-pyrite couple. However, the galvanic corrosion rate of steel-pyrrhotite couple was not impacted by the change of pH. In order to discover the reason behind this unusual outcome, it is necessary to explore the polarization behavior of mild steel and iron sulfides in different pH values as illustrated in Figure 35.



Figure 35. Comparison of potentiodynamic polarizations at pH 4 and pH 5 for A) steelpyrite couple, and B) steel-pyrrhotite couple at 30 °C, 1 wt.% NaCl, and cathode:anode surface area ratio of 1:1.

Focusing on the case of steel-pyrite couple, it is clear that the cathodic current of both mild steel and pyrite is higher at pH 4, which leads to the higher galvanic current as well as the total corrosion current. On the other hand, the cathodic current of pyrrhotite was not affected by the change of pH. Since the cathodic current of pyrrhotite is much higher than (more than an order of magnitude) the cathodic current of mild steel, the total corrosion current was not significantly impacted by the increase of cathodic current of mild steel alone. Therefore, the total galvanic corrosion rate was not altered by changing pH from 5 to 4. The effect of pH on the cathodic current of iron sulfides will be explored and discussed in detail in the next chapter, and it will be shown that the cathodic current of pyrrhotite is similar at pH 5 and 4. But for now, it suffices to conclude that the galvanic corrosion rate of steel-pyrite increases at pH 4, while it does not change for steel-pyrrhotite couple due to their different cathodic response to the change of pH. To close this topic, the validity of the experimental results was verified by comparing the corrosion rate obtained from ZRA with that obtained from polarization measurements. *Figure 36* compares the corrosion rates at two pH values, and once again, the results for two methods agree with each other. Once again, the experimental approaches used in this study was shown to be reliable.



Figure 36. Comparison of galvanic corrosion rate between ZRA and polarization measurements for different pH values for cathode:anode ratio of 1:1 at 30 $^{\circ}$ C, for A) pyrite, and B) pyrrhotite.

Effect of 100 ppm H₂S. Finally, it was important to consider the effect of dissolved H₂S on the galvanic corrosion between mild steel and iron sulfides. In this study, only low concentration of H₂S which was 100 ppm was investigated in order to discover its interaction with iron sulfides. It was a concerning hypothesis that H₂S could react with the surface of iron sulfides and impact their electrochemical behavior, and thus alter the galvanic corrosion rates. A more profound discussion regarding the impact of 100 ppm on the cathodic current of iron sulfides will be discussed in the next chapter. As H₂S is a weak acid, it could increase the corrosion of mild steel through buffering effect. However, low concentration of H₂S such as 100 ppm could merely produce enough H⁺ ions to buffer the depletion of this ion at the surface of electrode. Hence, any observed change in the galvanic corrosion rate is not associated with the buffering effect. Instead, it

could show that H₂S could possibly react with the surface of iron sulfides. In order to investigate the possible interaction between H₂S and iron sulfides, galvanic corrosion rates were measured in selected experimental conditions. The list of selected experiments measured for this purpose is shown in **Table 14**.

Table 14.

Test matrix for the experiments performed to investigate the effect of 100 ppm H_2S on galvanic corrosion between mild steel and iron sulfides.

Parameter	Conditions		
Material	X65, Pyrite	X65, Pyrrhotite	
Steel size	5 mm D	(0.196 cm^2)	
Iron sulfide size	5 mm D (0.196 cm ²) 1.27 cm ×1.27 cm (1.613 cm ²)		
Cathode/Anode ratio	1	1,8	
Temperature	30 °C		
Electrolyte	1 wt.% NaCl		
Sparge gas	N ₂		
Purge gas	$100 \text{ ppm } H_2S$		
Total pressure	1 bar		
pH	5.0 ± 0.1		
Exposure time	2 hours		
Electrochemical techniques	OCP, EIS, LPR, ZRA, Potentiodynamic sweep		

Figure 37 demonstrates the galvanic corrosion rate for different cathode:anode ratios for uncoupled steel, steel-pyrite couple and steel-pyrrhotite couples with and without 100 ppm H_2S .



Figure 37. Galvanic corrosion rates for different galvanic couples with and without the presence of 100 ppm H₂S at 30 $^{\circ}$ C, pH 5 for cathode:anode surface area ratio of A) 1:1, and B) 8:1.

As it is shown, the galvanic corrosion rates in presence of 100 ppm H₂S are very close to the those obtained in acidic solutions with no H₂S. In the case of cathode:anode surface area ratio of 8:1, as galvanic current is higher for a larger cathode to anode surface ratio, it is expected that the effect of 100 ppm H₂S is more distinguishable. However, 100 ppm H₂S does not show significant impact on the galvanic corrosion rates at this condition. The galvanic corrosion rates are slightly increased in presence of 100 ppm H₂S which could be due its minor contribution in buffering effect. Eventually, it could be deduced that 100 ppm H₂S has no major interaction with the surface of iron sulfide surface. Therefore, aqueous H₂S can influence the galvanic corrosion only by providing more H⁺ ions through buffering effect, and accordingly, it could be assumed

that galvanic corrosion rate between mild steel and iron sulfides will increase at high concentration of H₂S only due to the buffering effect.

Summary

- In the studied experimental conditions i.e., pH 5, at 30 °C, the galvanic behavior of steel-pyrite distinctly differed from that of steel-pyrrhotite couple. For cathode:anode surface area ratio of 1:1, coupling of steel to pyrite did not significantly change the corrosion rate of steel while its coupling to pyrrhotite increased the corrosion rate of steel by around an order of magnitude. This difference was correlated to the different electrochemical behavior of pyrite and pyrrhotite by analyzing their polarization response.
- When cathode:anode surface area ratio was increased to 8:1 and 91:1, the galvanic corrosion rate of both steel-pyrite and steel-pyrrhotite couples was increased by approximately the same order of magnitude.
- Improving the conductivity of solution by increasing the NaCl concentration from 0.1 wt.% to 1 wt.% increased the galvanic corrosion of steel for both cases. However, very high salt concentrations i.e., 10 wt.% NaCl did not increase the galvanic corrosion rate.
- The results obtained from ZRA measurements were compared with the results estimated graphically from potentiodynamic polarization curves. The outcome of the two methods agreed very well with each other, and thus validated the approaches used in this study.

- In addition, the effect of pH was examined. It was found that the corrosion rate of uncoupled steel as well as coupled steel-pyrite were increased by lowering the pH from 5 to 4, while the galvanic corrosion rate of steel-pyrrhotite couple was not influenced. The contradiction observed was related to the effect of pH on the cathodic current of different iron sulfides.
- Lastly, adding 100 ppm H₂S showed no impact on the galvanic corrosion rate between steel and iron sulfides and verified that H₂S does not react with the surface of iron sulfides.

Electrochemical Characterization of Iron Sulfides⁴

The galvanic coupling between steel and iron sulfides and the effect of experimental parameters including iron sulfide type, cathode:anode surface area ratio, and salt concentration, have been systematically investigated in the previous chapter. However, the prediction of galvanic current is not achievable without understanding the electrochemical characteristics of iron sulfides. Since iron sulfides act as the cathode in a steel-iron sulfide couple, the cathodic current of iron sulfides should be known to predict the accurate galvanic current. Therefore, this chapter aims to investigate the cathodic behavior of iron sulfides in various experimental conditions in strong acid solutions using rotating disk electrode (RDE) system.

Literature Review

Very few studies have investigated electrochemical reactions, specifically cathodic reactions, occurring on iron sulfides. The only systematic research to date was done by Navabzadeh et al., [123] which investigated the cathodic behavior of pyrite and pyrrhotite in various acidic solutions at different pH values using a rotating disk electrode (RDE) apparatus. The results were compared with the cathodic current of X65 mild steel in each condition. It was concluded that when H⁺ reduction reaction is dominant, i.e., low pH values, both iron sulfides showed similar cathodic current as X65 mild steel. In addition, pyrrhotite showed an extra cathodic reaction which was associated with the reduction of pyrrhotite to troilite [123].

⁴ A version of this chapter was published as a conference paper: Abdar, P.S., Brown, B. and Nesic, S. "Electrochemical Investigation and Modeling of Cathodic Reactions on Iron Sulfides in Acidic Solutions", AMPP Annual Conference, Mar. 2023.

Materials and Experimental Setup

In this study, a rotating disk electrode (RDE), as illustrated in *Figure 38*, has been used which is a very useful system for electrochemical measurements since its hydrodynamics and mass transfer have been well defined in the literature.



Figure 38. Overview of the RDE experimental setup.

Two types of iron sulfides (pyrite and pyrrhotite) have been used as well as API 5L X65 steel for comparison with the iron sulfide results. Mineral pyrite and pyrrhotite were purchased from Ward's Science. For purity analysis, these minerals were powdered by pestle and mortar, then characterized by XRD measurement using Cu K α radiation as shown in *Figure 39*. Very high purity was observed for the pyrite sample when compared to the reference pattern ICDD# 00-0042-1340. The purity of the pyrrhotite sample was also verified according to the reference pattern ICSD# 01-079-5969, however, minor impurities are present. These mineral iron sulfides were cut to the right shape and embedded in epoxy fitted in the rotating disk electrode system. In addition, a silver

conductive paste was placed on the back of the mineral samples to improve the conductivity for the gold spring contact inside the RDE holder.



Figure 39. XRD analysis of mineral iron sulfide samples. A) pyrite, B) pyrrhotite

A platinum mesh counter electrode (CE) and a saturated Ag/AgCl reference electrode (RE) were used. The experiments were performed in strong acid solutions with 1 wt.% NaCl. In order to characterize the nature of cathodic reactions, the experiments were done in various pH (3, 4, and 5) and rotational speeds (100 and 1000 rpm). Electrochemical impedance spectroscopy was utilized for the measurement and compensation of solution resistance. Cathodic polarizations were performed with the scan rate of 0.5 mV/s after running open circuit potential measurements for about 30 minutes using a Gamry Reference 600 potentiostat. The experiments were repeated twice for most of the conditions. The replicated results are shown as the average of two repeats with error bar being the standard deviation of the average values. The test matrix for the experimental conditions is shown in **Table 15**.

Table 15.

Parameter	Conditions		
Material	X65, Pyrite, Pyrrhotite		
Steel Size	5 mm ø		
pН	$3.0, 4.0, 5.0 \pm 0.1$		
rpm	100, 1000		
Temperature	25°C		
Electrolyte	1 wt.% NaCl		
Sparge Gas	N_2		
Electrochemical Techniques	Cathodic polarization 0.5 mV/s EIS for solution resistance		

Test matrix of experimental conditions.

Compositional Characterization of Mineral Pyrrhotite. As it was discussed in more details in earlier sections, pyrrhotite is a non-stoichiometric iron-deficient group of iron sulfides with the formulae of $Fe_{1-x}S$ where x is ranged from 0 to 0.2. Therefore, it is essential to quantify the structural composition of the purchased mineral pyrrhotite sample. To achieve this goal, two material characterization techniques have been used: Xray diffraction analysis (XRD), and energy dispersive spectroscopy analysis (EDS).

Numerous studies investigated the crystal structure as well as the composition of mineral pyrrhotite samples from different sources [146]–[149]. The main characterization techniques used in these studies is X-ray diffraction analysis (XRD), and the characteristics of pyrrhotites were associated with (1 0 2) peak around 2-theta of 44°.

Pyrrhotite has two crystal structures of hexagonal and monoclinic. Hexagonal structure is associated with two peaks, while monoclinic structure is associated with one peak at around 44° in XRD spectra [146]. Therefore, based on the XRD result shown in *Figure 39*, the crystal structure of pyrrhotite sample is monoclinic. The composition of pyrrhotite sample can also be corelated to the d-spacing of (1 0 2) plane which can be found from the position of (1 0 2) peak using Bragg's law as represented by Equation (61).

$$n\lambda = 2dsin\theta$$
 Equation (61)

where *n* is the diffraction order, λ is the wavelength of radiation, θ is the diffraction angle, and *d* is the d-spacing of the selected plane. The d-spacing for the (1 0 2) peak of the pyrrhotite sample was calculated to be 2.07 Å, based on its 43.7° position in its XRD pattern.

Having the d-spacing value, the composition of pyrrhotite sample was quantified using three different references. According to the reference table established by Arnold [146], the pyrrhotite sample has 47.8% iron which gives the formulae of $Fe_{0.92}S$. In addition, Toulmin et al. [148] provided an equation, as shown below, for the quantification of pyrrhotite composition.

%
$$Fe = 45.212 + 72.86(d_{(102)} - 2.04) +$$

 $311.5(d_{(102)} - 2.04)^2$ Equation (62)

Using the abovementioned equation, the iron content of the pyrrhotite sample was found to be 47.7% with the formulae $Fe_{0.91}S$. Finally, using the graphic reference from Yund et al. [147], the iron content was determined as 47.6% with the formulae $Fe_{0.91}S$.

Furthermore, the pyrrhotite sample was characterized by energy dispersive X-ray spectroscopy and the result is shown in *Figure 40*.

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
		Sum	93.81	100.00	100.00		
Iron	26	298714	55.66	59.33	41.59	1.63	2.92
Sulfur	16	599706	33.78	36.01	43.96	1.19	3.53
Carbon	6	5471	3.51	3.74	12.19	0.54	15.41
Oxygen	8	5022	0.87	0.92	2.26	0.14	15.64

Figure 40. EDS analysis of mineral pyrrhotite sample

Based on the EDS analysis, the iron content of pyrrhotite was defined to be around 48.6% which results in the composition of $Fe_{0.94}S$. Although the composition found from EDS is very close to that obtained from XRD analysis, it is less reliable due to around 2% of error of this technique as well as the presence carbon and oxygen at the surface of sample. As a result, the composition that was selected here is $Fe_{0.92}S$ (or $Fe_{11}S_{12}$ as more commonly shown in some literature), and it will be used for the further calculations in this study.

