The Effect of Organic Acids on Hydrogen Sulfide Corrosion of Mild Steel

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# This thesis titled:

The Effect of Organic Acids on Hydrogen Sulfide Corrosion of Mild Steel

by

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#### Abstract

The Effect of Organic Acids on Hydrogen Sulfide Corrosion of Mild Steel

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Individually, the corrosion mechanisms of  $H_2S$  and organic acid in the presence of  $CO_2$  have been studied extensively in upstream oil and gas pipelines, but minimal literature has been published about how organic acids will influence the corrosion mechanisms when an  $H_2S$  or  $H_2S/CO_2$  mixed environment is present. This research aims to identify gaps in the current understanding of  $H_2S$  and  $H_2S/CO_2$  corrosion in the presence of organic acids where hypotheses and research questions were developed to be tested by the proposed test matrices to fill the identified knowledge gaps.

A thorough analysis of the influence of up to 1000 ppm of free organic acid (namely acetic acid) on H<sub>2</sub>S and H<sub>2</sub>S/CO<sub>2</sub> corrosion mechanisms with 0 - 1 vol.% (0 - 10 mbar) of H<sub>2</sub>S at 30 °C, pH 4.0, and a 1000 rpm RDE was done by collecting and analyzing LPR corrosion rates and potentiodynamic sweeps. Environmental conditions such as free organic acid concentration, pH, temperature, and the mass transfer coefficient were also varied in an H<sub>2</sub>S/CO<sub>2</sub> environment to further investigate the influence of organic acid on the involved mechanisms. The results of this study showed that acetic acid will follow the buffering effect mechanism for all H<sub>2</sub>S partial pressures and organic acid concentrations that were tested in H<sub>2</sub>S and H<sub>2</sub>S/CO<sub>2</sub> corrosion environments. There existed an outlying case with 0.1 mbar of H<sub>2</sub>S and 1000 ppm of organic acid involving H<sub>2</sub>S corrosion where a

further analysis of the system must be done before any confident conclusion is made on whether organic acid will follow the buffering effect mechanism in this condition.

A surface analysis utilizing SEM/EDS, Raman spectroscopy, and profilometry was completed after corrosion testing for a prolonged time of 72 hours using 0 and 1000 ppm of free organic acid with 0.1 mbar of H<sub>2</sub>S in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0, and a 1000 rpm RDE to determine if a detectable layer of sulfide species had formed on the surface. The surface analysis using EDS was able to detect sulfide on the surface of the steel, but Raman Spectroscopy was not able to confirm the identity of the species of sulfide that had formed. This study also developed an electrochemical model for strong acid, H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>S/CO<sub>2</sub> corrosion to predict the influence organic acids have on the potentiodynamic sweeps and corrosion rates for the environments that were investigated in this study. An analysis of the results and comparison of the model to the experimental data showed that the model performed with sufficient accuracy.

# Dedication

То

*My family for their unconditional love and support My friends who make life worth living* 

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# **Table of Contents**

Abstract	3
Dedication	5
Acknowledgments	6
Table of Contents	7
List of Tables	.10
List of Figures	.11
Chapter 1: Introduction	.16
Chapter 2: Literature Review	.18
2.1 CO <sub>2</sub> Corrosion of Mild Steel	.18
2.2 H <sub>2</sub> S Corrosion of Mild Steel	.21
2.3 Organic Acid Corrosion of Mild Steel	.26
Chapter 3: Mechanistic Study of H <sub>2</sub> S Corrosion of Mild Steel	.30
3.1 Research Hypothesis and Questions	.30
3.2 Experimental Methodology	.30
3.2.1 Equipment	.30
3.2.2 H <sub>2</sub> S Health and Safety Information	.34
3.2.3 Test Matrix	.35
3.2.4 Procedure	.35
3.3 Results and Discussion	.37
3.3.1 Influence of H <sub>2</sub> S Partial Pressure	.37
3.3.2 Influence of Free Acetic Acid Concentration	.42
3.4 Conclusions	.50
Chapter 4. Mechanistic Study of H <sub>2</sub> S/CO <sub>2</sub> Corrosion of Mild Steel	.53
4.1 Research Hypothesis and Questions	.53
4.2 Experimental Methodology	.54
4.2.1 Equipment	.54
4.2.2 Test Matrix	.54
4.2.3 Procedure	.56
4.3 Results and Discussion	.56
4.3.1 Influence of H <sub>2</sub> S Partial Pressure	.56

4.3.2 Influence of Free Acetic Acid Concentration	64
4.3.3 Influence of pH	72
4.3.4 Influence of Temperature	
4.3.5 Influence of the Mass Transfer Coefficient	79
4.4 Conclusions	83
Chapter 5. H <sub>2</sub> S/CO <sub>2</sub> Corrosion Rate Over Time and Surface Analysis Study of M	ild Steel
	87
5.1 Research Hypothesis and Questions	87
5.2 Experimental Methodology	87
5.2.1 Experimental and Analytical Equipment	87
5.2.2 Test Matrix	88
5.2.3 Procedure	90
5.3 Results and Discussion	91
5.3.1 CO <sub>2</sub> Corrosion Without the Presence of Acetic Acid	91
5.3.2 H <sub>2</sub> S/CO <sub>2</sub> Corrosion Without the Presence of Acetic Acid	99
5.3.3 H <sub>2</sub> S/CO <sub>2</sub> Corrosion in the Presence of Acetic Acid	104
5.4 Conclusions	111
Chapter 6. Electrochemical Modeling of H <sub>2</sub> S and H <sub>2</sub> S/CO <sub>2</sub> Corrosion	115
6.1 Modeling of $H_2S$ and $H_2S/CO_2$ Corrosion in the Presence of Acetic Acid.	115
6.1.1 Introduction and Methodology	115
6.1.2 Hydrogen Ion Reduction Reaction	116
6.1.3 Mass Transfer Limiting Current from Hydrogen Ions	120
6.1.4 Water Reduction Reaction	124
6.1.5 Iron Oxidation Reaction	126
6.1.6 Mixed Potential Theory	131
6.2 Implication of the Model and Comparison to Experimental Data	133
6.2.1 Modeling of H <sub>2</sub> S Corrosion of Mild Steel in the Presence of Acetic	Acid 133
6.2.2 Modeling of H <sub>2</sub> S/CO <sub>2</sub> Corrosion of Mild Steel in the Presence of Ac Acid	etic:
6.3 Conclusions	158
Chapter 7. Conclusions and Future Work	160
7.1 Final Conclusions	160
7.2 Future Work	163

References	165
Appendix A: Determination of the RDE Mass Transfer Coefficient <i>via</i> the Dimen Sherwood, Reynolds, and Schmidt Number for RDE hydrodynamics	sionless 172
Appendix B: Determination of the Activation Energy for the $H^+$ Ion Reduction Rein an $H_2S/CO_2$ Corrosion Environment <sup>59</sup>	eaction

# List of Tables

10

Table 1. Reactions Involved in CO2 Corrosion of Mild Steel 19
Table 2. Equilibrium Constants for Chemical Reactions in CO <sub>2</sub> Corrosion 20
Table 3. Chemical Reactions Involved in H <sub>2</sub> S Corrosion of Mild Steel 22
Table 4. Equilibrium Constants for Chemical Reactions in H <sub>2</sub> S Corrosion 22
Table 5. Chemical Reaction Involved in Acetic Acid Corrosion of Mild Steel 27
Table 6. Equilibrium Constant for Chemical Reaction in Acetic Acid Corrosion
Table 7. Composition of the X65 pipeline steel working electrode (wt.%)
Table 8. Text matrix for investigating corrosion mechanisms involved in H <sub>2</sub> S corrosion in the presence of acetic acid
Table 9. Text matrix for investigating corrosion mechanisms for H2S/CO2 corrosion inthe presence of acetic acid
Table 10. Text matrix for investigating how acetic acid influences $H_2S/CO_2$ corrosion rates over time and if a detectable sulfide layer will form during a prolonged exposure. 90
Table 11. The parameters for the H <sup>+</sup> ion reduction reaction for each environment that was modeled.
Table 12. The parameters for the H <sub>2</sub> O reduction reaction for each environment that was modeled
Table 13. The parameters for the Fe oxidation reaction for each environment that was modeled.    129
Table 14. A summary of the parameters used in the electrochemical model 131
Table 15. Reaction orders for acetic acid in $H_2S$ corrosion with 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and $N_2$ as the sparge gas
Table 16. Reaction orders for acetic acid in CO <sub>2</sub> corrosion with 100 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and CO <sub>2</sub> as the sparge gas
Table 17. Summary of the important research hypotheses that were proposed in thisresearch and their results
Table 18. Summary of the important research questions that were proposed in thisresearch and their results

# List of Figures

11

Figure 1. A 3 dimensional rendering of the 1 L RDE glass cell was used for the collection of experimental data
Figure 2. A detailed drawing showing the internal parts of the 1 L RDE glass cell that was used for the collection of experimental data
Figure 3. The influence of 0 - 10 mbar of H <sub>2</sub> S at 30 °C, pH 4.0, 1000 rpm RDE, and N <sub>2</sub> as the sparge gas
Figure 4. The influence of 0 - 10 mbar of $H_2S$ with 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and $N_2$ as the sparge gas
Figure 5. Water chemistry calculation of the aqueous species concentration over a range of bulk pH values with 10 mbar of $H_2S$ and 1175 ppm of total acetic acid in a 30 °C, 1 bar total pressure, and $N_2$ sparged environment
Figure 6. The influence of 1000 ppm of free acetic with 0 mbar of $H_2S$ at 30 °C, pH 4.0, 1000 rpm RDE, and $N_2$ as the sparge gas
Figure 7. An illustration of a hypothetical potentiodynamic sweep assuming the buffering effect mechanism for acetic acid (HAc) is followed where a substantial amount of HAc is added to a system that causes a transition from mixed charge transfer controlled/mass transfer controlled kinetics to fully charge transfer controlled kinetics accompanied by a slight retardation of the anodic reaction in a constant pH environment
Figure 8. The influence of 1000 ppm of free acetic with 0.05 mbar of $H_2S$ at 30 °C, pH 4.0, 1000 rpm RDE, and $N_2$ as the sparge gas
Figure 9. The influence of 1000 ppm of free acetic with 0.1 mbar of $H_2S$ at 30 °C, pH 4.0, 1000 rpm RDE, and $N_2$ as the sparge gas
Figure 10. The influence of 1000 ppm of free acetic with 10 mbar of H <sub>2</sub> S at 30 °C, pH 4.0, 1000 rpm RDE, and N <sub>2</sub> as the sparge gas
Figure 11. LPR corrosion rates for experiments conducted with $0 - 10$ mbar of H <sub>2</sub> S and 0 & 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N <sub>2</sub> as the sparge gas
Figure 12. The influence of 0, 0.1, and 10 mbar of H <sub>2</sub> S in a H <sub>2</sub> S/CO <sub>2</sub> gas mixture at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub>
Figure 13. The influence of 0, 0.1, and 10 mbar of $H_2S$ in a $H_2S/CO_2$ gas mixture with 100 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of $CO_2$ 60
Figure 14. Water chemistry calculation of the aqueous species concentration over a range of bulk pH values with 10 mbar of H <sub>2</sub> S in a H <sub>2</sub> S/CO <sub>2</sub> gas mixture and 118 ppm of total acetic acid in a 30 °C, 1 bar total pressure, and 0.96 bar of CO <sub>2</sub>

Figure 15. The influence of 0, 0.1, and 10 mbar of H <sub>2</sub> S in a H <sub>2</sub> S/CO <sub>2</sub> gas mixture with 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub> 62
Figure 16. Water chemistry calculation of the aqueous species concentration over a range of bulk pH values with 10 mbar of $H_2S$ in a $H_2S/CO_2$ gas mixture and 1175 ppm of total acetic acid in a 30 °C, 1 bar total pressure, and 0.96 bar of $CO_2$
Figure 17. The influence of 0, 100, and 1000 ppm of free acetic acid with 0 mbar of $H_2S$ the presence of $CO_2$ at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of $CO_2$
Figure 18. An illustration of a hypothetical potentiodynamic sweep assuming the buffering effect mechanism for acetic acid (HAc) is followed where a substantial amount of HAc is added to a system that causes a transition from mixed charge transfer controlled/mass transfer controlled kinetics to fully charge transfer controlled kinetics accompanied by a substantial retardation of the anodic reaction in a constant pH environment
Figure 19. The influence of 0, 100, and 1000 ppm of free acetic acid with 0.1 a mbar H <sub>2</sub> S/CO <sub>2</sub> gas mixture at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub>
Figure 20. The influence of 0, 100, and 1000 ppm of free acetic acid with a 10 mbar H <sub>2</sub> S/CO <sub>2</sub> gas mixture at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub> 70
Figure 21. LPR corrosion rates for experiments conducted with a $0 - 10$ mbar H <sub>2</sub> S/CO <sub>2</sub> gas mixture and 0 & 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub>
Figure 22. The influence of pH with 0 ppm of free acetic acid and a 0.1 mbar H <sub>2</sub> S/CO <sub>2</sub> gas mixture at pH 4.0 and 5.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub> 73
Figure 23. The influence of pH with 100 ppm of free acetic acid and a 0.1 mbar $H_2S/CO_2$ gas mixture at pH 4.0 and 5.0, 30 °C, 1000 rpm RDE, and 0.96 bar of $CO_2$
Figure 24. The influence of pH with 1000 ppm of free acetic acid and a 0.1 mbar $H_2S/CO_2$ gas mixture at pH 4.0 and 5.0, 30 °C, 1000 rpm RDE, and 0.96 bar of $CO_2$ 75
Figure 25. The influence of temperature with 0 ppm of free acetic acid and a 0.1 mbar $H_2S/CO_2$ gas mixture at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of $CO_2$ 77
Figure 26. The influence of temperature with 100 ppm of free acetic acid and a 0.1 mbar $H_2S/CO_2$ gas mixture at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of $CO_2$ 78
Figure 27. The influence of temperature with 1000 ppm of free acetic acid and a 0.1 mbar $H_2S/CO_2$ gas mixture at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of $CO_2$ 79
Figure 28. The influence of the mass transfer coefficient with 0 ppm of free acetic acid and a 0.1 mbar H <sub>2</sub> S/CO <sub>2</sub> gas mixture with a 500, 1000, and 2000 rpm RDE at 30 °C, pH 4.0, and 0.96 bar of CO <sub>2</sub> . ( <i>kRDE</i> is equal to $2.06 \times 10^{-4}$ , $2.91 \times 10^{-4}$ , and $4.12 \times 10^{-4}$ m/s, respectively)
Figure 29. The influence of the mass transfer coefficient with 100 ppm of free acetic acid and a 0.1 mbar $H_2S/CO_2$ gas mixture with a 500, 1000, and 2000 rpm RDE at 30 °C, pH

steel surface after 72 hours of exposure (b) two dimensional profile measurement across of the steel surface where the path length is shown by the red line
Figure 40. Modeled potentiodynamic sweeps for experiments containing 0 - 10 mbar of H <sub>2</sub> S without the presence of acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N <sub>2</sub> as the sparge gas
Figure 41. Modeled potentiodynamic sweeps for experiments containing 0 mbar of H <sub>2</sub> S with 0 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N <sub>2</sub> as the sparge gas
Figure 42. Modeled potentiodynamic sweeps for experiments containing 0.05 mbar of H <sub>2</sub> S with 0 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N <sub>2</sub> as the sparge gas
Figure 43. Modeled potentiodynamic sweeps for experiments containing 0.1 mbar of H <sub>2</sub> S with 0 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N <sub>2</sub> as the sparge gas
Figure 44. Modeled potentiodynamic sweeps for experiments containing 10 mbar of H <sub>2</sub> S with 0 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N <sub>2</sub> as the sparge gas
Figure 45. Comparison between the corrosion rates calculated from the strong acid and $H_2S$ models and the LPR corrosion rates determined experimentally at 30 °C, pH 4.0, 1000 rpm RDE, and $N_2$ as the sparge gas
Figure 46. Modeled potentiodynamic sweeps for experiments containing 0 - 10 mbar of $H_2S$ in a $H_2S/CO_2$ mixed environment without the presence of acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of $CO_2$
Figure 47. Modeled potentiodynamic sweeps for experiments in $CO_2$ corrosion containing 0 – 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of $CO_2$ .
Figure 48. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 0 – 1000 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of $CO_2$
Figure 49. Modeled potentiodynamic sweeps for experiments in containing 10 mbar of $H_2S$ and $0 - 1000$ ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of $CO_2$
Figure 50. Comparison between the corrosion rates calculated from the CO <sub>2</sub> and H <sub>2</sub> S/CO <sub>2</sub> models and the LPR corrosion rates determined experimentally at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub>
Figure 51. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 0 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 °C, pH 4.0 and 5.0, 1000 rpm RDE, and 0.96 bar of $CO_2$

Figure 52. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 100 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 °C, pH 4.0 and 5.0, 1000 rpm RDE, and 0.96 bar of $CO_2$
Figure 53. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 1000 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 °C, pH 4.0 and 5.0, 1000 rpm RDE, and 0.96 bar of $CO_2$
Figure 54. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 0 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of $CO_2$
Figure 55. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 100 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of $CO_2$
Figure 56. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 1000 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of $CO_2$
Figure 57. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 0 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 °C, pH 4.0, 500 - 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub> . ( <i>kRDE</i> is equal to 2.06x10 <sup>-4</sup> , 2.91x10 <sup>-4</sup> , and 4.12x10 <sup>-4</sup> <i>m/s</i> , respectively). 156
Figure 58. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 100 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 °C, pH 4.0, 500 - 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub> . ( <i>kRDE</i> is equal to 2.06x10 <sup>-4</sup> , 2.91x10 <sup>-4</sup> , and 4.12x10 <sup>-4</sup> <i>m/s</i> , respectively)
Figure 59. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of $H_2S$ and 1000 ppm of free acetic acid in a mixed $H_2S/CO_2$ environment at 30 °C, pH 4.0, 500 - 1000 rpm RDE, and 0.96 bar of CO <sub>2</sub> . ( <i>kRDE</i> is equal to 2.06x10 <sup>-4</sup> , 2.91x10 <sup>-4</sup> , and 4.12x10 <sup>-4</sup> <i>m/s</i> , respectively)

#### **Chapter 1: Introduction**

Corrosion is a naturally occurring phenomenon that involves the process of metals wanting to revert to a more stable form akin to how they existed as their parent ore, which is how they are naturally found geologically. This process happens through two sets of electrochemical reactions, known as the cathodic and anodic reactions, that happen simultaneously. These electrochemical reactions alone, in 2014, cost the United States oil and gas industry \$27 billion US dollars in asset damage. Furthermore, they are responsible for many accidents seen in the United States over the years, associated with lack of inadequate mitigation strategies, maintenance. and improper analysis of production/transmission systems.<sup>1</sup> One case in particular involved the Prudhoe Bay oil field located in Alaska, USA. On March 2nd, 2006, an oil leak had been discovered by a worker that was driving near a deserted section of the pipeline while investigating a strong petroleum odor. The pipeline had been leaking for 5 days prior to its discovery. It was determined that 212,252 gallons were able to leak from a section of the pipeline that failed due to localized corrosion. At the time, this was the largest oil spill to ever happen in Alaska's North Slope.<sup>2</sup> This is yet another example that exemplifies the importance of this research as it helps engineers implement proper maintenance and mitigation measures in order to prevent catastrophic failures of metallic materials.

Identification of the corrosive species and characterizing how they influence the reactions involved is an essential step in understanding the corrosion process and finding ways for effective mitigation. Organic acids have been identified as corrosive species in oil and gas pipelines; they are weak acids that contribute additional H<sup>+</sup> ions that are reduced

during the cathodic reaction.<sup>3–5</sup> They do this by being able to buffer the pH at the surface of the metal by only partially dissociating in the aqueous phase, releasing more  $H^+$  ions that are consumed at the surface.<sup>4,5</sup> Consequently, this leads to increased mass transfer limiting currents pertaining to the cathodic reaction. How these organic acids, specifically acetic acid due to its abundance in oil and gas pipelines coupled with its similar pK<sub>a</sub> to other prevalent organic acids therein, influence CO<sub>2</sub> corrosion has been studied extensively, but their influence on H<sub>2</sub>S corrosion has yet to be studied to an appreciable extent. This is where the motivation for this research is derived. The next section will review the relevant literature that has been published on the topic of CO<sub>2</sub>, H<sub>2</sub>S, and organic acid corrosion to gain an understanding of what has already been researched thus far, and to identify the gaps in this knowledge that need to be investigated.

### **Chapter 2: Literature Review**

#### 2.1 CO<sub>2</sub> Corrosion of Mild Steel

Carbon dioxide (CO<sub>2</sub>) corrosion is one of the most extensively studied types of corrosion in the oil and gas industry. This is due to its abundance in upstream oil and gas pipelines. CO<sub>2</sub> in the gas phase is not corrosive, but upon dissolving into the aqueous phase will form carbonic acid (H<sub>2</sub>CO<sub>3</sub>). This is a corrosive weak acid that will deteriorate the inside of a mild steel pipe, creating safety concerns if left unnoticed or improperly mitigated. This section will discuss what is known thus far about CO<sub>2</sub> corrosion.

As CO<sub>2</sub> corrosion of mild steel is understood today, there are three electrochemical reactions that happen on the surface of the metal. The anodic reaction solely involves the oxidation of iron (Fe) whereas the cathodic reaction involves two reactions, the reduction of hydrogen ions (H<sup>+</sup>) and the reduction of water (H<sub>2</sub>O). Near the corrosion potential, the reduction of H<sup>+</sup> is the dominant cathodic reaction. When there is a large negative overpotential applied to the system, the reduction of H<sub>2</sub>O becomes the dominant cathodic reaction.

When evaluating a corrosion system, an understanding of the water chemistry is always an important factor in understanding how the system will behave.  $CO_2$  will dissolve into any aqueous phase that is present where the amount dissolved is mainly a function of temperature and partial pressure of  $CO_2$ . The concentration of dissolved  $CO_2$  under atmospheric pressure conditions can be found using Henry's law. Once dissolved into the aqueous phase,  $CO_2$  will go through a slow hydration step to form H<sub>2</sub>CO<sub>3</sub>. The H<sub>2</sub>CO<sub>3</sub> can then go through two dissociation steps. The first dissociation step will yield an H<sup>+</sup> ion and a bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) and the second step will yield another  $H^+$  ion and a carbonate ion (CO<sub>3</sub><sup>2-</sup>). The concentrations of each of these ions in the aqueous phase can be found using their respective equilibrium constants. When comparing the reaction rates of all the reactions mentioned above, the kinetics of the CO<sub>2</sub> hydration step is so slow such that it is considered to be the rate determining step. All the reactions mentioned above is a summary of knowledge from the open literature and are listed in Table 1.

Electrochemical Reactions			
Oxidation of <b>F</b>	$Fe \qquad Fe_{(s)} \to Fe_{(c)}^2$	$\frac{1}{2}(q) + 2$	2e <sup>-</sup> (1)
Reduction of I	$H^+ \qquad H^+_{(aq)} + e^- \rightarrow$	$\frac{1}{2}H_2$	e <sub>(g)</sub> (2)
Reduction of I	$H_2 \mathbf{O} \qquad \qquad H_2 \mathcal{O}_{(l)} + e^- \to \frac{1}{2} H_2 \mathbf{O}_{(l)}$	$I_{2(g)}$ -	$+ OH_{(aq)}^{-}$ (3)
Chemical Reactions Equilibrium Constant			Equilibrium Constant
Dissolution of CO2	$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$	(4)	$K_{H,CO_2} = C_{CO_2}/P_{CO_2}$
H <sub>2</sub> O dissociation	$H_2O_{(l)} \rightleftharpoons H_{(aq)}^+ + OH_{(aq)}^-$	(5)	$K_{wa} = C_{H^+} C_{OH^-}$
CO <sub>2</sub> hydration	$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$	(6)	$K_{hy} = C_{H_2CO_3}/C_{CO_2}$
H <sub>2</sub> CO <sub>3</sub> dissociation	$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^{3(aq)}$	(7)	$K_{ca} = C_{H^+} C_{HCO_3^-} / C_{H_2CO_3}$
HCO <sub>3</sub> - dissociation	$HCO_{3(aq)}^{-} \rightleftharpoons H_{(aq)}^{+} + CO_{3(aq)}^{2-}$	(8)	$K_{bi} = C_{H^+} C_{CO_3^{2-}} / C_{HCO_3^{-}}$

Table 1. Reactions Involved in CO<sub>2</sub> Corrosion of Mild Steel

Equations for the respective equilibrium constants for each chemical reaction are listed in Table 2.

Table 2. Equilibrium Constants for Chemical Reactions in CO<sub>2</sub> Corrosion

<b>Chemical Reaction</b>	Equilibrium Constant		
Dissolution of CO <sub>2</sub>	K <sub>H,CO2</sub>		
Reference: Oddo	14.5 $m_{10}^{-(2.27+5.65x10^{-3}T_f - 8.06x10^{-6}T_f^2 + 0.075I)} molar$		
and Tomson <sup>6</sup>	$=\frac{1.00258}{1.00258} \times 10^{-10}$		
H <sub>2</sub> O dissociation	$K_{wa} = (10^{-3}\rho_w)^2 \ 10^{\left(A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \left(E + \frac{F}{T} + \frac{G}{T^2}\right)\log(10^{-3}\rho_w)\right)} \ molar^2$		
Reference: Marshall	$A = -4.098, B = -3245.2, C = 2.2362 \times 10^5, D = -3.984 \times 10^7$		
and Franck <sup>7</sup>	$E = 13.957, F = -1262.3, G = 8.5641 x 10^5$		
CO <sub>2</sub> hydration			
Reference: Palmer	$K_{hy} = 2.58 \times 10^{-3}$		
and Van Eldik <sup>8</sup>			
H <sub>2</sub> CO <sub>3</sub> dissociation	$\left(-6.6216-1.594x10^{-3}T_f+8.52x10^{-6}T_f^2\right)$		
Reference: Ma <sup>9</sup>	$K_{ca} = 387.6 \times 10^{(} -3.07 \times 10^{-5} p CO_2 - 0.7379 I^{0.5}) molar$		
HCO <sub>3</sub> <sup>-</sup> dissociation			
Reference: Oddo	$K_{bi} = 10^{\begin{pmatrix} -10.61 - 4.97x10^{-3}T_f + 1.331x10^{-5}T_f^2 - 2.624x10^{-5}pCO_2 \\ -1.166I^{0.5} + 0.3466I \end{pmatrix}} molar$		
and Tomson <sup>6</sup>			

Note: In this table, *T* is temperature in Kelvin,  $T_f$  is temperature in Fahrenheit,  $\rho_w$  is the density of water in kg/m<sup>3</sup>, *pCO*<sub>2</sub> is partial pressure of CO<sub>2</sub> in psi, and *I* is ionic strength in molar.