Results and Discussions

The cathodic polarizations of steel at various pH values and rotational speeds are shown in Figure 41. The cathodic current of steel is necessary in order to compare with the cathodic current of iron sulfides. Two main cathodic reactions occur at the surface of steel in acidic solutions: hydrogen ion reduction (at more positive cathodic potentials close the open circuit potential), and water reduction (at lower cathodic potential). Hydrogen ion reduction includes charge transfer and mass transfer limiting current, while water reduction reaction has only charge transfer as water is always available at the surface of electrode.



Figure 41. Cathodic current densities on the surface of steel at pH 3, 4, and 5 for A) 100 and B) 1000 rpm (RDE, 25°C, 1 wt.% NaCl, 1 bar, sparged with N₂).

The presence of hydrogen ion reduction reaction can be verified by comparing the limiting current density of this reaction to the theoretical limiting current density developed for rotating disk electrode system using Levich equation as shown below [111].

$$i_L = 0.62 n F D^{(2/3)} \omega^{(1/2)} v^{(-1/6)} C_b$$
 Equation (63)

where *n* is the number of electrons transferred in the reaction, *F* is the Faraday constant, *D* is the diffusivity, ω is the rotational speed in rad/s, *v* is the kinematic viscosity of solution, and C_b is the concentration of species [H⁺] in the bulk solution. Therefore, the limiting current density depends on both H⁺ concentration, i.e., pH, and rotational speeds. On that account, the theoretical values of limiting current densities were calculated in the various experimental conditions and listed in Table 16.

Table 16.

рН	Rotational Speed (rpm)	Mass transfer limiting current density (A.m ⁻²)
2	100	9.52
3	1000	30.10
4	100	0.952
4	1000	3.010
5	100	0.095
3	1000	0.301

The values of theoretical mass transfer limiting current densities for hydrogen ion reduction at various conditions.

Comparing the theoretical values with the experimental values shown in Figure 41, it is clear that the limiting current densities agree very well specifically at pH values of 3 and 4. This result confirm the occurrence of hydrogen ion reduction at the surface of steel and the validity of experimental approach. However, at pH 5, the experimental
results deviates from the theoretical current densities due to the dominance of water reduction reaction at this condition. Very low concentration of H⁺ at pH 5 leads to the very low limiting current density which can not be clearly seen in the experimental polarization curves. Therefore, pH 5 is not an appropriate condition for verifying the hydrogen ion reduction reaction, and it will not be shown subsequently when comparing the current densities of iron sulfides with that of steel.

Characterization of Cathodic Reactions on the Surface of Pyrite. The cathodic current densities of pyrite at varied experimental conditions are compared with that obtained for steel are displayed in Figure 42. As seen in the plot, hydrogen ion reduction and water reduction reactions are seen at the surface of pyrite in potential ranges similar to that observed for steel. Furthermore, the limiting current densities of hydrogen ion reduction of pyrite at pH of 3 and 4, as well as for 100 and 1000 rpm are identical to that of steel, which proves the occurrence of this reaction at pyrite surface. The charge transfer part (~120 mV/dec Tafel slope) of this reaction does seem to be detectable for steel at 1000 rpm and pH 3, but not at the other tested conditions. However, the charge transfer part can be clearly identified for pyrite in all four cathodic sweeps in Figure 42. The charge transfer current density does not change with rotational speed at a constant pH which implies that it only depends on the concentration of H⁺. With regards to the water reduction reaction occurring at very low potentials, the results show that the onset potential of this reaction on the surface of pyrite is more negative than on the surface of steel. This observation signifies that the water reduction reaction was retarded at the surface pyrite.



Figure 42. Comparison of cathodic current densities on the surface of steel and pyrite for 100 and 1000 rpm at A) pH 3, and B) pH 4 (RDE, 25°C, 1 wt.% NaCl, 1 bar, sparged with N₂).

In addition to these two reactions, a third reduction reaction was observed to occur at even more positive potentials which was not observed for steel. The effect of rotational speeds seems to have very minor impact, considering the error bars, on the current density of this reaction based on Figure 42, which implies that H⁺ ion is not involved in this reaction. To provide further evidence on the effect of H⁺ ion on this unknown reaction, the cathodic current of pyrite was measured in the wide range of pH as exhibited in Figure 43.



Figure 43. Cathodic current densities on the surface of pyrite at various pH values for 100 rpm (RDE, 25°C, 1 wt.% NaCl, 1 bar, sparged with N₂).

As it is seen, the cathodic current of the unknown reaction does not not change significantly with the change of pH, even for very low pH 2, which supports the fact that either the H⁺ ion does not participate in this unknown reaction, or it is not a limiting factor for the reaction. Finding the true nature of this reaction is not easily accessible since it requires advanced surface characterization techniques as well as elaborate electrochemical analysis. However, investigating the previous studies could provide some clues about the nature of this cathodic reaction. To date, no direct research has been performed on exploring the cathodic polarization of pyrite, but several electrochemical studies as well as surface characterization analysis investigated the cathodic reactions of pyrite [126], [127], [141], [150]–[152]. The electrochemical studies suggested that pyrite can be converted to iron sulfide (i.e., troilite) through solid state conversion by Reaction (32) or to iron ion through reductive dissolution shown in Reaction (33) [141], [151], [152].

$$FeS_2 + 2H^+ + 2e^- \rightleftharpoons FeS + H_2S$$

$$FeS_2 + 4H^+ + 4e^- \rightleftharpoons Fe^{2+} + 2H_2S$$

$$Reaction (32)$$

$$Reaction (33)$$

The reduction of sulfur as shown in Reaction (34) was also proposed since the sulfur can be produced at the surface of pyrite during oxidation process [141], [152], [153].

$$S + 2H^+ + 2e^- \rightleftharpoons H_2 S$$
 Reaction (34)

However, all three above-mentioned reactions involve H^+ ion which contradicts with the conclusion obtained from experimental results. Another possible reaction proposed in the literature is the reduction of polysulfides according to Reaction (35), which does not involve H^+ ion [127], [129], [150], [154].

$$S_{n(s)}^{2^{-}} + 2(n-1)e^{-} \to nS^{2^{-}}$$
 Reaction (35)

Polysulfides are chains of sulfur atoms linked together by covalent bonds. These polysulfides can be formed during the natural formation of iron sulfide minerals, and due to oxidation in various oxidative environments such as air, water, and acidic solutions [126], [131]. Several surface characterization studies confirmed the presences of

polysulfides on the surface of different types of iron sulfides such as pyrite and pyrrhotite [126], [127], [131], [150], [152], [155]. Specifically, Mikhlin and co-workers, over the past decades, utilized electrochemical methods as well as surface characterization instruments to investigate the surface analysis of iron sulfides and their oxidation and reduction reactions [126], [129], [131], [154]. They used advanced surface characterization methods including advanced X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and etc. [126], [128], [131]. In addition, some earlier studies also confirmed the presence of polysulfides on the surface of pyrite using XPS and Raman spectroscopy [127], [150], [152]. On that account, reduction of polysulfides was selected to be associated to the reduction reaction of pyrite at more positive cathodic potential since its reaction does not include H⁺ ion which matches with the experimental results. To sum up, the cathodic reactions at the surface of pyrite are listed in Table 17.

Table 17.

Summary of Cathodic Reactions on Pyrite			
High cathodic potential	$S_{n(s)}^{2-} + 2(n-1)e^- \to nS^{2-}$		
Moderate cathodic potential	$H^+_{(aq)} + e^- \rightarrow \frac{1}{2} H_{2(g)}$		
Low cathodic potential	$H_2 O_{(l)} + e^- \rightarrow \frac{1}{2} H_{2(g)} + (OH)_{(aq)}^-$		

Summary of proposed cathodic reactions on the surface of pyrite

Characterization of Cathodic Reactions on the surface of Pyrrhotite. The same experiments and evaluation were performed for the characterization of the cathodic reactions on pyrrhotite surface. Figure 44 shows the cathodic polarization of pyrrhotite and steel at two pH values and two rotational speeds. Analogous to the pyrite case, three cathodic reactions can be distinguished at the surface of pyrrhotite, although it is less clear at pH 4. Similar to what was observed for pyrite, the water reduction reaction at more negative potentials was retarded on the surface of pyrrhotite compared with steel, showing similar behavior between pyrrhotite and pyrite regarding water reduction.



Figure 44. Comparison of cathodic current densities on the surface of steel and pyrrhotite for 100 and 1000 rpm at A) pH 3 and B) pH 4 (RDE, 25°C, 1 wt.% NaCl, 1 bar, sparged with N₂).

For pyrrhotite, the Tafel region of the hydrogen reduction reaction can be observed only for the cathodic sweeps at pH 3. Also, at pH 3, changing the rotational speed influenced the limiting current density of the hydrogen reduction reaction on pyrrhotite. The limiting current density on the surface of pyrrhotite is equal to the one obtained on the surface of steel at 1000 rpm and follows the Levich equation which confirms the presence of the hydrogen reduction reaction. At 100 rpm, the limiting current density of pyrrhotite is slightly higher than steel which is due to the effect of high current density associated with pyrrhotite reduction reaction. However, at pH 4, the limiting current density is masked due the presence of another reaction with a higher current density which starts at more positive cathodic potential. This reaction was also seen at pH 3 at potential higher than the hydrogen reduction reaction. While its current density is lower than the limiting current density of hydrogen reduction at pH 3, it dominates this limiting current density at pH 4 and masks the limiting current at both rotational speeds. This unknown reaction at high cathodic potential behaves differently at pH and pH 4; rotational speed impacts its current density at pH 3, but it does not impact the current density at pH 4. Hence, it is not clear whether this reaction involves H⁺ ion. For further elucidation, the effect of pH on this reaction was investigated and the results are plotted in Figure 45.A.



Figure 45. Cathodic current densities on the surface of pyrrhotite at various pH values for A) 1000 rm, the current study B) 2000 rpm, Esmaeely and Nesic [123] (RDE, 25°C, 1 wt.% NaCl, 1 bar, sparged with N₂).

Similar experiment on the effect of pH on the cathodic current of pyrrhotite has been done previously by Esmaeely and Nesic [123], which is shown in Figure 45.B. The results of the current study qualitatively agree with the previous research. The cathodic current density of the unknown reaction changes significantly with the change of pH specifically at low pH values; however, higher pH of 4 and 5 show almost similar current density. It can be concluded that the unknown reaction depends on H⁺ ion for low pH values, while it is independent of it at less acidic solutions. Once more, previous literature have been reviewed in order to find the most probable reaction which involves H⁺ ion [129], [130], [153], [154], [156]. Analyzing the previous studies leads to two main possible cathodic reactions at the surface of pyrrhotite: reductive dissolution of pyrrhotite as described via Reaction (36), and solid-state reduction of pyrrhotite to troilite shown by Reaction (37). The HS⁻ ion can be replaced by H₂S depending on the condition of experimental solutions.

$$Fe_{(1-x)}S + H^{+}_{(aq)} + 2xe^{-} \rightarrow (1-x)Fe^{2+} + HS^{-}_{(aq)} \qquad \text{Reaction (36)}$$

$$Fe_{(1-x)}S + xH^{+}_{(aq)} + 2xe^{-} \rightarrow (1-x)FeS + xHS^{-}_{(aq)} \qquad \text{Reaction (37)}$$

Replacing the determined composition of pyrrhotite sample, these two reactions can be rewritten as Reaction (38) and Reaction (39).

$$Fe_{0.92}S + H^{+}_{(aq)} + 0.16e^{-} \rightarrow 0.92Fe^{2+} + HS^{-}_{(aq)} \qquad \text{Reaction (38)}$$

$$Fe_{0.92}S + 0.08H^{+}_{(aq)} + 0.16e^{-} \rightarrow 0.92FeS + 0.08HS^{-}_{(aq)} \qquad \text{Reaction (39)}$$

The stoichiometry of these two reactions are different indicating that the number of electrons transfer for each H^+ ion is different. The number of electrons transferred is a parameter in the Levich equation for limiting current of the related reaction. Thus, the correct reaction can be verified by comparing the theoretical limiting current density to the experimental value. For pH 3 and 1000 rpm condition, the limiting current densities of Reaction (38) and Reaction (39) were calculated to be 4.82 and 60.2 A.m⁻², respectively. Comparing the obtained values with the experimental results in Figure 45.A evidently confirms that reductive dissolution of pyrrhotite is the most probable reaction.

With regard to higher pH of 4 and 5, in which the current density does not depend on H⁺ ion, similar to the pyrite case, the reduction of polysulfides was considered as the dominant reaction. Numerous studies corroborated the presence of polysulfides at the surface of mineral pyrrhotite [126], [127], [129], [131], [155]. Therefore, two parallel reactions were considered at higher cathodic potential: first reductive dissolution of pyrrhotite according to Reaction (38) which depends on the H⁺ ion (more dominant at higher H⁺, i.e., low pH values), and second reduction of polysulfides which is independent of H⁺ ion (more dominant at higher pH values). Table 18 summarizes all the cathodic reactions at the surface of pyrrhotite.

Table 18.

Summary of proposed cathodic reactions on the surface of pyrrhotite.