When the appropriate physiochemical conditions are present in the system,  $Fe^{2+}$  ions that are released into solution from the anodic reaction can react with  $CO_3^{2-}$  from the dissociated H<sub>2</sub>CO<sub>3</sub> and precipitate on the metal surface as iron carbonate (FeCO<sub>3</sub>).<sup>9,10</sup> This precipitated layer will in most cases retard the corrosion process.<sup>11–15</sup>

The reason why H<sub>2</sub>CO<sub>3</sub> is so corrosive is because of its ability to buffer the pH at the surface of the steel. As H<sup>+</sup> is being reduced during the cathodic reaction, H<sub>2</sub>CO<sub>3</sub> will readily dissociate and contribute H<sup>+</sup> near the corroding surface to replenish the concentration of H<sup>+</sup> that is being consumed. This only increases the cathodic mass transfer limiting current without influencing the charge transfer region near the corrosion potential. Because of the ability for H<sub>2</sub>CO<sub>3</sub> to act as a reservoir for H<sup>+</sup>, this mechanism is referred to as the buffering effect.<sup>16,17</sup> A previously used mechanism in the overall description for CO<sub>2</sub> corrosion of mild steel involved the direct reduction of H<sub>2</sub>CO<sub>3</sub> at the surface of the metal.<sup>18–</sup> <sup>22</sup> However, research conducted by Tran, *et al.*, and Kahyarian, *et al.*, demonstrated that this reaction is insignificant making the reduction of H<sup>+</sup> the only relevant cathodic reaction in CO<sub>2</sub> corrosion.<sup>16,17</sup>

#### 2.2 H<sub>2</sub>S Corrosion of Mild Steel

 $H_2S$  gas has also been identified as a corrosive species and its influence on the corrosion of carbon steel has been a topic of interest since as early as the 1960s.<sup>23</sup> It is known that when  $H_2S$  gas comes in contact with water, it will dissolve into the aqueous phase where the concentration is a function of temperature and its partial pressure. Once dissolved,  $H_2S$  will dissociate *via* two dissociation reactions; the first yielding  $H^+$  and bisulfide ions ( $HS^-$ ) and the second yielding  $H^+$  and sulfide ions ( $S^{2-}$ ). The concentration of each ion is dependent upon their respective equilibrium constants. The above reactions associated with  $H_2S$  corrosion can be found in the open literature and are included in Table 3, with equations for their associated equilibrium constants listed in Table 4. The same electrochemical reactions and water dissociation reaction that occurs in CO<sub>2</sub> corrosion,

reactions (1) - (3), respectively, also occur in  $H_2S$  corrosion and can be referred to in Table 1.

Table 3. Chemical Reactions Involved in H<sub>2</sub>S Corrosion of Mild Steel

	<b>Chemical Reactions</b>		Equilibrium Constant
Dissolution of H <sub>2</sub> S	$H_2S_{(g)} \rightleftharpoons H_2S_{(aq)}$	(9)	$K_{H,H_2S} = C_{H_2S} / P_{H_2S}$
H <sub>2</sub> S dissociation	$H_2S_{(aq)} \rightleftharpoons H^+_{(aq)} + HS^{(aq)}$	(10)	$K_{H_2S} = C_{H^+}C_{HS^-}/C_{H_2S}$
HS <sup>-</sup> dissociation	$HS^{(aq)} \rightleftharpoons H^+_{(aq)} + S^{2-}_{(aq)}$	(11)	$K_{HS^-} = C_{H^+} C_{S^{2-}} / C_{HS^-}$

Table 4. Equilibrium Constants for Chemical Reactions in H<sub>2</sub>S Corrosion

<b>Chemical Reaction</b>	Equilibrium Constant
<b>Dissolution of H<sub>2</sub>S</b> Reference: Ma <sup>24</sup>	$K_{H,H_2S} = 10^{-\binom{634.2593+0.2709T-0.00011132T^2 - \frac{16719}{T}}{-261.9\log(T) + 0.0656I}} \frac{molar}{bar}$
H <sub>2</sub> S dissociation Reference: Ma <sup>24</sup>	$K_{H_2S} = 10^{\binom{787.44055+0.36126T-0.00016722T^2 - \frac{20565.7315}{T}}{-142.741722\ln(T)+0.1672I}} molar$
HS <sup>-</sup> dissociation Reference: Migdisov <i>et al.</i> <sup>25</sup>	$K_{HS^-} = 10^{-17.4} molar$

## Note: In this table, T is temperature in Kelvin and I is ionic strength in molar

Recent research conducted by Kahyarian, *et al.*, investigated whether or not  $H_2S$  followed the buffering effect mechanism.<sup>26</sup> A mechanistic model was created postulating that the direct reduction of  $H_2S$  was insignificant, thus not including this additional cathodic reaction in the mechanistic model. Instead, it was assumed that  $H_2S$  will go

through a homogeneous dissociation inside the diffusion boundary layer that will buffer the surface pH. The model was compared to experimental data and was able to predict the behavior with reasonable accuracy over the range from pH 3 to pH 5 at 25 °C for H<sub>2</sub>S partial pressures up to 1 bar, thus further validating that H<sub>2</sub>S will follow the buffering effect mechanism in the conditions that were tested.

Through the use of potentiodynamic sweeps, insights as to how H<sub>2</sub>S influences mild steel corrosion mechanisms can be studied. Research conducted by Zheng aimed to investigate H<sub>2</sub>S corrosion mechanisms where select potentiodynamic sweeps were collected and analyzed.<sup>27</sup> Focusing on the cathodic reaction in a N<sub>2</sub> sparged 1 wt.% NaCl electrolyte at 30 °C and pH 4.0 shows that the addition of low partial pressures of H<sub>2</sub>S (100ppm<sub>v</sub>) in the gas phase above the test electrolyte induces significant retardation of the H<sub>2</sub>O reduction rate.<sup>27</sup> This retardation of the H<sub>2</sub>O reduction reaction occurred at partial pressures up to 10 vol.% of H<sub>2</sub>S and was described by how the adsorption of sulfide species can alter the capacitance of the electric double layer.<sup>27</sup>

When the H<sub>2</sub>S concentration is between 100 and 1000 ppm<sub>v</sub> at 30 °C and pH 4.0, the mass transfer limiting current resulting from the diminished H<sup>+</sup> concentration is unaffected when compared to a system with no H<sub>2</sub>S.<sup>27,28</sup> Research conducted by Kittel, *et al.*, observed this same trend of the H<sup>+</sup> limiting current not being influenced by  $\leq$  1000 ppm<sub>v</sub> of H<sub>2</sub>S.<sup>28</sup> Further increasing the H<sub>2</sub>S partial pressure to 1 and 10 vol.%, in addition to the typical H<sup>+</sup> mass transfer limiting current, a second mass transfer limiting current becomes apparent. This is denoted by a second limiting current seen at higher current densities in the cathodic sweep and is commonly referred to as the "double wave" phenomenon. The double wave phenomenon is typically only observed in low temperature and low pH environments.<sup>26–29</sup> The presence of the second limiting current was previously believed to be due to a second cathodic reaction, the direct reduction of H<sub>2</sub>S.<sup>27,28</sup> Recent research conducted by Kahyarian had found that the second limiting current is instead due to the increase in the surface pH as it reaches the pK<sub>a</sub> value of H<sub>2</sub>S. The current density will continue to increase after the first mass transfer limiting current due to the increase in the surface pH as it approaches 7.0, the approximate pK<sub>a</sub> of H<sub>2</sub>S. This allows for the dissociation of H<sub>2</sub>S to become a favorable reaction thus allowing it to act as a buffering species for the cathodic reaction close to the surface of the metal.<sup>26</sup> This shifts the mass transfer limiting current to higher current densities thus the presence of a second limiting current.

When evaluating corrosion systems, the corrosion rate is one of the most important factors to consider for a given condition. The corrosion rate in systems containing H<sub>2</sub>S is primarily influenced by the partial pressure of H<sub>2</sub>S present, the bulk pH value, and temperature. Zheng conducted linear polarization resistance (LPR) corrosion rate measurements with partial pressures ranging from 0 to 10 vol.% of H<sub>2</sub>S to examine how they influenced the corrosion rate in a N<sub>2</sub> sparged 1 wt.% NaCl electrolyte at 30 °C and pH  $4.0.^{27}$  At low concentrations of H<sub>2</sub>S, 100 and 1000ppm<sub>v</sub>, the corrosion was found to be significantly retarded. This decrease in corrosion rate in the presence of low partial pressures of H<sub>2</sub>S is consistently observed throughout the literature.<sup>28–36</sup> This retardation is due to a thin mackinawite corrosion product layer that forms relatively quickly on the surface of the metal.<sup>27,37</sup> What is unique about this thin mackinawite layer is that it will

form regardless of whether or not the saturation limit with respect to iron sulfide is achieved. At higher concentrations of  $H_2S$ , 1 and 10 vol.%, this retardation is no longer observed and corrosion rates will be accelerated as compared to the same environmental conditions with no  $H_2S$  ("Pure  $N_2$ ").<sup>27</sup>

In the presence of H<sub>2</sub>S, depending on the physicochemical conditions in the system, many types of iron sulfides can be formed. The most common form of iron sulfide is mackinawite (FeS), a metastable compound with relatively fast formation kinetics as compared to other forms of iron sulfide.<sup>37</sup> With time, mackinawite can form more stable structures of iron sulfide such as troilite (FeS), pyrrhotite (Fe<sub>1-x</sub>S), and pyrite (FeS<sub>2</sub>). Because of mackinawite's relatively fast formation kinetics, it is the most prevalent form of iron sulfide identified on samples in short term experiments at low temperatures.<sup>27,36–38</sup> During the formation of an iron sulfide layer, regardless of whether or not the saturation limit with respect to iron sulfide is achieved, H<sub>2</sub>S will react with iron immediately after dissolution to form a thin mackinawite layer on the surface of the steel.

This thin mackinawite layer was investigated by Lee using LPR and EIS measurements over time as well as by X-ray photoelectron spectroscopy (XPS) surface analysis on X65 steel.<sup>39</sup> EIS measurements collected at 20 minutes in the presence of 340ppm<sub>v</sub> H<sub>2</sub>S indicated that a thin sulfide layer had formed almost immediately after immersion into the test solution. This was consistent with the retarded corrosion rates measured *via* LPR during the same time period. Although SEM/EDS analysis could not confirm the presence of sulfides on the metal surface, the XPS analysis showed intensity peaks at binding energies as well as a surface composition that was indicative of

mackinawite. This thin mackinawite layer is believed to be much too thin to act as a diffusion barrier but it is postulated that the adsorption of the sulfide species will prevent the dissolution of iron and block active sites for the reduction of H<sup>+</sup> reaction thus decreasing the overall observed corrosion rate.<sup>27,35</sup> This thin layer will also allow for iron sulfide to favorably precipitate onto once the saturation limit is reached.<sup>27,37,39,40</sup> The conclusions from Lee's research further validates the presence of a thin mackinawite layer that will retard corrosion rates as reported in previous work.<sup>28–36</sup>

### 2.3 Organic Acid Corrosion of Mild Steel

When studying how the presence of organic acids influences the corrosion behavior of interest, it would be exhaustive of one's resources to investigate the influence of every organic acid that can be found in oil and gas pipelines. For this reason, typically only one organic acid is chosen for the analysis. The most common organic acid of choice is acetic acid as it is the most abundant in terms of mass concentration in oil and gas pipelines and its pKa of 4.76 is similar to other organic acids that can be found in oil and gas pipelines, such as butyric acid or propionic acid.<sup>41</sup> For this current research, acetic acid was chosen for the investigation of how organic acids influence H<sub>2</sub>S corrosion due to the reasons mentioned above.

Acetic acid corrosion and its effect on  $CO_2$  corrosion has been studied in some detail.<sup>11,12,42–46</sup> Acetic acid's presence in oil and gas pipelines can lead to the development of undesirable environmental conditions, especially at higher concentrations. Acetic acid is a weak acid with the formula CH<sub>3</sub>COOH (frequently written as HAc) that will partially dissociate in the aqueous phase to form an H<sup>+</sup> ion and an acetate ion (CH<sub>3</sub>COO<sup>-</sup> or Ac<sup>-</sup>).

The concentration of each ion is dependent upon their respective equilibrium constants. The reactions associated with HAc corrosion can be found in the open literature and are written as follows in Table 5. The same electrochemical reactions and water dissociation reaction that occurs in  $CO_2$  and  $H_2S$  corrosion, reactions (1) - (3), respectively, also occur in HAc corrosion and can be referred to in Table 1.

Table 5. Chemical Reaction Involved in Acetic Acid Corrosion of Mild Steel

	<b>Chemical Reactions</b>	Equilibrium Constant		
HAc dissociation	$HAc_{(aq)} \rightleftharpoons H^+_{(aq)} + Ac^{(aq)}$	(12)	$K_{HAc} = C_{H^+} C_{Ac^-} / C_{HAc}$	

The equation for the equilibrium constant associated with this chemical reaction is shown in Table 6.

|--|

Chemical Reaction	Equilibrium Constant
HAc dissociation	
Reference: Kharaka, et	$K_{HAc} = 10^{-(6.66104 - 0.0134916T + 2.37856x10^{-5}T^2)} molar$
al. <sup>47</sup>	

### Note: In this table, T is temperature in Kelvin

When studying the influence of acetic acid on corrosion mechanisms, the concentration of free acetic acid still available to dissociate becomes the species of interest. This is due to recent research that has shown that acetic acid is not an electroactive species, it will instead follow the buffering effect mechanism much like  $H_2CO_3$  in  $CO_2$ 

corrosion.<sup>4,5,43</sup> The buffering effect mechanism is defined by the buffering of the surface pH by a weak acid as H<sup>+</sup> is being consumed in the cathodic, reduction, reaction. When the surface pH naturally starts to increase due to the consumption of H<sup>+</sup>, the weak acid, in this case acetic acid, will partially dissociate near the corroding surface and contribute additional H<sup>+</sup>, thus buffering the surface pH. This is why the free (undissociated) acetic acid is a key species of interest. Increasing concentrations of acetic acid will only increase the mass transfer limiting current without much influence on the charge transfer region of the cathodic reaction. When acetic acid is added to a system, its influence on the corrosion rate can vary depending on the water chemistry and environmental conditions.

In CO<sub>2</sub> corrosion, low temperatures and high concentrations of acetic acid will typically have decreased corrosion rates when compared to pure CO<sub>2</sub> corrosion when the pH remains constant. This phenomenon has been observed in the literature and is attributed to acetic acid retarding the rate of the anodic reaction.<sup>3,42</sup> This retardation of the anodic reaction has also been observed in a strong acid environment in the presence of acetic acid at low temperatures, but the magnitude of the retardation is less than that seen in CO<sub>2</sub> corrosion.<sup>42,48</sup> Due to the less substantial influence acetic acid has on the anodic reaction in strong acid environments, the presence of acetic acid will result in increased corrosion rates due to the transition from mass transfer controlled kinetics to more charge transfer controlled kinetics. When the temperature is increased to higher values, the retardation of the anodic reaction is no longer observed.<sup>45,46</sup> Because of this, higher corrosion rates tend to occur when acetic acid is added to the system.

The influence of acetic acid has been investigated in  $H_2S/CO_2$  mixed environments inside of a flow loop.<sup>32</sup> Weight loss corrosion rates were collected at various partial pressures of  $H_2S$  in environments with and without the presence of 1000 ppm of free acetic acid. Two trends can be identified from the corrosion rate data that was collected over time in this study. Firstly, as time progresses, especially at higher partial pressures of  $H_2S$ , the corrosion rate decreased. Upon the addition of 1000 ppm of free acetic acid, there is no longer a clear relationship in corrosion rate effects over time. This could mean that acetic acid influenced the formation of the iron sulfide or iron carbonate layer causing it to not be able to form a protective corrosion product layer over time. Secondly, 1000 ppm of free acetic acid increased the corrosion rate at all partial pressures of  $H_2S$  that were tested. Research conducted by Camacho also studied the combined effect of  $H_2S/CO_2$  and acetic acid in a flow loop.<sup>49</sup> The conclusions of this research stated the observation of similar trends to those reported in research conducted by Singer.<sup>32</sup>

### Chapter 3: Mechanistic Study of H<sub>2</sub>S Corrosion of Mild Steel

### **3.1 Research Hypothesis and Questions**

After a thorough review of the literature, hypotheses and research questions have been developed to address the knowledge gaps that have been identified in our current understanding of how acetic acid will influence H<sub>2</sub>S corrosion. The relevant hypothesis to be tested is as follows:

• Like in CO<sub>2</sub> environments, acetic acid in H<sub>2</sub>S environments is not directly reduced, it only increases the limiting current associated with the cathodic reaction.

A research question to be answered was also developed from the gaps in the literature and is as follows:

• How does the concentration of free acetic acid influence the anodic and cathodic reactions in H<sub>2</sub>S environments?

A test matrix was developed with the purpose of testing and investigating the above hypothesis and research question.

### **3.2 Experimental Methodology**

### 3.2.1 Equipment

Experiments were conducted in a 1 L glass cell with a 1 wt.% NaCl electrolyte prepared with deionized water. A three-electrode setup was used for all electrochemical measurements. A platinum-coated titanium mesh was used as a counter electrode (CE). A rotating disk electrode (RDE) controlled by a speed controller was used as the working electrode (WE). An RDE was chosen for these experiments due to the high reproducibility

of results that can be obtained and its popularity of usage in bare metal corrosion mechanism investigations. A saturated silver-silver chloride (sat. Ag/AgCl) reference electrode (RE) electrically in contact with the test solution through a Luggin capillary was used. The Luggin capillary was filled with a 1 M potassium chloride (KCl) solution. The pH of the solution was measured by an electrode that was immersed in the solution during testing. The gaseous concentration of H<sub>2</sub>S was controlled by a gas rotameter and confirmed by use of a GasTec pump and colorimetric tubes. A 1 M NaOH solution followed by an activated carbon scrubber was used to treat the gas leaving the glass cell to remove as much H<sub>2</sub>S as possible. A 3-dimensional rendering of the RDE glass cell can be seen in Figure 1, and a detailed drawing of its internal components used for the collection of experimental data is neatly shown in Figure 2. Because acetic acid was not expected to exist in significant concentrations in the vapor phase and the loss of the electrolyte through evaporation was expected to be very low, a condenser on the gas outlet stream was not used.



Figure 1. A 3-dimensional rendering of the 1 L RDE glass cell used for the collection of experimental data.



Figure 2. A detailed drawing showing the internal parts of the 1 L RDE glass cell that was used for the collection of experimental data.

The material used in this experimental work was X65 pipeline steel. The composition provided by Laboratory Testing Inc. is shown in Table 7. The WE was machined into a small disk with a diameter of 5 mm and an exposed surface area of 0.196 cm<sup>2</sup>.

С	Mn	Мо	Ni	Nb	Cr	Si
0.054	1.40	0.072	0.25	0.036	0.23	0.22
	V	Ti	Р	Al	Fe	
	0.035	0.011	0.003	0.023	Balance	

Table 7. Composition of the X65 pipeline steel working electrode (wt.%)

#### 3.2.2 H<sub>2</sub>S Health and Safety Information

H<sub>2</sub>S is a hazardous gas that must be handled with extreme caution. According to the Occupational Health and Safety Administration (OSHA), concentrations of as little as 100ppm<sub>v</sub> can be harmful to humans. Concentrations above 700ppm<sub>v</sub> can lead to death if proper personal protection equipment (PPE) and action plans to remove yourself from the environment are not implemented.<sup>50</sup> Because of this, several steps were taken in order to ensure that there is no personal exposure to H<sub>2</sub>S. Completion of the ANSI/ASSP Z390.1 H<sub>2</sub>S certification course as well as fit testing for a self-contained breathing apparatus (SCBA) was done to become knowledgeable about H<sub>2</sub>S hazards and to have proper PPE when conducting experiments in the Institute for Corrosion and Multiphase Technology's (ICMT) H<sub>2</sub>S room when H<sub>2</sub>S concentrations exceed 100ppm<sub>v</sub>.

In addition to the SCBA, a personal  $H_2S$  monitor was worn that would alarm if concentrations above 10ppm<sub>v</sub> were detected. When experiments were conducted in the  $H_2S$ room, an equally trained and equipped buddy was always utilized outside of the  $H_2S$  room to monitor all activities and act accordingly if a loss of containment were to happen or their buddy were to become incapacitated. When the  $H_2S$  concentration does not exceed 100ppm<sub>v</sub>, experiments were conducted in a controlled fume hood where any loss of containment would be dealt with by safely venting. If any leaks in the experimental setup were detected, experiments were stopped, and the leak was repaired immediately.

### 3.2.3 Test Matrix

The environmental conditions for these experiments were chosen to ensure that the formation of an outer iron sulfide layer was highly unlikely so that the bare steel corrosion mechanisms could be studied with clarity. Test matrix 1 shown in Table 8 was developed to test the hypothesis and research question. Potentiodynamic sweeps were collected in an H<sub>2</sub>S environment at 30 °C and pH 4.0 with 0 – 1 vol.% of H<sub>2</sub>S with and without the presence of 1000ppm of free acetic acid.

Experimental Conditions		
Temperature	30 °C	
рН	4.0	
[HAc]free	0, 1000 ppm / 0, 16.7 mM	
WE	X65 RDE	
Electrolyte	1 wt.% NaCl	
Total Pressure	1 bar	
<b>RDE Rotation Velocity</b>	1000 rpm	
Sparge Gas	0, 0.05, 0.1, 10 mbar /	
	0, 50, 100, 10000 ppm <sub>v</sub> H <sub>2</sub> S in N <sub>2</sub>	
Exposure Time	2 hours	
Analytical Techniques	LPR, EIS, Potentiodynamic Sweeps	

Table 8. Text matrix for investigating corrosion mechanisms involved in H<sub>2</sub>S corrosion in the presence of acetic acid

### 3.2.4 Procedure

The test solution was sparged with  $N_2$  gas for at least 1 hour to deoxygenate the test solution; this was a crucial step to avoid elemental sulfur formation when  $H_2S$  was

introduced. Measurements with a Hach Orbisphere showed an O<sub>2</sub> concentration of 0.0 ppb after one hour of sparging, thus confirming that 1 hour of deoxygenation was sufficient for O<sub>2</sub> depletion. After the solution was deoxygenated, H<sub>2</sub>S gas was sparged into the solution to saturate it with dissolved H<sub>2</sub>S at the appropriate partial pressure. The desired H<sub>2</sub>S partial pressure was achieved by mixing the appropriate ratio of H<sub>2</sub>S and N<sub>2</sub> in the gas inlet with a rotameter. In experiments where acetic acid was used, the appropriate volume of glacial acetic acid was added to achieve the desired mass concentration of free acetic acid in the aqueous phase. The pH was adjusted to the desired value right before inserting the sample by adding either sodium hydroxide (NaOH) or hydrochloric acid (HCl) to the test solution. Before experiments were started, the specimen was sequentially polished with 600, 800, and 1200 grit silicon carbide (SiC) abrasive paper, then a mirror finish polish was obtained by using a 9µm, 3µm, then 0.25µm diamond suspension polishing formulation. The specimen was then cleaned and sonicated with isopropyl alcohol, inserted into the rotating shaft, and placed into the testing solution where it was ready for experiments to start.

The polarization resistance ( $R_p$ ) was obtained using the linear polarization (LPR) method. The WE was polarized  $\pm$  5mV from the open circuit potential (OCP) at a scan rate of 0.125 mV/s. The Tafel constant ("B value") used for the LPR analysis was 13 mV/decade. The solution resistance ( $R_s$ ) was obtained by using electrochemical impedance spectroscopy (EIS) so that the potentiodynamic sweeps and LPR measurements could be corrected for the solution resistance accordingly. The EIS measurements were conducted by applying an oscillating potential of  $\pm$ 5 mV around the OCP using a frequency range of 0.2 Hz to 8 kHz. The anodic and cathodic potentiodynamic sweeps were collected over a
range of overpotentials from 0 to 0.2 V vs. EOC and 0 to -1.2 V vs. EOC, respectively, at a scan rate of 0.5 mV/s and a sampling period of 0.5 s.

Due to the nature of RDE samples, weight loss corrosion rates could not be obtained. Because of this, all corrosion rates were calculated with the  $R_p$  obtained from the LPR measurements. In order to ensure the repeatability of the results, each experiment was completed at least twice. The standard deviation in the measured current was added as error bars to all potentiodynamic sweeps and LPR corrosion rates to present the repeatability in a clear and concise manner.

# **3.3 Results and Discussion**

# 3.3.1 Influence of H<sub>2</sub>S Partial Pressure

In this section, the partial pressure of H<sub>2</sub>S was varied between 0 and 10 mbar at 30 °C and pH 4.0 with and without the presence of 1000 ppm of free acetic acid. This facilitated investigation of how changing the H<sub>2</sub>S partial pressure (pH<sub>2</sub>S) will influence the corrosion mechanisms involved. The corrosion potential and corrosion current measured using the LPR method were collected for each experiment and plotted on the Evans diagram along with the corresponding potentiodynamic sweep. These points are represented by a triangle that is colored the same as its corresponding potentiodynamic sweep. The potentiodynamic sweeps in Figure 3 show the influence of pH<sub>2</sub>S at 30 °C and pH 4.0 without the presence of acetic acid.