Summary of Cathodic Reactions on Pyrrhotite		
High cathodic potential	$Fe_{0.92}S + H^+_{(aq)} + 0.16e^- \rightarrow 0.92Fe^{2+} + HS^{(aq)}$	
	$S_n^{2-} + 2(n-1)e^- \rightarrow nS^{2-}$	
Moderate cathodic potential	$H^+_{(aq)} + e^- \rightarrow \frac{1}{2} H_{2(g)}$	
Low cathodic potential	$H_2 O_{(l)} + e^- \rightarrow \frac{1}{2} H_{2(g)} + (OH)_{(aq)}^-$	

Comparison of Cathodic Reactions on Different Surfaces. To conclude this chapter, the cathodic currents on the surface of steel, pyrite, and pyrrhotite were compared at all the experimental conditions and presented in Figure 46. At pH 3, hydrogen reduction reaction including both mass transfer limiting as well as charge transfer regions are noticeable on the surface of both pyrite and pyrrhotite. Also, the limiting current densities of both rotational speeds are almost equal for all three electrodes which indicates the presence of hydrogen ion reduction reaction. The current density at more positive cathodic potential on pyrrhotite electrode is more than an order of magnitude larger than that on pyrite electrode. As discussed, this cathodic current at pH 3 is associated with the reductive dissolution of pyrrhotite, while it is associated with polysulfides reduction at the surface of pyrite. With respect to water reduction, it is clear that the onset potential differs for different surfaces, and the reaction is retarded on pyrite and pyrrhotite compared with steel.



Figure 46. Comparison of cathodic current densities on various surfaces at A) pH 3, 100 rpm, B) pH 3, 1000 rpm, C) pH 4, 100 rpm, D) pH 4, 1000 rpm, E) pH 5, 100 rpm, and F) pH 5, 1000 rpm. (RDE, 25°C, 1 wt.% NaCl, 1 bar, sparged with N₂).

At pH 4, the current density of pyrrhotite is generally higher than pyrite and steel. The limiting current of hydrogen ion reduction matches very well for the case of pyrite and steel at both rotational speeds; however, it was covered for the case of pyrrhotite due to very high current density of the more positive cathodic reaction which was related to polysulfides reduction as well as reductive dissolution of pyrrhotite. As it was mentioned, the polysulfides reduction reaction dominates at pH 4, still its current density on pyrrhotite surface is about an order of magnitude higher than the same reaction on pyrite surface. This observation can be explained by considering the higher stability of pyrite rather than pyrrhotite and the notion that pyrite is the most stable phase of iron sulfides. The oxidation of pyrite is lower than pyrrhotite when exposed to corrosive environments, which could result in lower amount of polysulfides formed on its surface. Mikhlin et at. examined the presence of polysulfides at the surface of both pyrite and pyrrhotite, and they found that the thickness of polysulfide layer at the surface of pyrrhotite is much thicker than that at the surface of pyrite [126], [131]. Their observation is in accordance with the experimental results of this study, and also with the higher oxidation rate and instability of pyrrhotite compared with pyrite.

At pH 5, the limiting current of hydrogen ion reduction can not be seen due to the dominance of water reduction reaction at the corrosion potential of steel. However, this limiting current is noticeable on the surface of pyrite specifically at 1000 rpm. As it is seen, the limiting current density of pyrite is clearly lower than the current density of water reduction at steel electrode. The same observation can be seen at pH 5 regarding the significant difference in the current density magnitude between the current density of

polysulfides reduction at the surface of pyrrhotite and pyrite. Similarly, the This high current density of pyrrhotite can be associated with its higher oxidation which leads to the formation of higher amount of polysulfides.

Effect of 100 ppm H₂S on the Cathodic Reactions of Iron Sulfides. In the last part of this section, the effect of 100 ppm H₂S on the electrochemical characteristics of iron sulfides is studied. The goal is to discover the potential interaction of H₂S with the surface of iron sulfides and its effect on the rate of cathodic reactions. If H₂S reacts with iron sulfides, the electrochemical reactions and the currents related to them could be different. However, if H₂S does not react with iron sulfides, adding H₂S could only influence the cathodic current through buffering effect, and thus the prediction of the electrochemical behavior of iron sulfides in H₂S aqueous solutions will be accessible. For this purpose, the cathodic current of pyrite, pyrrhotite, and mild steel was measured in acidic solutions with 100 ppm H₂S using rotating disk electrode. The test matrix of these experiments is shown in **Table 19**.

Table 19.

Parameter	Conditions		
Material	X65, Pyrite, Pyrrhotite		
Steel Size	5 mm ø		
pH	$4.0, 5.0 \pm 0.1$		
rpm	100, 1000		
Temperature	25°C		
Electrolyte	1 wt.% NaCl		
Sparge Gas	N_2		
Purge Gas	$100 \text{ ppm H}_2\text{S}$		
Electrochemical Techniques	Cathodic polarization 0.5 mV/s EIS for solution resistance		

Test matrix of experimental conditions.

The effect of 100 ppm H₂S on cathodic current has been initially obtained on the surface of X65 steel. The cathodic currents were measured for pH of 4 and 5 for the rotational speeds of 100 and 1000 rpm. As shown in *Figure 47*, the cathodic current of different experimental conditions in the absence of H₂S are compared with the results in presence of 100 ppm H₂S. At pH 4, 100 ppm H₂S does not significantly change the limiting current. However, a slight increase in the limiting current can be observed specifically for 100 rpm in presence of H₂S. This observation is expected and can be justified through buffering effect ability of H₂S. Thus, adding 100 ppm H₂S minimally

increases the concentration of H⁺ which leads to the higher limiting current density of hydrogen ion reduction reaction.



Figure 47. Comparison of cathodic current densities on steel surface in absence and presence of 100 ppm H_2S for 100 and 1000 rpm at A) pH 5 and B) pH 4 (RDE, 25°C, 1 wt.% NaCl, 1 bar).

Regarding the water reduction reaction, However, the presence of 100 ppm H_2S shifts the onset potential of this reaction to lower values, in other words, the presence of 100 ppm H_2S retards water reduction reaction. The same observation has been found in the previous study by Zheng et al. [47]. The influence of 100 ppm H_2S on water reduction reaction is more discernible at pH 5, since water reduction is the dominant reaction at this condition due to very low limiting current density of hydrogen ion reduction. Therefore, 100 ppm H_2S decreases the total current density of cathodic reactions on the surface of steel at pH 5.

Figure 48 reveals the results for cathodic current measured on the surface of pyrite in the absence and presence of 100 ppm H_2S at various conditions. As it can be

seen, 100 ppm H₂S does not significantly impact the cathodic current of hydrogen reduction reaction and its limiting current.



Figure 48. Comparison of cathodic current densities on pyrite surface in absence and presence of 100 ppm H₂S for 100 and 1000 rpm at A) pH 5 and B) pH 4 (RDE, 25°C, 1 wt.% NaCl, 1 bar).

Also, the water reduction reaction was also unaffected in the presence of 100 ppm H₂S. The reason might stem from the fact that water reduction reaction was already retarded at the surface of pyrite and can not be further retarded. In addition, the presence of 100 ppm H₂S showed minor effect on the current density of polysulfide reduction reaction at higher overpotential, proving that H₂S does not react with the surface of pyrite. These results show that 100 ppm H₂S does not have a major interaction with the surface of pyrite. Therefore, it can be concluded that at both pH values of 4 and 5, the presence of 100 ppm H₂S does not influence the cathodic current of pyrite.

The same experiments were performed on the surface of pyrrhotite. The results at pH 4 and 5 for different rotational speeds are shown in *Figure 49*. As can be observed, 100 ppm H₂S does not show any impact on the cathodic current of pyrrhotite. Since the

cathodic current is very high on the surface of pyrrhotite compared to previous cases, the cathodic currents are almost same for all the conditions.



Figure 49. Comparison of cathodic current densities on pyrrhotite surface in absence and presence of 100 ppm H_2S for 100 and 1000 rpm at A) pH 5 and B) pH 4 (RDE, 25°C, 1 wt.% NaCl, 1 bar).

These results reveals that H_2S does not affect the polysulfide as well as pyrrhotite dissolution reactions, and thereby it does not react at the surface of pyrrhotite. Therefore, it could be hypothesized that the presence of H_2S in acidic solution only increases the cathodic current through buffering effect. In fact, the effect of very high concentration of H_2S on the cathodic current of iron sulfides was already studied by Esmaeely et al., [123] and the results showed that the major contribution of H_2S on cathodic current is through increasing the current density of hydrogen evolution reaction via buffering effect. No other effect of H_2S on the cathodic current of iron sulfides was observed [123].

Summary

- The cathodic current as well as the nature of cathodic reactions were characterized at the surface of pyrite and pyrrhotite.
- Hydrogen reduction have been verified to occur on pyrite and pyrrhotite surfaces by comparing the experimental mass transfer limiting current with the theoretical one at various conditions.
- The water reduction reaction occurred on all surfaces at very low cathodic potentials. This reaction was retarded on the surface of pyrite and pyrrhotite compared with that on the surface of steel.
- At more positive cathodic potential (higher than corrosion potential of steel), the cathodic current at the surface of pyrrhotite was shown to be higher than that at the surface of pyrite. For pyrrhotite, this cathodic region was associated with the occurrence of two parallel reactions: reductive dissolution of pyrrhotite, and polysulfides reduction. On the other hand, for pyrite, this cathodic region was associated with polysulfides reduction.

Chapter 5.B: Modeling

This chapter contains the modeling section of the experimental parts presented in previous chapters. Similar to the experimental section, this chapter is divided into two main studies: modeling of electrochemical reactions on the surface of iron sulfides, and modeling of galvanic corrosion rate between steel ad iron sulfides. To achieve the final goal of this study which is the prediction of galvanic corrosion between steel and iron sulfides using polarization method as explained earlier, it is essential to firstly predict the cathodic current of iron sulfides. Therefore, this section will be provided first followed by the modeling of galvanic corrosion rate between mild steel and iron sulfides. It should be mentioned that the models proposed for both sections are the first model developed in the related topics. Therefore, it should be viewed as the first version which naturally includes several simplifications as well as shortcomings.

Modeling of Electrochemical Reactions on Iron Sulfide⁵

Hitherto, no model has been proposed for the prediction of cathodic current on the surface of iron sulfides [157]. Hence, the current study is the first attempt to provide such a model, and as is commonly seen for the first proposed model, it will suffer from some simplifications and shortcomings. With that being the case, the first model should be proposed in order to be improved in the next studies. The current mathematical model is based on the mechanistic understanding of cathodic reactions occurring on the surface of iron sulfides as it was described in previous chapter. A model for the cathodic current of steel will be provided initially in order to establish the foundation of the model. The values of the parameters for different cathodic reactions was proposed based on previous studies and also on the fitting to the experimental results. However, these values were attempted to follow consistent procedure as much as possible.

Mathematical Model

First the two well-established cathodic reactions were considered: hydrogen ion reduction, and water reduction. Hydrogen ion reduction consists of two regions of charge transfer current and mass transfer limiting current. The charge transfer current density for all the cathodic reactions proposed in this study was calculated using Tafel equation as represented in Equation (64).

⁵ A version of this chapter was published as a conference paper: Abdar, P.S., Brown, B. and Nesic, S. "Electrochemical Investigation and Modeling of Cathodic Reactions on Iron Sulfides in Acidic Solutions", AMPP Annual Conference, Mar. 2023.

$$i_{H^+,ct} = i_{0,H^+} \times 10^{-\frac{(E-E_{rev})}{b_c}}$$
 Equation (64)

where b_c (V.dec⁻¹) is the Tafel slope, E (V) is the applied cathodic potential, E_{rev} (V) is the reversible potential of reaction, and i_{0,H^+} (A.m⁻²) is the exchange current density which is determined from Equation (65) for hydrogen ion reduction and is constant for all other reactions.

$$i_{0,H^+} = i_{0,H^+}^{ref} \left(\frac{c_{H^+}}{c_{H^+,ref}} \right)^{0.5} \times e^{-\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)}$$
Equation (65)

where i_{0,H^+}^{ref} (A.m⁻²) is the reference exchange current density, c_{H^+} (M) is the concentration of H^+ ion, $c_{H^+, ref}$ (M) is the reference concentration, ΔH (kJ.mol⁻¹) is the enthalpy of reaction, R (J.K⁻¹.mol⁻¹) is the molar gas constant, T (K) is the temperature, and T_{ref} is the reference temperature.

The mass transfer limiting current density of hydrogen ion reduction follows Levich equation, as rotating disk electrode used in this study. Finally, the total current for the hydrogen reduction reaction consists of both charge transfer current and mass transfer limiting current, is calculated by Equation (66).

$$\frac{1}{i_{H^+}} = \frac{1}{i_{H^+,ct}} + \frac{1}{i_{H^+,lim}}$$
 Equation (66)

Regarding the water reduction reaction, since water is always available on the surface of electrode, the current density for the water reduction reaction is a sole charge transfer current which can be found using Tafel equation.

For the case of pyrite, in addition to the two reactions described above, the reduction of polysulfides was also considered. Similar to hydrogen ion reduction, this reaction has both charge transfer and limiting currents, with former calculated from Tafel equation and latter being a constant limiting current. The limiting current in this case is not mass transfer limited as it is not changing with the change of pH. The nature of this limiting current is unknown; however, it could be related to the reaction at the surface of pyrrhotite.