Upon adding 0.05 mbar of  $H_2S$  to the system, the rates of the anodic and cathodic reactions were significantly retarded. This is due to the formation of a thin mackinawite layer that is known to form in these conditions and cause a significant retardation of the

corrosion rate.<sup>27,31–33,35,49</sup> This mackinawite layer is much too thin to act as a diffusion barrier, but it is postulated that the adsorption of the sulfide species will prevent the dissolution of iron and block active sites for the reduction of  $H^+$  reaction thus decreasing the overall observed corrosion rate.<sup>27,35</sup> This was accompanied by a retardation of both the corrosion current and H<sub>2</sub>O reduction reaction rate, which is consistent with what has been observed in the literature.<sup>26–29</sup> It can also be seen that 0.05 mbar of H<sub>2</sub>S has no significant influence on the mass transfer limiting current, implying that there is not enough H<sub>2</sub>S dissolved in the aqueous phase to contribute to reduction of H<sup>+</sup> by buffering the pH at the surface of the metal, which is expected at this low of an H<sub>2</sub>S partial pressure.<sup>27,28</sup>

Increasing the partial pressure to 0.1 mbar of  $H_2S$ , similar trends to 0.05 mbar were observed. There was a further retardation of the rate of the anodic reaction with a small positive shift in the corrosion potential when compared to an environment without the presence of  $H_2S$ . A further retardation of the corrosion current was also observed, which was due to the anodic reaction becoming more retarded than it was when 0.05 mbar of  $H_2S$ was present. Because 0.1 mbar is still a relatively low partial pressure of  $H_2S$ , there was no significant influence on the mass transfer limiting current.

When 10 mbar of  $H_2S$  is present, both the anodic and cathodic reaction rate are increased in a relatively equal proportion that results in an overall increase in the corrosion current but does not yet exceed the corrosion current of the system without  $H_2S$  present. In addition to the increase in the corrosion current, two mass transfer limiting currents can be seen in the cathodic sweep. This is indicative of the double wave phenomenon and is caused by there being enough  $H_2S$  to become a buffering species when the surface pH approaches the pK<sub>a</sub> of H<sub>2</sub>S (~ pH 7). At 10 mbar of H<sub>2</sub>S, the concentration of H<sub>2</sub>S in the solution has become significant enough such that it will begin to buffer the surface pH as it approaches the pKa value of H<sub>2</sub>S at around  $7.^{26}$ 



Figure 3. The influence of 0 - 10 mbar of H<sub>2</sub>S at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.

The potentiodynamic sweeps in Figure 4 show the influence of pH<sub>2</sub>S at 30 °C and pH 4.0 in the presence of 1000 ppm of free acetic acid. When 0.05 mbar of H<sub>2</sub>S is added to this system, a significant retardation of the cathodic reaction without much influence on the anodic reaction resulting in an overall retardation of the corrosion rate and negative shift in the corrosion potential is observed. Because of the low partial pressure of H<sub>2</sub>S, there was no significant influence on the limiting current. Similarly to H<sub>2</sub>S corrosion without the presence of acetic acid, a retardation of the water reduction reaction was observed.

Increasing the partial pressure to 0.1 and 10 mbar of  $H_2S$ , there was not much variation in the system when compared to the 0.05 mbar results with 1000 ppm of acetic acid present. The anodic reaction remained relatively uninfluenced regardless of the partial pressure of  $H_2S$ . Looking at the cathodic reaction, there was a significant retardation of the cathodic reaction rate when 0.05 mbar of  $H_2S$  was added. With 0.05 – 10 mbar of  $H_2S$ , there seems to be a slight variation in the sweeps within the charge transfer region, but each respective sweep falls within the error bars of one another, thus they can be considered to be not significantly different. For all sweeps collected in this environment, the limiting current was not significantly influenced by the partial pressure of  $H_2S$  up to 10 mbar. This was due to the high concentration of free acetic acid compared to the other weak acid, aqueous  $H_2S$ , present in the system causing it to become the primary buffering species.



Figure 4. The influence of 0 - 10 mbar of H<sub>2</sub>S with 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.

In the system with 10 mbar of  $H_2S$  and 1000 ppm of free acetic acid at 30 °C, the aqueous concentration for each weak acid was calculated by solving each respective equilibrium equation for reactions (9-11) and reaction (12). The total acetic acid concentration was determined from the 1000 ppm of free acetic acid present at pH 4.0. This means that 1175 ppm of acetic acid was present in the aqueous phase to achieve this concentration of free acetic acid. This is relevant because the concentration of each respective weak acid species is a function of pH, so the total amount of each weak acid is required for the calculation.

The concentration of dissolved H<sub>2</sub>S was fixed with the partial pressure of the sparge gas and not a function of pH. The concentration profile over a range of bulk pH values is shown in Figure 5. With even the highest partial pressure of H<sub>2</sub>S that was tested, at pH 4.0, the concentration of free acetic acid is the most abundant weak acid species present until about pH 6. At pH 4.0, the ratio of free acetic acid to aqueous H<sub>2</sub>S is 19.3:1 which exemplifies the abundance of free acetic acid present in the system and why it is the dominant buffering species in this condition.



Figure 5. Water chemistry calculation of the aqueous species concentration over a range of bulk pH values with 10 mbar of H<sub>2</sub>S and 1175 ppm of total acetic acid in a 30 °C, 1 bar total pressure, and N<sub>2</sub> sparged environment.

# 3.3.2 Influence of Free Acetic Acid Concentration

In this section, at each  $H_2S$  partial pressure that was tested up to 10 mbar, the free acetic acid concentration was varied between 0 and 1000 ppm in order to investigate how it influenced the corrosion mechanisms involved. As a baseline, 1000 ppm of free acetic acid present in a system with no  $H_2S$  present (pure HAc corrosion) at 30 °C and pH 4.0 was investigated. The potentiodynamic sweeps are shown in Figure 6. A large positive shift in the corrosion potential is observed. The large increase in the corrosion potential results from the transition from mixed charge transfer controlled/mass transfer controlled kinetics to fully charge transfer controlled kinetics due to a significant increase in the limiting current accompanied by a slight retardation of the anodic reaction. Overall, 1000 ppm of

free acetic acid did not have a significant influence on the corrosion current. The retardation of the anodic reaction in strong acid environments has been reported in research conducted by Kahyarian.<sup>48</sup>

It is difficult to decipher whether the addition of acetic acid influenced the charge transfer region of the cathodic reaction due to the condition without the presence of acetic acid not exhibiting fully charge transfer controlled kinetics. Because of this, a theoretical potentiodynamic sweep was created in order to further investigate the influence of acetic acid on the anodic and cathodic reactions.



Figure 6. The influence of 1000 ppm of free acetic with 0 mbar of H<sub>2</sub>S at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas

The theoretical potentiodynamic sweep can be seen in Figure 7. This theoretical potentiodynamic sweep was produced assuming that acetic acid follows the buffering

effect mechanism in an extreme situation where a substantial amount of acetic acid will cause the system to transition from mixed charge transfer controlled/mass transfer controlled kinetics to fully charge transfer controlled kinetics with a slight retardation of the anodic reaction in a constant pH environment. What is shown is the total anodic and total cathodic current for each situation where the intersection of the respective net currents signifies where the corrosion potential and corrosion current is located. The theoretical potentiodynamic sweep exemplifies a positive shift in the corrosion potential without much influence on the corrosion current, which further validates the observations made in the experimental data and supports the conclusions seen in the literature that acetic acid will follow the buffering effect mechanism while also retarding the anodic reaction in these conditions.<sup>48</sup>



Current Density (A/m<sup>2</sup>)

Figure 7. An illustration of a hypothetical potentiodynamic sweep assuming the buffering effect mechanism for acetic acid (HAc) is followed where a substantial amount of HAc is added to a system that causes a transition from mixed charge transfer controlled/mass transfer controlled kinetics to fully charge transfer controlled kinetics accompanied by a slight retardation of the anodic reaction in a constant pH environment.

The partial pressure of  $H_2S$  was increased to 0.05 mbar where 1000ppm of free acetic was added to the system. The resulting potentiodynamic sweep can be seen in Figure 8. When 1000 ppm of free acetic acid was added to the system, a positive shift in the corrosion potential and no significant change in the corrosion current was observed. This was likely due to a transition from mixed charge transfer controlled/mass transfer controlled kinetics to fully charge transfer controlled kinetics combined with the slight of retardation of the anodic reaction, but to a smaller magnitude than before. The retardation of the anodic reaction from the presence of acetic acid is of a lesser magnitude due to 0.05 mbar of  $H_2S$  also retarding the rate of the anodic reaction. From this set of experiments, it is difficult to analyze the cathodic charge transfer rates near the corrosion potential when the system without the presence of acetic acid is not fully charge transfer controlled. Being that the system with 0.05 mbar of  $H_2S$  behaves similarly to the system with no  $H_2S$  present, just to a smaller magnitude, it can be assumed that acetic acid follows the buffering effect mechanism when 0.05 mbar of  $H_2S$  is present.



Figure 8. The influence of 1000 ppm of free acetic with 0.05 mbar of H<sub>2</sub>S at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas

The partial pressure of  $H_2S$  was then increased to 0.1 mbar where the resulting potentiodynamic sweep can be seen in Figure 9. When 1000 ppm of free acetic acid was added to this system, a significant increase in the corrosion current without any increase in the corrosion potential was observed. This increase in the corrosion current without a change in the corrosion potential was due to an increase in the anodic and cathodic reaction rates in an equally proportional manner. Because both systems are primarily under charge transfer controlled kinetics, it is unlikely that the large increase in the limiting current has an influence on the corrosion current and corrosion potential.

When 0.1 mbar of  $H_2S$  is present in the system, Figure 3 showed that it caused a large retardation of both the anodic and cathodic reaction as opposed to a system without  $H_2S$  present. In this significantly retarded system, it is under charge transfer controlled kinetics, meaning that 1000ppm of free acetic acid will buffer the surface pH as  $H^+$  is reduced, but it will not have any influence on the corrosion current because the system is not under mass transfer controlled kinetics. Yet, an increase in the corrosion current is still observed. If the increase in the corrosion current was only due to the increase in the anodic reaction rate, then a negative shift in the corrosion potential would have been observed, but this is not the case. Considering this observation, an increase in the rate of the cathodic reaction seems to have occurred due to the addition of acetic acid, but this could have been due to some complex interaction that was not studied further in this research. Due to this outstanding case, a further analysis of this phenomenon must be conducted to confidently determine whether acetic acid follows the buffering effect mechanism in this condition.



Figure 9. The influence of 1000 ppm of free acetic with 0.1 mbar of H<sub>2</sub>S at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas

Finally, 1000 ppm of free acetic acid was added to a system with 10 mbar H<sub>2</sub>S present. The potentiodynamic sweep from this set of experiments can be seen in Figure 10. The addition of 1000 ppm of free acetic acid had no significant influence on the corrosion current nor the anodic or cathodic reaction rate near the corrosion potential. The addition of the acetic acid did significantly increase the limiting current, but because both systems are primarily under charge transfer controlled kinetics, it is unlikely that corrosion current and corrosion potential were influenced. The appearance of two limiting currents is no longer visible when 1000 ppm of free acetic acid is present due to it becoming the main buffering species as noted in the discussion of Figure 5. The system is no longer in a significantly retarded environment, so the presence of the acetic acid no longer will increase the rate of the cathodic reaction near the corrosion potential as was seen

previously. Thus, it is concluded that in this condition, acetic acid will follow the buffering effect mechanism.



Figure 10. The influence of 1000 ppm of free acetic with 10 mbar of H<sub>2</sub>S at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas

A summary of the LPR corrosion rates for all  $H_2S$  environments that were tested is plotted in Figure 11. This figure illustrates that 1000 ppm of free acetic acid will only significantly influence the corrosion rate when 0.1 mbar of  $H_2S$  is present. The increase in the corrosion rate can be explained by the increase in the anodic and cathodic reaction rate seen in the potentiodynamic sweeps in Figure 9. This is where the system is at somewhat of a maximum retardation caused by the presence of  $H_2S$ . This means that the thin mackinawite layer that is formed in these conditions is most protective at 0.1 mbar of  $H_2S$ for all the pH<sub>2</sub>S values that were tested. For all conditions that were tested without the presence of acetic acid, the presence of  $H_2S$  significantly retarded the corrosion rate as compared to a system with no  $H_2S$  present where a maximum retardation was seen around 0.1 mbar of  $H_2S$ . This is consistent with the potentiodynamic sweeps collected in this study as well as in the literature.<sup>27,32,49</sup>



Figure 11. LPR corrosion rates for experiments conducted with 0 – 10 mbar of H<sub>2</sub>S and 0 & 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas

### **3.4 Conclusions**

When  $H_2S$  is added to a system at 30 °C and pH 4.0, a significant retardation of the corrosion rate will be observed up to 10 mbar of  $H_2S$  as compared to a system with no  $H_2S$  present. This is due to the formation of a thin mackinawite layer that is known to form in these conditions. The retardation is a result of the decrease in the rate of the anodic and cathodic reaction rate. A maximum retardation was observed at 0.1 mbar of  $H_2S$  where the thin mackinawite layer was the most protective. The presence of  $H_2S$  also significantly

retarded the rate of the water reduction reaction. This happened regardless of whether acetic acid was present or not. The retardation of the water reduction reaction was not found to be influenced by the amount of H<sub>2</sub>S present.

When glacial acetic acid was added to the system to aceive1000 ppm of free acetic acid at 30 °C and pH 4.0, it only had a significant influence on the corrosion rate at 0.1 mbar of H<sub>2</sub>S where the retardation of the system from H<sub>2</sub>S was at its highest. This was possibly due to acetic acid accelerating the rate of both the anodic and cathodic reactions. At every other pH<sub>2</sub>S that was tested, 1000 ppm of free acetic acid had no significant influence on the rate of the cathodic reaction, only influencing the rate of the anodic reaction. Because of this, the data collected further supports that acetic acid will follow the buffering effect mechanism in all tested conditions where the tests completed with 0.1 mbar of H<sub>2</sub>S require further investigation as to whether the buffering effect mechanism is still followed.

Revisiting the hypothesis stated in section 3.1 Research Hypothesis and Questions, acetic acid was found to only increase the limiting current associated with the cathodic reaction when 0.05 and 10 mbar of H<sub>2</sub>S was present. Because of this, the hypothesis was accepted in these conditions. Experiments conducted with 0.1 mbar of H<sub>2</sub>S observed a possible increase in the cathodic reaction rate which does not exactly coincide with observations indicative of acetic acid following the buffering effect mechanism.<sup>26</sup> For that reason, the hypotheses could not be confidently tested in this condition. In addition to this, at every pH<sub>2</sub>S that was tested, 1000 ppm of free acetic acid significantly increased the

limiting current of the system where because of its abundance, it became the dominating buffering species.

# Chapter 4. Mechanistic Study of H<sub>2</sub>S/CO<sub>2</sub> Corrosion of Mild Steel

### 4.1 Research Hypothesis and Questions

In this section, a thorough review of the  $H_2S$ ,  $CO_2$ , and acetic acid literature has been undertaken where gaps in the current understanding of the corrosion mechanisms involved have been identified. Research hypotheses and questions have been proposed in order to fill the identified knowledge gaps in the literature. The proposed research hypothesis is as follows:

• Like in CO<sub>2</sub> environments, acetic acid in H<sub>2</sub>S/CO<sub>2</sub> mixed environments will retard the anodic dissolution rate at low temperatures.

The proposed research questions are as followed:

- Considering that acetic acid follows the buffering effect mechanism in strong acid and CO<sub>2</sub> environments, will the same be true in a H<sub>2</sub>S/CO<sub>2</sub> mixed environment?
- How do the following environmental parameters influence the anodic and cathodic reactions in H<sub>2</sub>S/CO<sub>2</sub> mixed environments?
  - Free acetic acid concentration
  - Bulk solution pH
  - Temperature
  - Mass transfer coefficient (RDE rotation rate)

From these hypotheses and research questions, a test matrix was developed with the purpose of their testing and investigation.

### 4.2 Experimental Methodology

#### 4.2.1 Equipment

The test apparatus, electrochemical equipment, and sample material that was used for the N<sub>2</sub> sparged H<sub>2</sub>S experiments were also used for the CO<sub>2</sub> sparged H<sub>2</sub>S/CO<sub>2</sub> mixed system experiments. Because of this, specific details of the equipment used can be found in section 3.2.1 Equipment. H<sub>2</sub>S at partial pressures between 0.1 and 10 mbar was used in these experiments so precautions were taken to ensure that the research is completed in a safe manner. The relevant H<sub>2</sub>S health and safety information can be found in section 3.2.2 H<sub>2</sub>S Health and Safety Information.

#### 4.2.2 Test Matrix

The environmental conditions for these experiments were chosen to ensure that the formation of an outer iron carbonate or iron sulfide layer is highly unlikely so that the bare steel corrosion mechanisms can be studied with clarity. Test matrix 1 shown in Table 9 was developed to test the proposed hypothesis and research questions. The hypothesis that pertains to whether acetic acid will retard the rate of the anodic reaction in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment was tested at 30 °C, pH 4.0, and 0.1 & 10 mbar of H<sub>2</sub>S with a 1000 rpm RDE. The free acetic acid concentration was increased to 100 and 1000 ppm while keeping all other environmental factors constant, this facilitated isolating its influence on the anodic reaction. The first research question pertaining to whether acetic acid will follow the buffering effect mechanism was addressed in the same manner as stated for testing the hypothesis. The free acetic acid concentration was increased to 100 and 1000 ppm while keeping all other environmental conditions constant to isolate its influence on the cathodic

reaction. The second research question was addressed one at a time by varying the free acetic acid concentration, bulk solution pH, temperature, and mass transfer coefficient *via* the RDE rotation rate where the baseline condition was defined to be 0 ppm of free acetic acid, 0.1 mbar of  $H_2S$ , pH 4.0, 30°C, and a 1000 rpm RDE.

For example, when investigating the influence of temperature, all other environmental parameters will remain at their baseline value. Therefore, the test was completed at pH 4.0 with 0 ppm of free acetic acid, 0.1 mbar of H<sub>2</sub>S, and a 1000 rpm RDE while the temperature was changed from 30 to 50 °C. This was done for each respective acetic acid concentration as defined in Table 9 below. LPR corrosion rates and potentiodynamic sweeps were collected for each experiment that was conducted. All experiments from this test matrix were completed at least twice in order to validate the repeatability of the procedure and results.

Experimental Conditions	
Temperature	30, 50 °C
рН	4.0
[HAc]free	0, 100, 1000 $ppm_m$ / 0, 1.67, 16.7 mM
WE	X65 RDE
Electrolyte	1 wt.% NaCl
<b>Total Pressure</b>	1 bar
<b>RDE Rotation Velocity</b>	500, 1000, 2000 rpm
Sparge Gas	0, 0.1 mbar / 0, 100 ppm <sub>v</sub> H <sub>2</sub> S in CO <sub>2</sub>
Exposure Time	2 hours
Analytical Techniques	LPR, EIS, Potentiodynamic Sweeps

Table 9. Text matrix for investigating corrosion mechanisms for H<sub>2</sub>S/CO<sub>2</sub> corrosion in the presence of acetic acid

# 4.2.3 Procedure

The experimental procedure that was used for these sets of experiments was identical to the procedure defined in section 3.2.4 Procedure. The only change that was made to the procedure from the previous chapter was that CO<sub>2</sub> was used as a sparge gas rather than N<sub>2</sub>. Because of this, a detailed procedure to these sets of experiments can be found in section 3.2.4 Procedure.

#### 4.3 Results and Discussion

#### 4.3.1 Influence of H<sub>2</sub>S Partial Pressure

In this section, the partial pressure of  $H_2S$  was varied between 0 and 10 mbar at 30 °C and pH 4.0 in the presence of 100 and 1000 ppm of free acetic acid, as well as its absence, in order to investigate how changing the  $H_2S$  partial pressure (pH<sub>2</sub>S) will influence the corrosion mechanisms involved. Just as stated in the previous section, the corrosion potential and corrosion current measured using the LPR method were collected for each experiment and plotted on the Evans diagram along with the corresponding potentiodynamic sweep. These points are represented by a triangle that is colored the same as its corresponding potentiodynamic sweep.

The first set of potentiodynamic sweeps can be seen in Figure 12 where the  $pH_2S$  was varied in an environment where acetic acid was not present. When 0.1 mbar of  $H_2S$  was added to the system, there was a significant retardation of the anodic and cathodic reaction rate in an equally proportional manner that resulted in a retardation of the corrosion current with no significant change in the corrosion potential. This is similar to what was observed in a pure  $H_2S$  environment where the cause of the retardation of the corrosion

current is due to a thin mackinawite layer that will form relatively quickly in this environment.<sup>27,31–33,35,49</sup>

As discussed previously, this mackinawite layer is much too thin to act as a diffusion barrier, but it is postulated that the adsorption of the sulfide species will prevent the dissolution of iron and block active sites for the reduction of  $H^+$  reaction thus decreasing the overall observed corrosion rate.<sup>27,35</sup> A significant retardation of the H<sub>2</sub>O reduction reaction is also observed which is expected when any amount of H<sub>2</sub>S is present in a system.<sup>26–29</sup> Because 0.1 mbar of H<sub>2</sub>S is a relatively low concentration of H<sub>2</sub>S, it is not expected to have a significant influence on the limiting current in these conditions.<sup>27,28</sup> It can be seen that this is also the case in this set of experiments, there is simply not enough H<sub>2</sub>S dissolved in the aqueous phase to be able to buffer the pH at the surface of the metal.

Increasing the pH<sub>2</sub>S to 10 mbar, an increase in the corrosion current and a negative shift in the corrosion potential was observed. This was a result of a significant increase in the rate of the anodic reaction without much influence on the rate of the cathodic reaction. The acceleration that was observed in the anodic reaction caused an increase in the corrosion current. In addition to this, the presence of two limiting currents were visible in the cathodic reaction. The first limiting current corresponds to the H<sup>+</sup> mass transfer limitation that appears when the H<sup>+</sup> concentration becomes depleted on the surface of the steel, and the second limiting current corresponds to the buffering capability of H<sub>2</sub>S. As the surface pH approaches the pK<sub>a</sub> of H<sub>2</sub>S (around pH 7) at higher negative overpotentials, the dissociation of H<sub>2</sub>S becomes more favorable and will then buffer the surface pH, thus the presence of a second mass transfer limiting current.<sup>26</sup>



Figure 12. The influence of 0, 0.1, and 10 mbar of H<sub>2</sub>S in a H<sub>2</sub>S/CO<sub>2</sub> gas mixture at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

In the next set of experiments, the  $pH_2S$  was varied between 0 and 10 mbar with 100 ppm of free acetic acid present in the system where the resulting sweeps can be seen in Figure 13. Much like what was observed in the system with no acetic acid present, when 0.1 mbar of  $H_2S$  was added, there was a significant retardation of the corrosion rate. This was caused by a significant retardation of the cathodic reaction rate as well as a slight retardation of the anodic reaction rate. There was a negative shift in the corrosion potential due to the retardation of the cathodic reaction being more substantial than the anodic reaction. As seen before, there was also a retardation of the  $H_2O$  reduction reaction as well as no significant influence on the limiting current, which is expected with such low partial pressures of  $H_2S$ .

When the pH<sub>2</sub>S was increased to 10 mbar, similar to what was observed previously, there was a further retardation of the cathodic reaction followed by an acceleration of the anodic reaction rate that overall resulted in an increase in the corrosion current. With 100 ppm of free acetic acid, an increase in the limiting current was seen despite there not being any obvious double wave in the cathodic reaction. This could have been due to the nature of the experiment itself. Polarizing this system to the high negative overpotentials that are required to study the limiting current region of the cathodic reaction will force the reduction of H<sup>+</sup> reaction to proceed at a high rate. This will produce a substantial amount of H<sub>2</sub> gas that will accumulate on the surface of the sample because of the laminar flow regime at the RDE tip. This does not influence the validity of data that is collected, but it will cause the data to appear noisy as compared to data that is collected that does not require applying a high negative overpotential. Nevertheless, an increase in the limiting current was observed and is likely due to the double wave phenomenon.



Figure 13. The influence of 0, 0.1, and 10 mbar of H<sub>2</sub>S in a H<sub>2</sub>S/CO<sub>2</sub> gas mixture with 100 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

This observation can be validated by calculating the aqueous concentration of the involved weak acid species with 10 mbar of  $H_2S$  and 100 ppm of free acetic acid. The aqueous concentrations of the weak acid species were calculated in the same way as they were in Figure 5 with the addition of reaction equations (4) and (6) - (8) because of the presence of CO<sub>2</sub> gas in this system. The concentration of  $H_2CO_3$  was fixed with the partial pressure of the sparge gas (CO<sub>2</sub>) and dissolved CO<sub>2</sub> and not a function of pH. The total amount of acetic acid that was present in the aqueous phase in order to achieve a concentration of 100 ppm of free acetic acid at pH 4.0 was 118 ppm. The species concentrations as a function of bulk pH can be seen in Figure 14. At pH 4.0, the ratio of free acetic acid to dissolved H<sub>2</sub>S is 1.92:1 which is much closer than what has been seen previously when 1000 ppm of free acetic acid was present. This means that in this

environment, acetic acid has not become the dominating buffering species and  $H_2S$  is still able to contribute to the buffering involved in the cathodic reaction.



Figure 14. Water chemistry calculation of the aqueous species concentration over a range of bulk pH values with 10 mbar of H<sub>2</sub>S in a H<sub>2</sub>S/CO<sub>2</sub> gas mixture and 118 ppm of total acetic acid in a 30 °C, 1 bar total pressure, and 0.96 bar of CO<sub>2</sub>.

The concentration of free acetic acid was then increased to 1000 ppm where the pH<sub>2</sub>S was held at 0, 0.1, and 10 mbar. The potentiodynamic sweeps shown in Figure 15 can provide insight on what happens when the pH<sub>2</sub>S is changed. When 0.1 mbar of H<sub>2</sub>S was introduced to the system, a retardation of the cathodic reaction could be seen but the anodic reaction remained relatively unaffected. This resulted in a decrease in the corrosion current and a negative shift in the corrosion potential. This is slightly different than what has been observed in the previous two sets of experiments. Upon increasing the pH<sub>2</sub>S to

10 mbar, the system exhibited similar behavior near the corrosion potential where it caused a further decrease in the cathodic reaction rate and an acceleration of the anodic reaction rate that overall resulted in an increase in the corrosion current and a further negative shift in the corrosion potential.