For the case of pyrrhotite, in addition to two reactions considered for steel and the polysulfide reduction reaction considered for pyrite, the reductive dissolution of pyrrhotite was also added. Once more, analogous to hydrogen ion reduction, this reaction has both charge transfer and mass transfer limiting currents. The charge transfer current density was found from Tafel equation. As this reaction was shown to be H⁺ concentration dependent, Levich equation was used for the mass transfer limiting current density with 0.16 (found previously from the stoichiometry of reaction based on pyrrhotite composition) as the number of charges transferred which gives n = 0.16 in Levich equation. All the equations are summarized as listed in **Table 20**. Also, the values for different parameters used in the modeling are listed in **Table 21**.

Table 20.

List of equations used in the mathematical model.

Equation	Number
$\frac{1}{i_{H^+}} = \frac{1}{i_{H^+,ct}} + \frac{1}{i_{H^+,lim}}$	Equation (66)
$i_{H^+,ct} = i_{0,H^+} \times 10^{-\frac{(E-E_{rev})}{b_c}}$	Equation (64)
$i_{0,H^+} = i_{0,H^+}^{ref} \left(\frac{c_{H^+}}{c_{H^+,ref}}\right)^{0.5} \times e^{-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{T_{ref}})}$	Equation (65)
$i_{H^+,lim} = 0.62 F D^{2/3} v^{(-\frac{1}{6})} \omega^{1/2} c_{H^+}$	Equation (63)
$i_{H_2O} = i_{0,H_2O} \times 10^{-\frac{\eta}{b_c}}$	Equation (67)
$\frac{1}{i_{ps_pyrite}} = \frac{1}{i_{ps_pyrite,ct}} + \frac{1}{i_{ps_pyrite,lim}}$	Equation (68)
$i_{ps_pyrite,ct} = i_{0,ps_pyrite} \times 10^{-\frac{(E-E_{rev})}{b_c}}$	Equation (69)
$i_{ps_pyrite,lim} = 0.13 \ (A. m^{-2})$	Equation (70)
$\frac{1}{i_{ps_pyrrhotite}} = \frac{1}{i_{ps_pyrrhotite,ct}} + \frac{1}{i_{ps_pyrrhotite,lim}}$	Equation (71)
$i_{ps_pyrrhotite,ct} = i_{0,ps_pyrrhotite} \times 10^{-\frac{(E-E_{rev})}{b_c}}$	Equation (72)
$i_{ps_pyrrhotite,lim} = 4 \ (A. m^{-2})$	Equation (73)
$\frac{1}{i_{diss_pyrrhotite}} = \frac{1}{i_{diss_pyrrhotite,ct}} + \frac{1}{i_{diss_pyrrhotite,lim}}$	Equation (74)
$i_{diss_pyrrhotite,ct} = i_{0,diss_pyrrhotite} \times 10^{-\frac{(E-E_{rev})}{b_c}}$	Equation (75)
$i_{diss_pyrrhotite,lim} = 0.1 F D^{2/3} v^{(-\frac{1}{6})} \omega^{1/2} c_{H^+}$	Equation (76)

* i_{ps} is current density of polysulfide reduction and i_{diss} is current density of reductive dissolution

Table 21.

Parameter	Steel	Pyrite	Pyrrhotite
i_{0,H^+}^{ref} (A.m ⁻²)	3×10 ⁻²	1.5×10 ⁻³	3×10 ⁻⁵
$C_{H^{+,ref}}$ (M)	10 ⁻⁴	10^{-4}	10 ⁻⁴
$\Delta H \ (kJ. mol^{-1})$	30	30	30
b_{c,H^+} (V. dec^{-1})	0.12	0.10	0.10
$T_{ref}(K)$	293	293	293
$E_{rev,H^+}(V)$	-0.059×pH	-0.059×pH	-0.059×pH
i_{0,H_20} (A. m^{-2})	3×10 ⁻⁴	10 ⁻⁵	2×10 ⁻⁴
$b_{c,H_20} (V.dec^{-1})$	0.16	0.16	0.18
E_{rev,H_2O} (V)	-0.2	-0.2	-0.2
$i_{0,ps}$ (A. m^{-2})	-	10-2	5×10 ⁻²
$b_{c,ps}$ (V. dec^{-1})	-	0.28	0.28
$E_{rev,ps}$ (V)	-	0.2	0.1
$i_{0,diss_pyrrhotite} (A.m^{-2})$	-	-	10-3
$b_{c,diss_pyrrhotite} (V. dec^{-1})$	-	-	0.12
$E_{rev,diss_pyrrhotite}$ (V)	-	-	0.3

The values of parameters used in the mathematical model.

Model Verification

In order to validate a model, the crucial step is to compare the performance of the model with experimental data at different conditions. On that account, the model developed for the cathodic current was compared with the experimental measurements from previous chapter at various experimental conditions using rotating disk electrode. Starting with verifying the model for the case of steel, *Figure 50* compares the experimental cathodic current with the predicted cathodic current at various conditions.



Figure 50. Comparison of experimental and predicted cathodic current densities on the surface of steel at pH 3, 4, and 5 for A) 100 rpm, and B) 1000 rpm.

Figure 50 shows the model successfully predicted the limiting current values as well as the charge transfer current for both hydrogen and water reduction reactions at various pH values and rotational speeds. Specifically, the model can capture the effect of change in H^+ ion concentration on the limiting current. It should be noticed that the anodic reaction was not taken into account in the model, so there is a deviation between the predicted and measured values above the open circuit potential as anodic current lies in this region in experimental situation. The charge transfer region was kept here as it

aids in analysis as the pure charge transfer cathodic Tafel can be seen and compared with the case of iron sulfides. According to earlier discussion, at pH 5, the limiting current is very low and cannot be clearly defined in experimental results, thus the model show slight deviation at this condition. Overall, the modeling results agree very well with the experimental results.

For the case of pyrite, *Figure 51* shows the cathodic currents measured by experiments as well as the predicted cathodic current from the model. The model successfully predicted the charge transfer as well as limiting current of hydrogen reduction reaction at various pH and rotational speeds. It should be emphasized here that the values for the parameters do not change with the change of condition. A model is verified based on fitting to the experimental data when constant values are able to predict the experiments at various conditions. Therefore, the values shown in **Table 21** were used for all conditions in order to verify the model, and the outcome confirmed the validity of the model.



Figure 51. Comparison of experimental and predicted cathodic current densities on the surface of pyrite at pH 3, 4, and 5 for A) 100 rpm, and B) 1000 rpm.

The water reduction reaction was also predicted reasonably, even though it has minor importance in the galvanic corrosion modeling as the galvanic potential is around and above corrosion potential of steel. Only at pH 5, water reduction has more contribution as the limiting current of hydrogen ion reduction decreases. Furthermore, the prediction of polysulfide reduction was also promising. Since polysulfide reduction does not depend on H⁺ ion, its current density does not vary with the change of pH and rotational speed. The slight deviation from experimental results stems from a slight increase of the current density in higher rotational speeds. Also, the modeling results fall in the range of errors, but it is not clear here as the error bars are not shown due to clarity of the figures. Overall, the modeling results match very well with the experimental results and was able to capture the effect of experimental parameters.

Finally, *Figure 52* displays the comparison between experimental and modeled cathodic currents on the surface of pyrrhotite at different conditions. The charge transfer and limiting current density of hydrogen ion reduction was successfully predicted at pH 3 condition. Furthermore, the current density of reductive dissolution of pyrrhotite was also predicted at pH 3 for both rotational speeds. This reaction was H⁺ ion dependent and this dependency was captured by the model.



Figure 52. Comparison of experimental and predicted cathodic current densities on the surface of pyrrhotite at pH 3, 4, and 5 for A) 100 rpm, and B) 1000 rpm.

As it was explained, the limiting current of hydrogen ion reduction for pyrrhotite could not be seen at pH 4 and 5. In these conditions the polysulfide reduction is dominant, and the current density does not alter with the change of pH and rotational speed. Thus, the current densities are very similar at these pH values which was reasonably predicted by the model. The model also reasonably well predicted the current density of water reduction reaction. The slight deviation between the experimental and predicted cathodic current density on pyrrhotite originates from the very peculiar cathodic behavior of pyrrhotite as well as its high instability in acidic solutions. The model could be improved by deeper understanding of the mechanism of pyrrhotite cathodic reactions in acidic solutions. In general, although the model seems less accurate for pyrrhotite as compared to pyrite, the agreement is still acceptable.

Summary

• A mathematical model was developed for prediction of cathodic current density on the surface of steel, pyrite and pyrrhotite.

- The model was based on the cathodic reactions found previously based on the characterization of cathodic reactions on iron sulfides.
- The model was verified by comparing the experimental measurements of cathodic current density on iron sulfides at various pH and rotational speeds using rotating disk electrode.
- The model was able to successfully predict the cathodic current density of steel, pyrite, and pyrrhotite at various experimental conditions.

Modeling of Galvanic Corrosion Between Mild Steel and Iron Sulfides

The ultimate goal and the final step of the current study is to provide a predictive model for the galvanic corrosion rate between mild steel and iron sulfides. The model will be verified by comparing it to the experimental data obtained from Chapter 4.A. As it was discussed, this is the first attempt to provide a mathematical model for the galvanic corrosion between mild steel and iron sulfides, and thus it is based on several simplifying assumptions which will be discussed later in more detail. It is important to mention that the modeling approach proposed in this section is a general method which can be applicable to various types of experimental systems, even though the specific characteristics of experimental setup used in this study were considered here in order to compare with the obtained experimental results. Therefore, the proposed modeling approach could be used in future research in this area for different experimental designs.

Modeling Approach

The modeling of galvanic corrosion between mild steel and iron sulfides is based on the graphical estimation of the parameters from polarization curves. This approach has been used in the experimental section (Chapter 4.A) in order to verify the results obtained for galvanic corrosion rate by ZRA method. Also, the scientific fundamentals of this approach has been exhaustively explained in the same chapter. Consequently, an in-depth description of the basics of the method is not required anymore. However, an example of the methodology used for the modeling of galvanic corrosion is shown in *Figure 53*, and will be briefly explained.



Figure 53. An example of polarization method for modeling of galvanic corrosion rate between mild steel and iron sulfides (steel-pyrite couple, pH 5, RDE with 1000 rpm, 30 °C, 1 wt.% NaCl, Cathode: Anode = 1:1)

Having the cathodic and anodic polarizations of the cathode and anode in a galvanic couple, the galvanic or coupled potential can be found as the intersection of total cathodic current with total anodic current. The first assumption in the case of this study is that the anodic current of iron sulfides is ignored since it is several orders of magnitude smaller than the anodic current of mild steel. The open circuit potential of iron sulfides is much higher than that of mild steel (~0 V vs. -0.7 V) which causes a very low anodic current in the region near the open circuit potential of mild steel. Therefore, the total anodic current is identical to the anodic current of mild steel as seen in *Figure 53*. The total cathodic current is the summation of cathodic current of mild steel and that of iron sulfide (pyrite in this example). As a result, the coupled or galvanic potential (E_{gal}) can be graphically found as the intersection of total anodic and total cathodic current. The galvanic current (i_{gal}) is the cathodic current of iron sulfide, i.e., pyrite, at the galvanic potential which is illustrated with dashed red line in *Figure 53*. More importantly, the

total galvanic corrosion current $(i_{gal,corr})$ is the anodic current of mild steel at the galvanic potential which is represented by dashed black line. Noticing that blue dashed line represents the corrosion current (i_{corr}) of mild steel when it is not coupled to the iron sulfide. It can be clearly seen from *Figure 53* that the corrosion current of mild steel increased due to the coupling to the iron sulfide, $i_{gal,corr}$ is higher than i_{corr} . Using this methodology, the galvanic corrosion rate was calculated for various experimental conditions.

The prerequisite to predict the galvanic corrosion rate is to model the cathodic current of mild steel and iron sulfides as well as the anodic current of mild steel. The previous chapter developed a mathematical model for prediction of cathodic currents for rotating disk electrode (RDE) system. As it was described in the experimental chapter, the experimental setup designed for the galvanic corrosion measurements was specific characteristics which differs from rotating disk electrode, particularly the mass transfer parameters are totally different due to the stagnant condition. Therefore, some modifications are required for the values used in the modeling of cathodic current. However, the modifications were attempted to be as few as possible in order to keep the consistency of the proposed model. The mass transfer coefficient of the galvanic corrosion setup was calculated based on the experimental results obtained at pH 4. The value of mass transfer coefficient is very low which corresponds to the experimental condition of stagnant solution. Based on the calculations, the limiting current of galvanic corrosion setup can be governed from Levich equation using the rotational speed of 0.03 rpm ($\omega = 0.03$). All other equations used for the modeling of cathodic current are the

same as described in previous chapter in **Table 20**. Also, the cathodic currents of the water reduction and the polysulfides reduction were slightly changed in the experimental results of galvanic corrosion setup. These deviations could originate from the different shape of electrodes as well as the geometry of the setup, and also from the fact that these two reactions are mainly controlled by charge transfer. Reviewing the literature also shows that the Tafel slope and exchange current density of water reduction reaction varies, sometimes significantly, depending on the experimental conditions [47], [67]. On that account, the values for the exchange current densities were modified based on the galvanic corrosion setup and the modified values are listed in **Table 22**. The values for all other parameters remained exactly the same as reported in **Table 21**.

Table 22.

Parameter	Steel	Pyrite	Pyrrhotite
i_{0,H_20} (A. m^{-2})	1.5×10 ⁻⁴	3×10 ⁻⁵	8×10 ⁻⁴
$i_{0,ps}$ (A.m ⁻²)	-	3×10 ⁻⁴	1.5×10 ⁻²

The modified exchange current density for galvanic corrosion setup.

The anodic current of mild steel was also modeled, in a simplistic way, as a charge transfer current found from Tafel equation as shown below.

$$i_{Fe} = i_{0,Fe} \times 10^{\frac{(E - E_{rev})}{b_a}}$$
Equation (77)

In Equation (77), E_{rev} (V) is the eversible potential of iron dissolution reaction equal to -0.488 V, b_a (V.dec⁻¹) is the Tafel slope of reaction equal to 0.04, and $i_{0,Fe}$ (A.m⁻²) is the exchange current density defined as Equation (78).

$$i_{0,Fe} = 0.25 \times \theta_{OH^-} \times e^{\frac{-\Delta H}{R}(\frac{1}{T} - \frac{1}{T_{ref}})}$$
Equation (78)

The exchange current density of iron dissolution reaction depends on the surface coverage of OH⁻ ions which depends on its concentration following the Langmuir adsorption model as described in Equation (79) [47]. All other parameters have the same values as they have in exchange current density of hydrogen ion reduction reaction.

$$K_1 C_{OH^-} = \frac{\theta_{OH^-}}{1 - \theta_{OH^-}}$$
 Equation (79)

where the value for the constant K_1 is 2×10^{10} . Therefore, the current density of iron dissolution reaction only depends on the pH of the solution.

Model Verification

The final step of the modeling section is to verify the developed model by comparing to the experimental results gained in the previous sections. As the polarization measurements slightly changes due to the specific design of galvanic corrosion setup, it is worthful to first verifies the modeling of polarization results. *Figure 54* compares the experimental and modeling results of the polarization curves for mild steel and iron sulfides.



Figure 54. Comparison of experimental and predicted polarization curves for A) steel-pyrite , and B) steel-pyrrhotite, at pH 5, 30°C, 1 wt.% NaCl, cathode:anode = 1:1. (solid lines are the experimental data, and dashed lines are the modeling results).

A good agreement can be observed between the experimental and modeled polarization curves. For the iron dissolution reaction, the anodic current deviates from the Tafel behavior with the increase of potential. This behavior originates from the change of mechanism from active region to transition region in iron dissolution reaction. The exact mechanism for the transition region is very complex and still not known, therefore its modeling needs complex mathematical calculations and is not in the scope of this study. This deviation could cause major errors for the modeling of galvanic corrosion current at high cathode:anode surface area ratios since the coupled potential is higher in those conditions. Also, slight deviation in the cathodic current of mild steel stems from very low limiting current due to the stagnant condition as well as high pH of solution. Despite these facts, the mathematical model can reasonably predict the polarization behavior of mild steel and iron sulfides. Even though the experimental setup differs from rotating disk electrode, the cathodic behavior of iron sulfides qualitatively agrees with that observed in rotating disk electrode. The cathodic current of pyrrhotite is much larger than the cathodic current of pyrite and mild steel. Also, the cathodic current of pyrite is lightly lower than that of mild steel.

Finally, the performance of the model to predict the galvanic corrosion rates between mild steel and iron sulfides could be verified by comparing to the experimental results gathered in the previous sections. *Figure 55* shows the galvanic corrosion rate of coupled steel-pyrite obtained from different experimental approaches and its comparison with the modeling data.



Figure 55. Comparison of experimental and predicted galvanic corrosion rates for steel-pyrite couple for different cathode:anode surface area ratio at pH 5, 30°C, 1 wt.% NaCl.
As the modeling of galvanic corrosion rates was based on the polarization method, the more accurate way is to compare the modeling results with the results obtained from polarization. In all cathode:anode surface area ratios, the modeled corrosion rates are very close to the experimental polarization results. The model slightly underpredicts the corrosion rates at high cathode:anode surface area ratios which could be related to the several assumptions considered to simplify the mathematical modeling (e.g., anodic current was assumed to follow Tafel equation which deviates from reality). The most important feature of the model is its ability to capture the effect of cathode:anode surface area ratio with reasonable precision which will be very beneficial for the modeling of real situations. The same comparison has been done for the case of coupled steel-pyrrhotite, and the results are shown in *Figure 56*.



Figure 56. Comparison of experimental and predicted galvanic corrosion rates for steel-pyrrhotite couple for different cathode:anode surface area ratio at pH 5, 30°C, 1 wt.% NaCl.

Once more, the predicted corrosion rates match very well with the experimental data of polarization measurements at different cathode:anode surface area ratios. The agreement in this case is even better than the case of coupled steel-pyrite, although the model slightly overpredicts the galvanic corrosion rates in all conditions. So far, the performance of the model to capture the effect of type of iron sulfides and cathode:anode surface area ratio was examined. The effect of conductivity (NaCl concentration) can not be investigated since its effect on the polarization curves are not know. The concentration of NaCl changes the solution resistance, and more importantly, changes the activity of the solution which leads to non-ideal solutions at high concentration of NaCl. This effect was independently studied in several previous papers, and therefore it is out of the scope of current research. The polarization curves can not be predicted for various NaCl solutions due to the complexity of mathematical correlations. Hence, the effect of NaCl concentration on the galvanic corrosion rates was not investigated. Instead, the effect of another important factor, namely pH, was discovered and the results are presented in Figure 57.



Figure 57. Comparison of experimental and predicted galvanic corrosion rates at different pH values for A) steel-pyrite couple, and B) steel-pyrrhotite couple for cathode:anode surface area ratio of 1:1 at 30°C, 1 wt.% NaCl.

As can be seen, the experimental and modelling results agree very well for both steel-pyrite and steel-pyrrhotite couples at both pH values of 4 and 5. The galvanic corrosion rate of steel-pyrite couple is increased at pH 4 which was successfully predicted by the model. On the other hand, the galvanic corrosion rate of steel-pyrrhotite couple did not alter with the change of pH, which was also predicted by the model. Therefore, it can be concluded that the developed model is able to capture the effect of pH on the galvanic corrosion rate between mild steel and iron sulfides. Overall, the model was successful in predicting the galvanic corrosion rates at various experimental conditions and it was able to predict the effect of different influential factors on the galvanic corrosion rates. Thus, the developed model could be a valuable tool for future studies in this area and could facilitate the development of a predictive model for the localized corrosion of mild steel in H₂S environments.

Summary

- A mathematical model was developed for prediction of galvanic corrosion rates between mild steel and iron sulfides.
- The model was based on the graphical estimation of galvanic corrosion current from polarization curves of mild steel and iron sulfides.
- The model was verified by comparing with the experimental measurements of galvanic corrosion rate at various experimental conditions.
- The model was able to successfully predict the galvanic corrosion rates at different experimental conditions and to capture the effect of iron sulfide type, cathode:anode surface area ratio, and solution pH.

Chapter 6: Conclusions and Future Works

Conclusions

Current research investigated the galvanic coupling between mild steel and iron sulfide by applying both experimental and modeling approaches in order to elucidate the mechanism involved in this process. As a basis for the modeling of galvanic corrosion research, new approaches were proposed for the modeling of electrochemical reactions as well as uniform corrosion rate of mild steel in aqueous H₂S solutions. Afterward, systematic studies with new design for the electrochemical cell were used for the investigation of galvanic corrosion between mild steel and iron sulfides. The main findings are:

- The effect of influential experimental parameters on the galvanic coupling between steel and iron sulfides was discovered. Cathode to anode surface area ratio was shown to significantly impact the galvanic current while conductivity of solution did not affect the process significantly. Also, steel-pyrrhotite showed higher galvanic corrosion rates than steel-pyrite.
- The cathodic current on the surface of iron sulfides was investigated in order to reveal the difference in their cathodic characteristics. Pyrrhotite showed higher cathodic reactions than pyrite. In addition, the cathodic reactions at the surface of each iron sulfide was discovered.
- A mathematical model for the rate of electrochemical reactions on the surface of iron sulfides was developed. The model was based on the cathodic reactions occurring at the surface of iron sulfides as well as the constants obtained from

experimental data. The model successfully predicted the cathodic current in various experimental conditions.

• A model, for the first time, was developed for predicting the galvanic corrosion rate between mild steel and iron sulfides. The model was based on the polarization behavior of mild steel and iron sulfides. The model was verified by comparing with the experimental results in various experimental conditions, and very good agreement was found between experimental and modeling results.

Recommendations for Future Work

The research on the understanding of the mechanism of localized corrosion in H_2S environments is in its early stages. The current study unraveled some aspects of this complex process by improving the mechanistic understanding of the galvanic corrosion between mild steel and iron sulfides. However, the following areas need further investigation in order to obtain a conclusive understanding of this system.

- It was shown that galvanic coupling occur between mild steel and iron sulfides, but the cause of this galvanic coupling in the case of H₂S corrosion of mild steel is still unknown. Iron sulfides are formed mostly during the H₂S corrosion of mild steel, but it is not clear if they always lead to the galvanic coupling and therefore localized corrosion. Therefore, an extensive investigation is required in order to understand the effect of galvanic coupling in situations similar to real H₂S corrosion of mild steel. For instance, different types of iron sulfides could be formed in controlled experimental conditions in H₂S environments, then their effect on the localized corrosion of mild steel could be examined.
- According to the current study, cathode to anode surface area ratio has a significant impact on the galvanic corrosion rate. In real situations, the iron sulfides formed in the H₂S corrosion of mild steel are very porous in some cases. The porosity increases the surface area of the cathode and thereby the rate of galvanic corrosion. On that account, the determination

of the porosity of different iron sulfides and its effect on the galvanic coupling could be the topic of a future project.

The current study deals with the interaction of mild steel with single-phase iron sulfides. However, in real situations, the iron sulfides formed during H₂S corrosion of mild steel are mixture of various polymorphs. As the current study showed, pyrite and pyrrhotite behave differently when coupled to mild steel. Therefore, the mixture of iron sulfides could show different cathodic behavior due to the specific physicochemical characteristics of each polymorph. Hence, their galvanic interaction with mild steel is also different and depends on the composition of the mixture. Studying the galvanic corrosion between mixed sulfide layers and mild steel is also another interesting topic for future research. A systematic investigation could be designed to reveal the composition of iron sulfides formed during H₂S corrosion of mild steel in different experimental conditions.

The current study also proposed the first model for the cathodic current on the surface of iron sulfides as well as the galvanic corrosion between steel and iron sulfides. Since it is the first attempt in this topic, the proposed model has some limitations which could be improved in future studies. The model could be modified and improved based on the advancement on the mechanistic understanding of this system which will be revealed in future research. In addition, modeling of localized attacks on the surface of mild steel in H₂S environment, which is the final goal of all studies in this area, could be

founded, in simple format, upon the proposed model. For instance, a two-dimensional model could be developed for a pit under a layer of iron sulfides based on the galvanic corrosion model developed in the current study. However, obtaining a comprehensive mechanistic model for the localized corrosion of mild steel in H₂S environments needs significant improvement in the understanding and modeling of this system which could be obtained with a long-term plan for future studies.

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Appendix A: Supplemental Information for Modeling of Cathodic Current for Weak Acids

This supplemental section provides the detail of the mathematical calculations for the derivation of the cathodic limiting current density for the general case of weak acids with one dissociation, as shown below.

$$HA \rightleftharpoons H^+ + A^-$$

The kinetic constant of this reaction depends on the rate of forward (k_f) and backward (k_b) reactions.

$$K = \frac{C_H + C_A}{C_{HA}} = \frac{k_f}{k_b}$$

It was assumed that the concentration of conjugate base (C_{A^-}) is a constant value. Therefore, the equation for the new kinetic constant can be written as below.

$$K' = \frac{C_{H^+}}{C_{HA}} = \frac{k_f}{k_b C_{A^-}} = \frac{k_f}{k_b'}$$

Based on the assumption and simplifications shown in the related chapter, the final equations to be solved are as follows.

$$\frac{\partial^2 C_{HA}}{\partial x^2} + \frac{k'_b}{D_{HA}} C_{H^+} - \frac{k_f}{D_{HA}} C_{HA} = 0$$
$$\frac{\partial^2 C_{H^+}}{\partial x^2} + \frac{k_f}{D_{H^+}} C_{HA} - \frac{k'_b}{D_{H^+}} C_{H^+} = 0$$

With the boundary conditions as defined below.

@
$$x = \delta_m$$
, $C_{HA} = C_{HA}^b$, $C_{H^+} = C_{H^+}^b$

@
$$x = 0$$
, $(\frac{\partial C_{HA}}{\partial x})_{x=0} = 0$, $C_{H^+} = 0$

The following mathematical procedure describes the derivation of concentration profiles by simultaneously solving the abovementioned two differential equations with the defined boundary conditions.