Figure 15. The influence of 0, 0.1, and 10 mbar of H<sub>2</sub>S in a H<sub>2</sub>S/CO<sub>2</sub> gas mixture with 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

Now that 1000 ppm of free acetic acid is present in the system, partial pressures of  $H_2S$  up to 10 mbar has no significant influence on the limiting current in the cathodic reaction. This was also observed in section 3.3.1 Influence of  $H_2S$  Partial Pressure and was found to be because of the abundance of free acetic acid that is present at pH 4.0 compared to the dissolved  $H_2S$  concentration. To validate this finding in a mixed  $H_2S/CO_2$  environment, the aqueous weak acid species concentration was calculated as a function of

bulk pH for a system with 10 mbar of H<sub>2</sub>S, 1000 ppm of free acetic acid at pH 4.0, and CO<sub>2</sub> as a sparge gas. The total amount of acetic acid that was present in the aqueous phase to achieve a concentration of 1000 ppm of free acetic acid at pH 4.0 was 1175 ppm. Looking at Figure 16 in a pH 4.0 environment, the ratio of free acetic acid to dissolved H<sub>2</sub>S and H<sub>2</sub>CO<sub>3</sub> is 19.3:1 and 241:1, respectively. This confirms that at pH 4.0, acetic acid is the most abundant and will be the dominate buffering species when determining the value of the limiting current.



Figure 16. Water chemistry calculation of the aqueous species concentration over a range of bulk pH values with 10 mbar of H<sub>2</sub>S in a H<sub>2</sub>S/CO<sub>2</sub> gas mixture and 1175 ppm of total acetic acid in a 30 °C, 1 bar total pressure, and 0.96 bar of CO<sub>2</sub>.

# 4.3.2 Influence of Free Acetic Acid Concentration

This next set of experiments shown in Figure 17 involves varying the free acetic acid concentration at 30 °C and pH 4.0 with partial pressures of H<sub>2</sub>S between 0 and 10 mbar. When 100 ppm of free acetic acid was added to the system, a large increase in the mass transfer limiting current accompanied by a retardation of the anodic reaction rate is observed. As a result, there is a positive shift in the corrosion potential and a decrease in the overall corrosion current. Further increasing the free acetic acid concentration to 1000 ppm, the mass transfer limiting current continued to be increased along with a more significant retardation of the anodic reaction. Just as before, this caused a further positive shift in the corrosion potential and a decrease in the overall corrosion current. The increase of the limiting current occurs due to the availability of undissociated acetic acid that is free to dissociate in order to buffer the surface pH, providing additional H<sup>+</sup> ions to the surface of the metal to be consumed by the cathodic reaction. The retardation has been attributed to the ability of HAc to adsorb onto the surface of the metal and inhibit the anodic charge transfer rates.<sup>4</sup> This retardation of the anodic reaction is consistent with the literature for low temperature and constant pH environments.<sup>42,43,48</sup>



Figure 17. The influence of 0, 100, and 1000 ppm of free acetic acid with 0 mbar of H<sub>2</sub>S the presence of CO<sub>2</sub> at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

Because the baseline condition without the presence of acetic acid is under mixed mass transfer/charge transfer controlled kinetics, it makes it difficult to study the charge transfer region of the cathodic reaction. Because of this, other means such as modeling are used to help evaluate this region. Just as was performed in section 3.3 Results and Discussion where the baseline strong acid condition was under mixed mass transfer/charge transfer controlled kinetics, a theoretical potentiodynamic sweep was created that assumes that acetic acid follows the buffering effect mechanism. This theoretical potentiodynamic sweep can be seen in Figure 18.

The model simulates a system where a substantial amount of free acetic acid causes the system to transition from mixed mass transfer/charge transfer controlled kinetics to fully charge transfer controlled kinetics with a substantial retardation of the anodic reaction in a constant pH environment. What is shown is the total anodic and total cathodic current for each situation where the intersection of the respective net currents signifies where the corrosion potential and corrosion current is located. The theoretical potentiodynamic sweep exemplifies a significant positive shift in the corrosion potential and a decrease in the corrosion current which further validates the observations made in the experimental data and supports the conclusions seen in literature that acetic acid will follow the buffering effect mechanism while also retarding the anodic reaction in these conditions.<sup>42,43,48</sup>



Current Density (A/m<sup>2</sup>)

Figure 18. An illustration of a hypothetical potentiodynamic sweep assuming the buffering effect mechanism for acetic acid (HAc) is followed where a substantial amount of HAc is added to a system that causes a transition from mixed charge transfer controlled/mass transfer controlled kinetics to fully charge transfer controlled kinetics accompanied by a substantial retardation of the anodic reaction in a constant pH environment.

The next set of experiments, data for which is plotted in Figure 19, involves varying the free acetic acid concentration with 0.1 mbar of H<sub>2</sub>S. When 100 ppm of free acetic acid is added to the system, as expected, a large increase in the mass transfer limiting current is observed, but 100 ppm of free acetic acid had no significant influence on the rate of the anodic reaction. Further increasing the free acetic acid concentration to 1000 ppm, an increase in the mass transfer limiting current was observed but, once again, 1000 ppm of free acetic acid had no significant influence on the rate of the anodic reaction rate remained unaffected by the concentration of free acetic acid which was different than that observed when adding 100 and 1000 ppm of free acetic acid in a pure CO<sub>2</sub> corrosion environment. As a result, there was a small increase in the corrosion current as the free acetic acid concentration was increased due to the transition from mixed charge transfer/mass transfer to fully charge transfer reaction kinetics without much change in the anodic reaction rate.

The reason behind the anodic reaction rate remaining unaffected by changes in the free acetic acid concentration when 0.1 mbar of H<sub>2</sub>S was present could be due to the formation of the thin mackinawite layer that is known to form in these conditions.<sup>27,28,35</sup> This thin layer could be interfering with the adsorption process of acetic acid that will happen at these low temperatures.<sup>48</sup> Examining the charge transfer controlled region of the cathodic sweep, it can be seen that there is no significant acceleration or retardation of the cathodic reaction rate; consistent with previous research that concluded HAc to not be an electroactive species, thus likely following the buffering effect mechanism in these

conditions.<sup>51,52</sup> This can be further validated by the very small increase in the corrosion current as the free acetic acid concentration is increased.



Figure 19. The influence of 0, 100, and 1000 ppm of free acetic acid with 0.1 a mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

Finally, 100 and 1000 ppm of free acetic acid is added to a system in the presence of 10 mbar of H<sub>2</sub>S. Figure 20 shows the resulting potentiodynamic sweeps. The addition of 100 and 1000 ppm of free acetic acid had no significant influence on the rate of the anodic reaction which is parallel to what was observed with 0.1 mbar of H<sub>2</sub>S present. Studying the cathodic reaction, 100 and 1000 ppm of free acetic acid had a significant influence on the limiting current but because the system was primarily controlled by charge transfer controlled kinetics, it had a little to no influence on the corrosion current. The presence of a double wave in the cathodic reaction becomes less apparent when 100 ppm of free acetic acid is added, then nonexistent when 1000 ppm of free acetic acid is added. This is because at this high of a free acetic acid concentration, it becomes the main buffering species near the surface of the metal thus the main contributor to the magnitude of the limiting current.

The reason for the rate of the anodic reaction remaining unaffected by the presence of acetic acid with 10 mbar of H<sub>2</sub>S could be due to the same reason as discussed in the 0.1 mbar of H<sub>2</sub>S environment. At these conditions, a thin mackinawite layer is known to form and become protective of the surface from further corrosion.<sup>27,28,35</sup> Because of the formation of this layer at a relatively fast rate, it could possibly be interfering with the adsorption process of acetic acid onto the surface of the metal that is also known to occur in these conditions.<sup>48</sup> Once again, studying the charge transfer region of the cathodic reaction, there is no significant acceleration or retardation of the cathodic reaction rate. This can be confirmed from the lack of change in the corrosion current when the free acetic acid concentration is increased. From this, it can be concluded that in these conditions, acetic acid contributes to the cathodic reaction *via* the buffering effect mechanism and not by direct reduction.



Figure 20. The influence of 0, 100, and 1000 ppm of free acetic acid with a 10 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

To summarize the observations made in the first two sections of this chapter, the corrosion rates determined *via* LPR were plotted for each environment that was tested. This plot can be seen in Figure 21. The observations from these sets of experiments can be summarized by three conclusions that are able to be deduced from this figure.

The first conclusion is that without the presence of  $H_2S$ , increasing the free acetic acid concentration up to 1000 ppm will cause a decrease in the corrosion rate due to the retardation of the anodic reaction caused by acetic acid adsorption. When  $H_2S$  is present in the system, the corrosion rate will increase when increasing the free acetic acid concentration up to 1000 ppm because acetic acid no longer retards the anodic reaction. There is rather an increase in the corrosion rate due to the transition to fully charge transfer controlled kinetics resulting from the large increase in the limiting current. The second conclusion can be made by studying the magnitude of the corrosion rate with and without the presence  $H_2S$ . When  $H_2S$  is added to the system, a significant retardation of the corrosion rate is observed. This happens regardless of whether acetic acid is present or not. This was explained by a thin mackinawite layer that forms on the surface of the metal that retards the rate of the anodic and cathodic reaction when up to 10 mbar of  $H_2S$  is present.

The third conclusion can be made by again studying the magnitude of the corrosion rate for each partial pressure of H<sub>2</sub>S that was tested. Irrespective of the presence of acetic acid, there is a significant decrease in the corrosion rate when 0.1 mbar of H<sub>2</sub>S is added to the system, then an increase in the corrosion rate when increasing it further to 10 mbar of H<sub>2</sub>S. This was found to be due to a retardation of both the anodic and cathodic reaction rate when 0.1 mbar of H<sub>2</sub>S was added, then an increase in the anodic reaction rate when 10 mbar of H<sub>2</sub>S was added that resulted in an overall increase in the corrosion rate.



Figure 21. LPR corrosion rates for experiments conducted with a 0 – 10 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture and 0 & 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

# 4.3.3 Influence of pH

In a system with 0.1 mbar of  $H_2S$ , the pH was increased from pH 4.0 to pH 5.0 while keeping the temperature and mass transfer conditions constant at 30 °C and 1000 rpm RDE with each 0, 100, and 1000 ppm concentrations of free acetic acid to investigate how the bulk pH would influence the involved mechanisms. The potentiodynamic sweep collected with 0 ppm of acetic acid present can be seen in Figure 22. A significant decrease in the cathodic reaction rate as well as a less apparent limiting current was observed at pH 5.0. This is due to less H<sup>+</sup> being available to be reduced on the surface of the steel, thus decreasing the rate of the cathodic reaction combined with the H<sub>2</sub>O reduction reaction becoming the more dominant cathodic reaction at higher pH values. The anodic reaction
showed an increase in the anodic Tafel slope ( $\beta_a$ ) near the corrosion potential from the value found commonly found in literature of 40 mV/decade to about 60 mV/decade. This increase in the anodic Tafel slope has been previously reported in the literature and is said to be due to the anodic reaction mechanism no longer being within the active dissolution range near the corrosion potential.<sup>48,53,54</sup> Overall this resulted in a decrease in the corrosion current.



Figure 22. The influence of pH with 0 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture at pH 4.0 and 5.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

The same set of experiments was conducted with 100 ppm of free acetic acid. The resulting potentiodynamic sweeps can be seen in Figure 23. Increasing the pH to 5.0 resulted in a significant decrease in the rate of the cathodic reaction followed by a decrease

in the limiting current that resulted in an overall decrease in the corrosion current and corrosion potential. This is again a result of there being less  $H^+$  available to be reduced on the surface of the steel. In this set of experiments, there is still a very apparent limiting current at pH 5.0 which is likely due to the free acetic acid replenishing the  $H^+$  as it is consumed in the cathodic reaction. With the addition of 100 ppm of free acetic acid, the anodic Tafel slope was calculated at pH 4.0 and pH 5.0 and no significant difference was found between the two slopes. The slope close to the literature value of 40 mV/decade.<sup>53</sup>



Figure 23. The influence of pH with 100 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture at pH 4.0 and 5.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

The final set of experiments shown in Figure 24 were conducted by changing the pH from pH 4.0 to pH 5.0 with 1000 ppm of free acetic acid in the same environmental conditions as before. Increasing the pH to 5.0 influenced the involved mechanisms in a

similar manner as was observed with 100 ppm of free acetic acid. There was a significant decrease of the cathodic reaction rate and limiting current that resulted in an overall decrease in the corrosion current and corrosion potential. The anodic Tafel slopes were calculated for the experiment completed at pH 4.0 and pH 5.0 and was found to be close to 40 mV/decade for both reactions signifying that the increase in pH had no influence on the anodic Tafel slope.



Figure 24. The influence of pH with 1000 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture at pH 4.0 and 5.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

## 4.3.4 Influence of Temperature

In a system containing 0.1 mbar of  $H_2S$ , the temperature was varied at 30 and 50 °C while keeping the pH and mass transfer conditions constant at 4.0 and a 1000 rpm RDE with each 0, 100, and 1000 ppm of free acetic acid. It should be noted that when the

temperature is increased, the partial pressure of  $CO_2$  will decrease from 0.96 to 0.88 bar due to the increase in vapor pressure of water. For these sets of experiments, the partial pressure of  $CO_2$  was not held constant so the concentration of  $H_2CO_3$  in the aqueous phase will decrease with increasing temperature. At 30 °C, there is 27.0 mmol of  $H_2CO_3$  in the aqueous phase which decreased to 17.8 mmol when the temperature was increased to 50 °C.