Defining two functions of f_1 and f_2 as below:

$$f_{1} = C_{HA} + \frac{D_{H^{+}}}{D_{HA}}C_{H^{+}}$$

$$f_{2} = C_{HA} - \frac{1}{K'}C_{H^{+}}$$

$$\frac{\partial^{2}f_{1}}{\partial x^{2}} = 0$$

$$\frac{\partial^{2}f_{2}}{\partial x^{2}} = \left(\frac{k_{f}}{D_{HA}} + \frac{k_{b}'}{D_{H^{+}}}\right) \cdot f_{2} = (\frac{1}{\delta_{r}})^{2} \cdot f_{2} , \qquad \frac{1}{\delta_{r}} = \sqrt{\left(\frac{k_{f}}{D_{HA}} + \frac{k_{b}'}{D_{H^{+}}}\right)}$$

The solution of the functions f_1 and f_2 are as below:

$$f_1(x) = C_1 x + C_2$$

$$f_2(x) = C_3 \cosh\left(\frac{x}{\delta_r}\right) + C_4 \sinh\left(\frac{x}{\delta_r}\right)$$

$$\frac{\partial f_1(x)}{\partial x} = C_1$$

$$\frac{\partial f_2(x)}{\partial x} = \frac{1}{\delta_r} C_3 \sinh\left(\frac{x}{\delta_r}\right) + \sqrt{n} C_4 \cosh\left(\frac{x}{\delta_r}\right)$$

Implementing boundary conditions:

$$f_{1}(\delta_{m}) = C_{1}\delta_{m} + C_{2} = C_{HA}^{b} + \frac{D_{H^{+}}}{D_{A}}C_{H^{+}}^{b} \rightarrow C_{2} = C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}}C_{H^{+}}^{b} - C_{1}\delta_{m}$$

$$f_{2}(\delta_{m}) = C_{3}\cosh\left(\frac{\delta_{m}}{\delta_{r}}\right) + C_{4}\sin h\left(\frac{\delta_{m}}{\delta_{r}}\right) = 0 \rightarrow C_{3} = -C_{4}tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)$$

$$f_{1}(0) = C_{1} \times 0 + C_{2} = C_{HA}^{s} \rightarrow C_{2} = C_{HA}^{s}$$

$$f_{2}(0) = C_{3}\cosh(0) + C_{4}\sin h(0) = C_{HA}^{s} \rightarrow C_{3} = C_{HA}^{s} = C_{2}$$
$$\frac{\partial f_1(0)}{\partial x} = C_1 = \frac{D_{H^+}}{D_{HA}} \frac{\partial C_{H^+}}{\partial x}$$
$$\frac{\partial f_2(0)}{\partial x} = \frac{1}{\delta_r} C_3 \sinh(0) + \frac{1}{\delta_r} C_4 \cos h(0) = -\frac{1}{K'} \frac{\partial C_{H^+}}{\partial x} \to C_4 = -\frac{1}{\frac{K'}{\delta_r}} \frac{\partial C_{H^+}}{\partial x}$$

Two relations can be found between C_3 and C_1 :

$$C_{1} = -\frac{D_{H^{+}}K'}{D_{HA}}\delta_{r}C_{4} \xrightarrow{replacing C_{4} by C_{3}} C_{1} = \frac{D_{H^{+}}K'}{D_{HA}}\frac{C_{3}}{\delta_{r}} \frac{C_{3}}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}$$
$$C_{3} = C_{2} \xrightarrow{replacing C_{2} by C_{3}} C_{3} = C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}}C_{H^{+}}^{b} - C_{1}\delta_{m}$$

From two equations above, all the constants can be calculated:

$$C_3 = C_{HA}^b + \frac{D_{H^+}}{D_{HA}} C_{H^+}^b - \frac{D_{H^+}}{D_{HA}} \frac{K'}{\delta_r} \frac{C_3}{\tanh\left(\frac{\delta_m}{\delta_r}\right)} \delta_m$$

$$C_{3} = \frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}}C_{H^{+}}^{b}}{1 + \frac{D_{H^{+}}}{D_{HA}}\frac{K'\frac{\delta_{m}}{\delta_{r}}}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}} = C_{2}$$

$$C_{4} = -\frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}}C_{H^{+}}^{b}}{1 + \frac{D_{H^{+}}}{D_{HA}}\frac{K'\frac{\delta_{m}}{\delta_{r}}}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}} \times \frac{1}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)} = -\frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}}C_{H^{+}}^{b}}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) + \frac{D_{H^{+}}}{D_{HA}}K'\frac{\delta_{m}}{\delta_{r}}}$$
$$C_{1} = \frac{D_{H^{+}}K'}{D_{HA}}\frac{C_{A}^{b} + \frac{D_{H^{+}}}{D_{HA}}C_{H^{+}}^{b}}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) + \frac{D_{H^{+}}}{D_{HA}}K'\frac{\delta_{m}}{\delta_{r}}} = \frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}}C_{H^{+}}^{b}}{\frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{D_{H^{+}}K'}{\delta_{r}}} + \delta_{m}}$$

Now functions f_1 and f_2 can be calculated:

$$f_{1}(x) = C_{1}x + C_{2} = \frac{C_{HA}^{b} + \frac{D_{H}^{+}}{D_{HA}}C_{H}^{b}}{\frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{D_{H}^{+}}{D_{HA}}K'\frac{\delta_{m}}{\frac{\delta_{m}}{\delta_{r}}}} + \delta_{m}} x + \frac{C_{HA}^{b} + \frac{D_{H}^{+}}{D_{HA}}C_{H}^{b}}{1 + \frac{D_{H}^{+}}{D_{HA}}\frac{K'\frac{\delta_{m}}{\delta_{r}}}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}}$$

$$f_{2}(x) = C_{3}\cosh\left(\frac{x}{\delta_{r}}\right) + C_{4}\sin h\left(\frac{x}{\delta_{r}}\right)$$

$$= \frac{C_{HA}^{b} + \frac{D_{H}^{+}}{D_{HA}}C_{H}^{b}}{1 + \frac{D_{H}^{+}}{D_{HA}}C_{H}^{b}}\cosh\left(\frac{x}{\delta_{r}}\right) - \frac{C_{HA}^{b} + \frac{D_{H}^{+}}{D_{HA}}C_{H}^{b}}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) + \frac{D_{H}^{+}}{\delta_{r}}sinh\left(\frac{x}{\delta_{r}}\right)}$$

Now C_{HA} and C_{H^+} can be calculated:

$$\begin{split} f_{1} - f_{2} &= C_{H^{+}} \left(\frac{D_{H^{+}}}{D_{HA}} + \frac{1}{K'} \right) \\ C_{H^{+}} &= \frac{f_{1} - f_{2}}{\left(\frac{D_{H^{+}}}{D_{HA}} + \frac{1}{K'} \right)} = \frac{\frac{D_{H^{+}}K'}{D_{HA}} \frac{C_{3}}{\delta_{r}} x + C_{3}(1 - \cosh\left(\frac{x}{\delta_{r}}\right)) + \frac{C_{3}}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)} sin h\left(\frac{x}{\delta_{r}}\right)}{\left(\frac{D_{H^{+}}}{D_{HA}} + \frac{1}{K'}\right)} \\ C_{H^{+}} &= \frac{\left[\frac{D_{H^{+}}K'}{D_{HA}} \frac{x}{\delta_{r}} + 1 - \cosh\left(\frac{x}{\delta_{r}}\right) + \frac{sin h\left(\frac{x}{\delta_{r}}\right)}{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)} \right] C_{3}}{\left(\frac{D_{H^{+}}}{D_{HA}} + \frac{1}{K'}\right)} \\ C_{H^{+}} &= \frac{\left[\frac{D_{H^{+}}K'}{D_{HA}} \frac{x}{\delta_{r}} + tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) - tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) cosh\left(\frac{x}{\delta_{r}}\right) + sin h\left(\frac{x}{\delta_{r}}\right)}{1 + \frac{D_{H^{+}}}{D_{HA}}} \frac{K'\frac{\delta_{m}}{\delta_{r}}}{tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)} \right] \\ C_{H^{+}} &= \frac{C_{H^{+}}^{b} \left[\frac{D_{H^{+}}}{D_{HA}} K'\frac{x}{\delta_{r}} + tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) - tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) cosh\left(\frac{x}{\delta_{r}}\right) + sin h\left(\frac{x}{\delta_{r}}\right)}{1 + \frac{D_{H^{+}}}{D_{HA}}} \frac{K'\frac{\delta_{m}}{\delta_{r}}}{tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)} \right] \\ C_{H^{+}} &= \frac{C_{H^{+}}^{b} \left[\frac{D_{H^{+}}}{D_{HA}} K'\frac{x}{\delta_{r}} + tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) - tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) cosh\left(\frac{x}{\delta_{r}}\right) + sinh\left(\frac{x}{\delta_{r}}\right)}{1 + \frac{D_{H^{+}}}{D_{HA}}} \frac{K'\frac{\delta_{m}}{\delta_{r}}}{tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)} \right] \\ C_{H^{+}} &= \frac{C_{H^{+}}^{b} \left[\frac{D_{H^{+}}}{D_{HA}} K'\frac{x}{\delta_{r}} + tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) - tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) cosh\left(\frac{x}{\delta_{r}}\right) + sinh\left(\frac{x}{\delta_{r}}\right)}{s_{r}} \right] \\ c_{H^{+}} &= \frac{C_{H^{+}}^{b} \left[\frac{D_{H^{+}}}{D_{HA}} K'\frac{x}{\delta_{r}} + tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) - tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) cosh\left(\frac{x}{\delta_{r}}\right) + sinh\left(\frac{x}{\delta_{r}}\right)}{s_{r}} \right] \\ s_{m} + \frac{D_{HA}}{D_{H^{+}}} \frac{tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{K'}{\delta_{r}}}} \right] \\ c_{H^{+}} &= \frac{C_{H^{+}} \left[\frac{D_{H^{+}}}{D_{HA}} \frac{tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) + sinh\left(\frac{x}{\delta_{r}}-\frac{\delta_{m}}{\delta_{r}}\right)}{s_{r}}}{s_{r}}} \right] \\ c_{H^{+}} &= \frac{C_{H^{+}} \left[\frac{D_{H^{+}}}{D_{H^{+}}} \frac{tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) + sinh\left(\frac{\delta_{m}}{\delta_{r}}-\frac{\delta_{m}}{\delta_{r}}\right)}{s_{r}}}{s_{r}}} \\ c_{H^{+}} &= \frac{C_{H^{+}} \left[\frac{D_{H^{+}}}{D_{H^{+}}} \frac{tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) + sinh\left(\frac{\delta_{m}}{\delta_{r}}-\frac{\delta_{m}}}{\delta_{r}}\right) + sinh\left(\frac{\delta_{m}}{\delta_{r}}-\frac{\delta_{m}}{\delta_{r}}-$$

The final equation for C_{H^+} is as follows:

$$\frac{C_{H^{+}}}{C_{H^{+}}^{b}} = \frac{x + \frac{D_{HA}}{D_{H^{+}} \frac{K'}{\delta_{r}}} \left[\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) + \frac{\sinh\left(\frac{x - \delta_{m}}{\delta_{r}}\right)}{\cosh\left(\frac{\delta_{m}}{\delta_{r}}\right)} \right]}{\delta_{m} + \frac{D_{HA}}{D_{H^{+}} \frac{K'}{\delta_{r}}} \tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}$$

The same procedure can be done for C_{HA} .

$$\begin{split} C_{HA} &= f_{1} - \frac{D_{H^{+}}}{D_{HA}} C_{H^{+}} \\ C_{HA} &= \frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}} C_{H^{b}}^{b}}{\frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{D_{H^{+}}K'}{D_{HA}} \delta_{r}}} \times + \frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}} C_{H^{b}}^{b}}{1 + \frac{D_{H^{+}}}{D_{HA}} C_{H^{b}}^{b}}} - \frac{\frac{D_{H^{+}}}{\delta_{r}} C_{B}^{b} \times + \frac{C_{H}^{b}}{K'}}{\frac{K'}{\delta_{r}}}}{\delta_{m} + \frac{D_{HA}}{D_{H^{+}}} \frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{K'}}{\delta_{r}}} \\ C_{HA} &= \frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}} C_{H^{+}}^{b}}{\frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{D_{H^{+}}K'}{D_{HA}} \delta_{r}}} + \delta_{m}} \times + \frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}} C_{H^{b}}^{b}}{\frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{D_{H^{+}}K'}{D_{HA}} \delta_{r}}} \\ & - \frac{\frac{D_{H^{+}}}{D_{HA}} C_{H}^{b} + x + \frac{C_{HA}^{b} + \frac{D_{H^{+}}}{D_{HA}} C_{H^{+}}^{b}}{\frac{\Delta_{H^{+}}}{\delta_{H}} \delta_{r}}} + \delta_{m}} \times \frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{D_{H^{+}}K'}{\delta_{r}}} \\ & - \frac{\frac{D_{H^{+}}}{D_{HA}} C_{H^{+}}^{b} + x + \frac{C_{H^{+}}^{b}}{D_{HA}} \sum_{r}^{t}} \left[\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) + \frac{\sinh\left(\frac{x - \delta_{m}}{\delta_{r}}\right)}{\cosh\left(\frac{\delta_{m}}{\delta_{r}}\right)}} \right]}{\delta_{m} + \frac{D_{HA}}}{D_{H^{+}}} \frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{\delta_{r}}}} \\ & - \frac{C_{HA}^{b} x + \frac{C_{HA}^{b} \tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{D_{H^{+}}K'}{\delta_{r}}} - \frac{C_{HA}^{b} \sinh\left(\frac{x - \delta_{m}}{\delta_{r}}\right)}{\frac{\delta_{r}}}{\delta_{r}}} \\ & - \frac{C_{HA}^{b} x + \frac{C_{HA}^{b} \tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{D_{H^{+}}K'}{\delta_{r}}} - \frac{C_{HA}^{b} \sinh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\delta_{m} + \frac{D_{HA}}{\delta_{r}}} \frac{\sinh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\delta_{m} + \frac{D_{HA}}{D_{H^{+}}} \frac{\sinh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{\delta_{r}}}{\delta_{r}}} \\ \end{array}$$

The final equation for C_{HA} is as follows:

$$\frac{C_{HA}}{C_{HA}^{b}} = \frac{x + \frac{D_{HA}}{D_{H^{+}}\frac{K'}{\delta_{r}}} \left[\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right) - \frac{K'D_{H^{+}}}{D_{HA}} \frac{\sinh\left(\frac{x - \delta_{m}}{\delta_{r}}\right)}{\cosh\left(\frac{\delta_{m}}{\delta_{r}}\right)} \right]}{\delta_{m} + \frac{D_{HA}}{D_{H^{+}}\frac{K'}{\delta_{r}}} \tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}$$

Now the cathodic limiting current density can be calculated.

$$\left(\frac{dC_{H^{+}}}{dx}\right)_{x=0} = \left(\frac{C_{H^{+}}^{b}x + \frac{C_{H^{+}}^{b}}{\overline{\Delta_{r}}}\frac{D_{HA}}{D_{H^{+}}}\frac{\sinh\left(\frac{x-\delta_{m}}{\delta_{r}}\right)}{\cosh\left(\frac{\delta_{m}}{\delta_{r}}\right)}\right)_{x=0} = \frac{C_{H^{+}}^{b} + \frac{C_{H^{+}}^{b}}{\overline{A_{H^{+}}}}\frac{D_{HA}}{D_{H^{+}}}}{\delta_{m} + \frac{D_{HA}}{D_{H^{+}}}\frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{K'}{\delta_{r}}}} = \frac{C_{H^{+}}^{b} + \frac{C_{H^{+}}^{b}}{\overline{A_{H^{+}}}}\frac{D_{HA}}{D_{H^{+}}}}{\delta_{m} + \frac{D_{HA}}{D_{H^{+}}}\frac{\tanh\left(\frac{\delta_{m}}{\delta_{r}}\right)}{\frac{K'}{\delta_{r}}}}$$

The final expression for the cathodic limiting current density can be written below.

$$i_L = F \frac{D_{H^+} C_{H^+}^b + D_{HA} C_{HA}^b}{\delta_m + \frac{D_{HA}}{D_{H^+} \frac{K'}{\delta_r}} \tanh\left(\frac{\delta_m}{\delta_r}\right)}$$

The same mathematical procedure can be implemented in order to derive the correlation for the cathodic current density of the entire cathodic region, including both charge transfer controlled, and mass transfer controlled. The only variation is to implement the flux boundary condition for H^+ at the surface of electrode instead of zero-concentration boundary condition. One more important consideration is to define the reaction order with respect to H^+ concentration at the surface of electrode. For hydrogen evolution reaction, the reaction order is mostly considered as 0.5. However, the calculations have been done with the order of reactions of 0.5 and 1. Here, only the final correlations are presented.

For reaction order of 1, the correlation for the cathodic current density is as follows.

$$i = F \frac{D_{HA}C_{HA}^b + D_{H^+}C_{H^+}^b}{\left(\frac{D_{HA}\delta_r}{D_{H^+}K'} \tanh\left(\frac{\delta_m}{\delta_r}\right) + \delta_m\right) + \frac{D_{H^+}}{K_{r,H^+}} + \frac{D_{HA}}{K'K_{r,H^+}}}$$

Where K_{r,H^+} is the contribution of charge transfer reaction and can be found from the equation below.

$$K_{r,H^+} = K_{r,H^+}^0 \exp(\frac{\alpha F(E-E^0)}{RT})$$

In the above equation, K_{r,H^+}^0 is the rate reaction constant and should be found based on the fitting to experimental results. Other parameters have their usual meanings. For reaction order of 0.5, which is the usual case for the hydrogen evolution reaction in acidic solutions, the correlation for the cathodic current density is as follows.

$$i = FK_{r,H^+} \frac{-Y + \sqrt{Y^2 + Z^2 C_{H^+}^b}}{Z}$$

With *Y* and *Z* parameters found from the following equations.

$$Y = \frac{D_{HA}\delta_r}{D_{H^+K}} \tanh\left(\frac{\delta_m}{\delta_r}\right) + \delta_m$$
$$Z = 2\left(\frac{D_{H^+}}{K_{r,H^+}} + \frac{D_{HA}}{KK_{r,H^+}}\right)$$

The verification of the equations derived for cathodic current density could be a topic for future studies. Also, it should be noted that due to the several simplifications and assumptions that have been considered, these equations might not perfectly fit to the experimental data. Therefore, further modifications can be made, also in future studies, to improve the validity of the proposed equations.

Appendix B: Simulation of Uniform and Galvanic Corrosion in Acidic Solutions Using Ansys Fluent Software

This section includes the works that has been done on the simulation of different corrosion cases using Ansys Fluent Software based on the collaboration with Ansys company. In the oil and gas industry, use of models for prediction of corrosion to develop appropriate mitigation strategies is widespread. one-dimensional models such as MULTICORP[™] rely on dimensionless number mass transfer correlations in order to predict pipe flow conditions which are used to make the corrosion predictions. These correlations are effective in laminar and turbulent, single phase, straight pipe flow. Using a one-dimensional system gives the advantage of having significantly fewer points at which calculations must be performed. It also avoids performing complex calculations to account for the flow values, instead replacing them with the dimensionless number correlations. A downside to this approach is that in systems where these correlations do not currently exist, such as for many multiphase flow systems or when a more complex geometry is present (bends, valves, fittings, obstacles), these models cannot accurately predict corrosion. In addition, the one-dimensional model can not be implemented for two-dimensional and three-dimensional cases which includes numerous situations in corrosion industries. To model corrosion in such systems, CFD (computational fluid dynamics) software can be implemented along with the appropriate understanding of the corrosion mechanisms. The main goal of this section is to validate a proof-of-concept for using CFD simulations software specifically Ansys Fluent for predicting corrosion rates

in various geometries. The geometries used for the validation process are the one that have well-defined correlations for flow, mass transfer, and corrosion rates.

To concisely summarize the basics of CFD software, it generally functions by taking a 2D or 3D geometry and breaking it down into a system of points at which flow variables and other system variables like temperature, pressure, species concentration will be calculated; this process is also known as discretization or meshing. Once the mesh has been created for the system the software then solves a number of equations simultaneously at each point inside the system using numerical methods. The equations solved will partly depend on what system variables are of interest to the user, those that must always be solved are the continuity and the Navier-Stokes equations as shown respectively as follows.

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_i)}{\partial x_i} = 0$$

$$\frac{\partial \rho u_j}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_j u_i) = \rho f_j - \frac{\partial P}{\partial x_j} + \frac{\partial}{\partial x_i} (\mu \frac{\partial u_j}{\partial x_i}) + \frac{1}{3} \frac{\partial}{\partial x_j} (\mu \frac{\partial u_i}{\partial x_i})$$

In the case of a corrosion calculation the only thing left out in the above equations are the concentrations of species which are relevant to the corrosion reactions. These can be solved for by including the species conservation equation which is shown below.

$$\frac{\partial}{\partial t}(m^s) + \frac{\partial}{\partial x_i}(m^s u_i) = \frac{\partial}{\partial x_i} \left(D^s \frac{\partial m^s}{\partial x_i} \right) + R^s$$

From this point the local concentration of species at any point inside the system can be calculated and utilized in the calculation of the corrosion rate. To calculate the corrosion rate itself, another equation must be solved, this time at the wall where the corrosion occurs. For this the Butler-Volmer equation, which can be seen below, is implemented as what is known as a boundary condition. Boundary conditions play a big role in CFD simulations as these are the ways in which information is transferred into the system, such as specifying a particular velocity or flow rate at an inlet, or a pressure at an outlet.

$$i_F = i_0 \left(\frac{c}{c_{ref}}\right)^n \left[\exp\left(\frac{2.303\eta}{\beta_a}\right) - \exp\left(\frac{2.303\eta}{\beta_c}\right)\right]$$

This implementation allows for the calculation by the CFD software of the current density of the electrochemical corrosion reaction, which can then be transformed into a corrosion rate.

For the purposes of this project, the focus is the verification of the hydrodynamics, mass transfer, electrochemical reactions, and corrosion rates in different experimental systems. In order to verify these parameters in these experimental systems, first literature sources are found which provide either experimental data in these systems, or correlations which can be used to calculate these parameters based on the conditions tested. When direct comparison with experimental data is to be performed, the experimental systems are designed in the Ansys software, carefully replicating the significant physical dimensions of the experimental systems used in the literature source. The parameters of the simulation are input to exactly recreate the conditions seen in the experiments being referenced. The relevant simulation results are then compared with the data present in the literature to determine the accuracy of the simulated results. If a correlation is being used for verification, the experimental system is created to satisfy any requirements that the correlation might have to ensure its validity in the simulated system. A range of conditions may then be simulated by changing the simulation parameters such as flow rate and the trend of relevant parameters can be compared against the trend predicted by the correlation.

Simulation of Rotating Disk Electrode. Rotating disk electrode (RDE) is one of the most common systems used for corrosion studies due to its well-known hydrodynamic and mass transfer characteristics. *Figure 58* shows an overview of the geometry used for the simulation of a laboratory glass cell containing only a rotating disk electrode with its shaft.



Figure 58. Geometry for simulation of rotating disk electrode (RDE) system.

The simulation was done using 2-dimensional geometry, in steady state condition and with laminar flow. As boundary conditions for mass transfer simulation, the concentration of the bulk of solution was set at 1 (mol.m⁻³), and it was zero at the surface of disk. An example of such simulation is presented in *Figure 59*. The behavior of flow close to the disk surface is crucial for characterizing the hydrodynamics and mass transfer of this system and comparing with the experimental data. The flow pattern near disk as shown in *Figure 59* agrees well with the pattern observed in the literatures.



Figure 59. The simulated velocity streamlines for the rotating disk system for 100 (rad.s⁻¹) rotational speed with $v = 10^{-6}$ (m².s⁻¹) and $\rho = 1000$ (kg.m⁻³).

In order to verify the results obtained from simulation, three important parameters are compared with their theoretical value found in literatures: shear stress, hydrodynamic boundary layer thickness, and mass transfer boundary layer thickness. For rotating disk system, the circumferential shear stress can be calculated using equation below [158].

$$\tau_w = 0.61 \rho v^{0.5} \omega^{1.5} r$$

The result of the simulation in comparison with the calculated value is shown in *Figure 60*. It is seen that the simulation result is very close to the theoretical value at the middle of the disk ,but it deviates at the edge of the disk which could be due to the edge effect and disturbance of flow in simulation which is not considered in theoretical equation. In the case of hydrodynamics, the thickness of boundary layer and the maximum velocity for rotating disk system can be calculated using Levich equations as shown below [111], [159].

$$\delta_{\rm h} = 2.8 v^{0.5} \omega^{-0.5} = 0.28 \ mm$$

 $U_0 = -0.884 (v\omega)^{0.5} = 0.0088 \ m/s$

As it is seen in *Figure 60*, the simulated maximum velocity as well as the simulated hydrodynamic boundary layer thickness agree very well with the theoretical values.



Figure 60. Comparison of simulated and theoretical values for circumferential shear stress (left), and axial velocity (right).

In addition, for the verification of mass transfer, the equation for concentration profile as well as the mass transfer boundary layer thickness are calculated using Levich equations for rotating disk system [111], [159].

$$\frac{C}{C_b} = \frac{1}{0.8934} \int_0^{y/(3B)^{1/3}} \exp\left(\frac{-y^3}{3B}\right) dy, \qquad B = \frac{1}{0.51} D\omega^{-3/2} v^{1/2}$$
$$\delta_m = 1.61 D^{1/3} v^{1/6} \omega^{-1/2} = 34.7 \,\mu m$$

The comparison of theoretical and simulated results shown in *Figure 61* verifies that the simulation is in very good agreement with the theoretical value.



Figure 61. Comparison of simulated and theoretical values for concentration profile and thickness of mass transfer boundary layer.

Finally, the electrochemical reaction rate was simulated for rotating disk electrode system. In order to verify the electrochemical reaction, the cathodic reaction of hydrogen ion reduction was considered since both charge transfer current as well as mass transfer limiting current are involved in this reaction. For this purpose, the boundary condition for the mass transfer at the surface of electrode is given by Butler-Volmer equation as described below.

$$i_F = i_0 \left(\frac{c}{c^{ref}}\right)^n \left[\exp\left(\frac{2.303(E - E_{rev})}{\beta_a}\right) - \exp\left(\frac{2.303(E - E_{rev})}{\beta_c}\right) \right]$$

Figure 62 compares the theoretical and simulated current density of hydrogen ion reduction reaction. As it is seen, the current density includes charge transfer and mass transfer limiting. The theoretical current density for the charge transfer and mass transfer limiting were calculated from Butler-Volmer and Levich equations, respectively [111], [159].



Figure 62. Comparison of simulated and theoretical values for current density of hydrogen ion reduction reaction.

Simulation of Pipe Flow. Corrosion of oil and gas transmission pipelines is one of the major issues for industries and thus modeling and prediction of corrosion rate in such systems are crucial for these industries in order to mitigate and control the failures due to corrosion. Hence, it was selected as another system for CFD simulation. The geometry and dimension of the simulation for pipe flow is shown in *Figure 63*.



Figure 63. Geometry for simulation of pipe flow.

It is a 2-dimensional simulation in steady state condition and turbulent flow with the velocity of 10 m.s⁻¹. As boundary conditions for mass transfer simulation, the concentration of the bulk of solution was set at 1 (mol.m⁻³), and it was zero at the wall of pipe. It should be noted that the results shown for this simulation are related to the fully developed region of the flow. *Figure 64* displays an example of velocity profile for a simulation of pipe flow.



Figure 64. The simulated velocity profile for pipe flow with V = 10 (m.s⁻¹), v= 10^{-6} (m²·s⁻¹), and $\rho = 1000$ (kg.m⁻³).

Same as the previous case, the flow as well as the mass transfer of the system were verified first. The shear stress for pipe flow can be calculated using Colebrook

equation for the Darcy friction assuming zero roughness for the pipe's wall as shown below [106], [107].

$$C_d = 0.25 \left[\log\left(\frac{\frac{\mathcal{E}}{D_{eq}}}{3.7} + \frac{5.74}{Re^{0.9}}\right) \right]^{-2} = 0.25 \left[\log\left(\frac{5.74}{Re^{0.9}}\right) \right]^{-2} = 0.0104$$
$$\tau_w = \frac{1}{2}\rho C_f V^2 = \frac{1}{8}\rho C_d V^2 = 130 \ Pa$$

Figure 65 shows the simulated wall shear stress of pipe starting from inlet when the flow is not fully developed to the outlet. As can be observed, the average shear stress in the fully developed region from simulation is close to the theoretical value. The average shear stress is the average shear stress in the fully developed region of the pipe.



Figure 65. The simulated wall shear stress in the pipe flow

According to the theory of turbulent flow, three different regions should be considered for the flow when plotting non-dimensional velocity versus non-dimensional distance: viscous sublayer, buffer region, and log-law layer [160]. Some empirical equations exist in the literature for viscous sublayer and log-law region as shown on *Figure 66*. The buffer region is actually a transition between these two regions. By comparing the simulated results with the theoretical one, a good agreement can be found for viscous sublayer and log-law regions, and some deviations exist in buffer layer.

For verifying mass transfer, the mass transfer coefficient has a relationship with the thickness of mass transfer boundary layer according to the literatures. Mass transfer coefficient for the pipe flow can be found from Berger and Hau correlation [92] and then mass transfer boundary layer thickness can be calculated as below. It should be mentioned that in this case the velocity of 1 m.s⁻¹ was used as the thickness of the mass transfer boundary layer is larger and therefore more observable at lower velocity.

$$k_{pipe} = 0.0165 Re^{0.86} Sc^{0.33} \frac{D}{d_{pipe}} = 1.365 \times 10^{-4}$$
$$\delta_m = \frac{D}{k_{pipe}} = 73 \ \mu m$$

Figure 66 shows the simulated concentration profile. As it can be seen, the thickness of mass transfer boundary layer found from simulation agrees very well with the theoretical value.



Figure 66. Comparison of simulated and theoretical values for velocity profile (left) and concentration profile (right).

In order to simulate the corrosion rates, it is necessary to initially establish the boundary conditions for electrochemical reactions including both anodic and cathodic reactions. The electrochemical reactions involved in the corrosion of mild steel in strong acid solutions are hydrogen ion reduction and iron dissolutions reactions. For this purpose, the boundary condition for the mass transfer at the wall of pipe is given by Butler-Volmer equations as described below.

$$i_F = i_0 \left(\frac{c}{c^{ref}}\right)^n \left[\exp\left(\frac{2.303(E - E_{rev})}{\beta_a}\right) - \exp\left(\frac{2.303(E - E_{rev})}{\beta_c}\right) \right]$$

For the simulation of corrosion rates in strong acid solutions for this study, the values of parameters used in Butler-Volmer equation are listed in **Table 23**.

Table 23.

Parameter	Hydrogen ion Reduction	Iron Dissolution
Exchange current density (A.m ⁻²)	0.037	1
Species concentration (M)	0.001, 0.0001, 0.00001	-
Reference mass fraction H ⁺	10-7	10 ⁻⁷
Reaction order	1	0
β_a	0.12	0.04
βc	0.12	0.04
Equilibrium potential (V)	-0.24	-0.488

The parameters used for the simulation of corrosion rates in pipe flow.

In order to verify the simulation performed by Fluent, the results were compared with the mathematical calculation of corrosion rates from Butler-Volmer equation. The comparison of corrosion rates as well as corrosion potential between Fluent simulation and mathematical calculations in different pH values are shown in *Figure 67*.



Figure 67. Comparison of simulated and calculated results for corrosion rate (left), and corrosion potential (right), at various pH values.

A very good agreement can be found between the simulated and calculated results for both cases of corrosion rate and corrosion potential. In the final step, the corrosion rate was simulated in CO_2 solutions. To simulate CO_2 corrosion, four homogenous chemical reactions as shown below were added which incorporate the hydration of CO_2 , and subsequent dissociation reactions that provide an additional source of H⁺ ions to be used in the corrosion reaction.

 $CO_{2} + H_{2}O \leftrightarrow H_{2}CO_{3}$ $H_{2}CO_{3} \leftrightarrow HCO_{3}^{-} + H^{+}$ $HCO_{3}^{-} \leftrightarrow CO_{3}^{2-} + H^{+}$ $H_{2}O \leftrightarrow H^{+} + OH^{-}$

The rate constants for these four chemical reactions were also shown in **Table 24**. It should be considered that the electrochemical reactions involved in CO_2 corrosion are still the same cathodic and anodic reactions with the same values shown in **Table 23**.

Table 24.

Reaction	Forward Rate Constant	Backward Rate Constant
CO ₂ Hydration	0.0348 s ⁻¹	24.5 s ⁻¹
H ₂ CO ₃ Dissociation	1.9×10 ⁷ s ⁻¹	4.7×10 ¹⁰ M ⁻¹ .s ⁻¹
HCO ₃ ⁻ Dissociation	181 s ⁻¹	$3.67 \times 10^{12} \text{ M}^{-1} \text{.s}^{-1}$
H ₂ O Dissociation	0.00126 M.s ⁻¹	1.4×10 ¹¹ M ⁻¹ .s ⁻¹

The rate constants for the homogenous chemical reactions in CO₂ corrosion

For validating the simulation results, the data were compared with the simulations from FREECORP software. *Figure 68* compares the simulation that was performed using Fluent with that obtained using FREECORP software at various partial pressure of CO₂.



Figure 68. Comparison between Fluent and FREECORP simulations for various partial pressure of CO₂ at pH 4.

As can be observed from the figure, the corrosion rate increased by the increase of the partial pressure of CO_2 , due to the buffering effect originating from contribution of homogenous chemical reactions. Also, simulation using Fluent was able to capture the effect of CO_2 through homogenous chemical reactions, and successfully predict the increase of corrosion rates. To investigate the effect of various pH values on the corrosion of mild steel in CO_2 environments, the simulation was performed at two pH values as well as different partial pressure of CO_2 , as represented in *Figure 69*.



Figure 69. Comparison between Fluent and FREECORP simulations for various partial pressure of CO₂ at pH 4 (left), and pH 3 (right).

The results show that the effect of partial pressure of CO₂ is stronger at pH 3 compared with that at pH 4. The reason might be that the corrosion rate at pH 3 is very high and mostly charge transfer controlled, and thus buffering effect has slight impact on the corrosion current. In general, good agreement was obtained between the Fluent simulation and FREECORP simulation in different environmental conditions. Therefore, we can conclude that Fluent is able to successfully simulate the corrosion of mild steel in strong acidic solutions as well weak acid solutions.

Simulation of Galvanic Corrosion. The galvanic corrosion was the main topic of this dissertation. It was discussed that the modeling galvanic corrosion specifically in the field of oil and gas corrosion remained in its elementary stage mainly due to the complexity of the galvanic corrosion phenomena. However, the prediction and modeling of galvanic corrosion as well as localized attacks are crucial for oil and gas industries in order to mitigate and control the failures. Hence, using CFD simulations could be a very useful tool in order to aid these industries to predict the localized attacks due to galvanic corrosion. In this study, Fluent software was used in order to provide an elementary simulation of the galvanic corrosion using the similar experimental setup used in this dissertation. The simulation was first used to demonstrate the proof-of-concept that Fluent software is capable of simulating galvanic corrosion. Afterwards, the simulation results was compared with the experimental results of this study. However, the complexity of the electrochemical reactions occurring at the surface of iron sulfides can not be entirely implemented into the simulation.

Figure 70 shows an overview of the geometry used for the simulation of the experimental setup used in this dissertation. A 3-dimensional geometry was used for this simulation. The geometry includes two electrodes facing each other in a glass cell similar to the experimental setup. It should be mentioned that the fluid of the glass cell in the simulation is stagnant similar to the experimental condition.



Figure 70. The geometry of galvanic corrosion simulation: overview (left), clos-up of electrodes (right).

In real experimental situations, the electrodes are connected, or in other words coupled, using ZRA method through potentiostat. In order to couple them in the simulation, the boundary condition for the potential of the top part of the electrodes were kept at zero. In order to show the proof-of-concept for the general case, the galvanic corrosion was simulated by implementing an anodic reaction on one electrode, and a cathodic reaction on the other one. The values of the parameters for the cathodic and anodic reactions are listed in **Table 25**.

Table 25.

Parameter	Cathodic Reaction	Anodic Reaction
Exchange current density (A.m ⁻²)	0.0007	0.3
Reaction order	0	0
β_a	0.28	0.04
β_{c}	0.28	0.04
Equilibrium potential (V)	0.2	-0.488

The parameters used for the simulation of galvanic corrosion.

Figure 71 shows the simulated galvanic current density at the surface of the electrodes. The current density at the surface of anode is equal to that at the surface of cathode. However, based on the definition of the current in Fluent software, the anodic current is positive and the cathodic current is negative which means that the current is flowing from cathode to anode.



Figure 71. The simulated galvanic current density at the surface of anode (left), and cathode (right).

In order to confirm the simulation, the results for the galvanic corrosion rate as well as galvanic potential were compared with the theoretical value found from the intersection of anodic and cathodic reaction calculated with Butler-Volmer reaction as discussed in the previous sections. *Figure 72* compares the theoretical and simulated values.



Figure 72. The comparison between the theoretical and simulated values for galvanic corrosion rate and galvanic potential.

The results show very good agreement between the experimental and the theoretical values for galvanic corrosion rate as well as galvanic potential. This confirms that Fluent software is able to predict the galvanic corrosion between two separated metals.

Steel-Pyrrhotite Couple. Considering the capability of the software to predict galvanic corrosion, the experimental conditions studied in this dissertation was simulated. The first case was to simulate the galvanic coupling between steel and pyrrhotite for the case of anode to cathode ratio of 1:1. The complexity of electrochemical reaction occurring at the surface of electrodes specifically the electrochemistry related to pyrrhotite reduction can not be completely implemented into the software. For instance, the limiting current at higher potential related to reductive dissolution of pyrrhotite can not be implemented as input, since only charge transfer reactions can be implemented in

Fluent software and the mass transfer limiting current are simulated based on the flow properties. It was shown that at the experimental conditions, i.e., pH 5, with stagnant solution, the entire cathodic reaction of reductive dissolution of pyrite could be neglected due to its low current density and therefore its mass transfer limiting current can also be neglected. Therefore, the only remaining cathodic current is polysulfide reduction reaction. This reaction also has a limiting current component which has a chemical nature and is related to the surface reaction. This component can not be also implemented into simulation as explained earlier. Therefore, the simulation was done with pyrrhotite as cathode considering that the only cathodic reaction at its surface is the charge transfer part of polysulfide reduction reaction as presented in Equation (72). The cathodic reactions at the surface of steel was also neglected (it seems that Fluent does not consider a cathodic reaction for the anode of galvanic couple). Therefore, the only anodic reaction at the surface of steel is iron dissolution reaction as represented in Equation (77). All the parameters and constants are similar to what was used for the modeling of steelpyrrhotite couple as shown in the modeling chapter.

On that account, the galvanic corrosion between mild steel and pyrrhotite was simulated in a simpler format. *Figure 73* shows the results of the simulation and compares the galvanic corrosion rate as well as the coupled potential between experimental data and simulation.



Figure 73. The comparison between the experimental and simulated values for galvanic corrosion rate and galvanic potential of steel-pyrrhotite couple.

Although the model was simplified, the simulated values for galvanic corrosion rate and coupled potential are in good agreement with the experimental data. This validates the capability of Fluent to predict galvanic corrosion cases.

Steel-Pyrite Couple. The second case that was simulated was the galvanic corrosion between mild steel and pyrite. The simulations were done similar to the case of steel-pyrrhotite couple. For anodic reaction, only iron dissolution reaction was considered at the surface of anode (mild steel). Based on the discussion in previous chapters of this dissertation, the only cathodic reaction occurring at the surface of pyrite is the reduction of polysulfides. This reaction includes charge transfer and chemically limiting current components. The limiting current can not be implemented in the software. Therefore, the only cathodic reaction at the surface of cathode is the charge transfer part of polysulfide reduction as represented in Equation (69). Based on these considerations, the galvanic corrosion between mild steel and pyrite was simulated and the results are presented in *Figure 74*.



Figure 74. The comparison between the experimental and simulated values for galvanic corrosion rate and galvanic potential of steel-pyrite couple.

As can be seen, the simulated results can not predict the galvanic corrosion rate and galvanic potential very well in the case of steel-pyrite. The discrepancies can emerge from two sources: first the cathodic current at the surface of anode (steel) was ignored which has a significant contribution in the total cathodic current in the case of steel-pyrite couple when cathode to anode ratio is 1:1, second the limiting current component of polysulfide reduction was ignored which has a major contribution in the total cathodic current at the surface of cathode. Therefore, the simulated galvanic corrosion rate is much lower than that obtained in experiments. These results show that the accuracy of the simulation depends on the parameters implemented into the software. When the electrochemical reactions are complex, a simplified approach might not always lead to accurate simulation, and therefore it should be chosen wisely. Also, the results suggest that Fluent software could be improved in order to handle the more complex cases, but the software is capable of simulating general galvanic corrosion cases.



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