The first set of experiments shown in Figure 25 was conducted with 0 ppm of free acetic acid. When the temperature was increased to 50 °C, an increase in the anodic and cathodic reaction rate as well as the overall corrosion current was observed. This is expected due to the acceleration of the reaction kinetics when temperature is increased. The acceleration of the reaction kinetics overshadows any influence that may be observed due to the decrease in  $H_2CO_3$  concentration.



Figure 25. The influence of temperature with 0 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of CO<sub>2</sub>.

The next set of experiments studying the influence of temperature is shown in Figure 26 and was done with 100 ppm of free acetic acid present in the system. When the temperature was increased to 50 °C, the rate of both the anodic and cathodic reaction increased as well as the overall corrosion current. The increase in the reaction kinetics is more pronounced in the 100 ppm of free acetic acid experiments than for the set completed without the presence of acetic acid. Just as before, the increase in reaction rate kinetics overshadows any influence that may have resulted from the decreased concentration of  $H_2CO_3$  in the bulk solution.



Figure 26. The influence of temperature with 100 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of CO<sub>2</sub>.

The last set of experiments investigating the influence of temperature are shown in Figure 27 and were completed with 1000 ppm of free acetic acid. Once again, when the temperature was increased to 50 °C, the rate of both the anodic and cathodic reaction was increased which caused the overall corrosion current to increase as well. This again was due to how chemical reaction kinetics are accelerated when temperature is increased. It can also be seen that the increase in reaction rate kinetics overshadows any influence that the decreased concentration of  $H_2CO_3$  may have on the system.



Figure 27. The influence of temperature with 1000 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of CO<sub>2</sub>.

## 4.3.5 Influence of the Mass Transfer Coefficient

In a system containing 0.1 mbar of H<sub>2</sub>S, the mass transfer coefficient ( $k_{RDE}$ ) was varied while keeping the temperature and pH constant at 30 °C and pH 4.0 each containing 0, 100, and 1000 ppm of free acetic acid. The mass transfer coefficient was varied by changing the rotation rate of the RDE where the 3 RDE rotation rates used were 500, 1000, and 2000 rpm; corresponding to mass transfer coefficients of  $2.06 \times 10^{-4}$ ,  $2.91 \times 10^{-4}$ , and  $4.12 \times 10^{-4}$  m/s, respectively. The mass transfer coefficient was found using the relationship between the dimensionless Sherwood number, Reynolds number, and Schmidt number for RDE hydrodynamics. These equations and calculation of the mass transfer coefficient *via* the

Dimensionless Sherwood, Reynolds, and Schmidt Number for RDE hydrodynamics. The first set of experiments shown in Figure 28 were completed without the presence of free acetic acid. As the rotation rate increases, a few observations can be made. The limiting current was increased without much influence on the anodic reaction. The corrosion current has a small variation with the increase in the rotation rate, but this is expected due to the system being controlled by mixed charge transfer controlled/mass transfer controlled kinetics.



Figure 28. The influence of the mass transfer coefficient with 0 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture with a 500, 1000, and 2000 rpm RDE at 30 °C, pH 4.0, and 0.96 bar of CO<sub>2</sub>. ( $k_{RDE}$  is equal to 2.06x10<sup>-4</sup>, 2.91x10<sup>-4</sup>, and 4.12x10<sup>-4</sup> m/s, respectively).

The next set of experiments shown in Figure 29 involved changing the rotation rate with 100 ppm of free acetic acid with the same environmental conditions as before. Similar results to the system without acetic acid were expected to be observed in this set of experiments. This is indeed true when looking at how there is an increase in the limiting current without much influence on the anodic reaction when the rotation rate is increased. What appears to be different about this set of experiments is the corrosion currents that were measured. The corrosion current for 2000 rpm was measured to be lower than both the 500 and 1000 rpm corrosion currents which is not the expected result considering the mass transfer coefficient for 2000 rpm is larger than that of 500 and 1000 rpm. This observation was studied further to investigate why this phenomenon occurred.

It was concluded that during the first 3 hours of immersion, the surface is actively changing due to the formation of a thin mackinawite layer. After the 1 hour OCP measurement, the continued formation of the thin mackinawite layer causes a variation of the LPR measurement that is so great such that the measurements seen in the potentiodynamic sweep will fall within each of their own respective standard deviations. This is what is expected due to the fact that this system is under mostly charge transfer controlled kinetics, therefore, the change in the mass transfer coefficient should not have much influence on the corrosion current, which is precisely what was observed.



Figure 29. The influence of the mass transfer coefficient with 100 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture with a 500, 1000, and 2000 rpm RDE at 30 °C, pH 4.0, and 0.96 bar of CO<sub>2</sub>. ( $k_{RDE}$  is equal to 2.06x10<sup>-4</sup>, 2.91x10<sup>-4</sup>, and 4.12x10<sup>-4</sup> *m/s*, respectively).

The last set of mass transfer experiments shown in Figure 30 involved changing the rotation rate with 1000 ppm of free acetic acid in the same environmental parameters as mentioned previously. The results of this set of experiments closely mimics the results of the previous set of experiments with 100 ppm of free acetic acid. When the rotation rate increased, an increase in the limiting current without much influence on the anodic reaction is observed. The corrosion current also does not vary significantly with the increase in the rotation rate due to the system exhibiting fully charge transfer controlled kinetics.



Figure 30. The influence of the mass transfer coefficient with 1000 ppm of free acetic acid and a 0.1 mbar H<sub>2</sub>S/CO<sub>2</sub> gas mixture with a 500, 1000, and 2000 rpm RDE at 30 °C, pH 4.0, and 0.96 bar of CO<sub>2</sub>. ( $k_{RDE}$  is equal to 2.06x10<sup>-4</sup>, 2.91x10<sup>-4</sup>, and 4.12x10<sup>-4</sup> *m/s*, respectively).

## 4.4 Conclusions

In a CO<sub>2</sub> corrosion environment (without the presence of H<sub>2</sub>S) at 30 °C and pH 4.0, increasing the free acetic acid concentration up to 1000 ppm will cause a decrease in the corrosion rate due to the retardation of the anodic reaction that is caused by the adsorption of acetic acid onto the surface of the metal. This is said to happen because the adsorbed acetic acid will interfere with the charge transfer rates associated with the anodic reaction and only occurs in low temperature and low pH environments.<sup>48</sup> When H<sub>2</sub>S is present in the system up to 10 mbar at 30 °C and pH 4.0, the corrosion rate will increase when increasing the free acetic acid concentration up to 1000 ppm because acetic acid no longer

retards the anodic reaction. There is rather an increase in the corrosion rate due to the transition to a fully charge transfer controlled kinetics resulting from the large increase in the limiting current. The lack of retardation from the acetic acid in these conditions could be due to the formation of the thin mackinawite layer that is known to form in these conditions.<sup>27,28,35</sup> This thin layer could be interfering with the adsorption process of acetic acid that will happen at these low temperatures.<sup>48</sup>

Revisiting the hypothesis that was proposed in section 4.1 Research Hypothesis and Questions, its purpose was to investigate whether the anodic reaction would be retarded by the adsorption of acetic acid when  $H_2S$  was present much like it does in  $CO_2$  corrosion. This was found to be false, thus, the hypothesis was rejected. When  $H_2S$  was present up to 10 mbar in the system, acetic acid was found to not retard the rate of the anodic reaction.

Studying the magnitude of the corrosion rates as outlined in Figure 21, it was seen that when  $H_2S$  was introduced into the system up to 10 mbar, a significant retardation of the corrosion rate is observed with the maximum retardation occurring at 0.1 mbar of  $H_2S$ . This trend was seen with every concentration of free acetic acid that was tested. The potentiodynamic sweeps supporting these measured corrosion rates showed that there was a significant retardation of both the anodic and cathodic reaction when 0.1 mbar of  $H_2S$ was introduced. This consequently was the reason behind the decrease in the overall corrosion rate. After increasing the partial pressure of  $H_2S$  to 10 mbar, an acceleration of the anodic reaction was observed and caused an increase in the overall corrosion rate but did not yet reach the corrosion rate measured for CO<sub>2</sub> corrosion. Increasing the bulk pH of the system from pH 4.0 to pH 5.0 at 30 °C with 0.1 mbar of H<sub>2</sub>S caused a decrease in the rate of the cathodic reaction and the limiting current that ultimately led to a decrease in the corrosion current. This was due to less H<sup>+</sup> being available to be reduced on the surface of the steel, thus decreasing the rate of the cathodic reaction. Without the presence of acetic acid, an increase in the pH caused an increase in the Tafel slope. This was found to be typical for this particular system. When 100 and 1000 ppm of free acetic acid was present, the change in Tafel slope was no longer observed when the pH was increased.

Increasing the solution temperature from 30 °C to 50 °C at pH 4.0 with 0.1 mbar of H<sub>2</sub>S caused an increase in the reaction rate of both the anodic and cathodic reaction resulting in an increase in the corrosion current. This is expected to happen because when the temperature is increased, it will in most cases cause an increase the rate of the chemical reaction, or in this case, the electrochemical reaction. This was observed regardless of the free acetic acid concentration up to 1000 ppm.

Increasing the mass transfer coefficient by increasing the RDE rotation rate of a system at 30 °C and pH 4.0 with 0.1 mbar of H<sub>2</sub>S will not have much of an influence on the anodic reaction, but it will increase the limiting current that is observed in the system. Depending on whether the corrosion is flow dependent or not will determine if the corrosion current is expected to increase when the mass transfer coefficient is increased. For this system, when 0 and 100 ppm of free acetic acid was present, the system was under mass transfer controlled/charge transfer controlled kinetics. This means that when the mass transfer coefficient was increased, the corrosion was only slightly flow dependent, so only

a slight variation was seen in the measured corrosion current. When 1000 ppm of free acetic acid was present, the system was now fully controlled by charge transfer controlled kinetics where the flow dependence becomes insignificant. This was why when the mass transfer coefficient was increased, there was no variation in the corrosion current.

# Chapter 5. H<sub>2</sub>S/CO<sub>2</sub> Corrosion Rate Over Time and Surface Analysis Study of Mild

#### Steel

# 5.1 Research Hypothesis and Questions

A thorough review of the literature on how acetic acid influences corrosion rates in  $H_2S/CO_2$  corrosion and the formation of corrosion product layers has been completed where gaps in the current understanding of this subject area have been identified. From these knowledge gaps, a research hypothesis and research questions have been developed in order to fill these identified knowledge gaps. The proposed hypothesis is as follows:

• Acetic acid will increase the steady state corrosion rate in H<sub>2</sub>S/CO<sub>2</sub> mixed environments.

The research questions to be investigated are as follows:

- Will exposing mild steel to a low partial pressure H<sub>2</sub>S environment for an extended period of time allow for a detectable sulfide layer to form?
- Are the experiments conducted previously involving short term testing still valid at longer exposure times when small amounts of H<sub>2</sub>S are present?

A test matrix was developed with the purpose of testing and investigating the hypothesis and research questions proposed above.

## **5.2 Experimental Methodology**

## 5.2.1 Experimental and Analytical Equipment

The test apparatus, electrochemical equipment, and sample material that was used for the N<sub>2</sub> sparged H<sub>2</sub>S experiments and CO<sub>2</sub> sparged H<sub>2</sub>S/CO<sub>2</sub> experiments were also used for this set of prolonged H<sub>2</sub>S/CO<sub>2</sub> corrosion exposure tests. Because of this, specific details of the equipment used can be found in section 3.2.1 Equipment.  $H_2S$  at a partial pressure of 0.1 mbar was used in these experiments so precautions will need to be taken to ensure that the research is completed in a safe manner. The relevant  $H_2S$  health and safety information can be found in section 3.2.2  $H_2S$  Health and Safety Information.

In addition to the electrochemical equipment that collected the LPR corrosion rates over time, surface analysis techniques were used to characterize the surface of the steel after the tests were completed. A scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) analysis capabilities was utilized to characterize the condition and elemental composition of the steel surface. Raman spectroscopy was used to attempt to measure if there was a detectable amount of sulfide species, specifically mackinawite, on the surface of the steel. To ensure that the oxidation of the sulfide layer after removal from the test solution is kept to a minimum, Raman spectroscopy was completed immediately after the experiment was ended. Lastly, profilometry measurements were utilized to characterize the surface roughness and though unlikely, detect any potential localized attacks on the surface of the steel.

### 5.2.2 Test Matrix

This set of experiments is designed to test the proposed hypothesis and investigate whether a detectible sulfide layer will form after 72 hours as well as verify the current short term exposure work at longer exposure times. The test matrix for this set of experiments is outlined in Table 10. These experiments were completed at 30 °C and pH 4.0 with and without the presence of 0.1 mbar of H<sub>2</sub>S (CO<sub>2</sub> and H<sub>2</sub>S/CO<sub>2</sub> Corrosion) where the free acetic acid concentration was varied between 0 and 1000 ppm only for the set of experiments containing 0.1 mbar of  $H_2S$ .

To obtain a sound baseline set of data, the free acetic acid concentration was also varied between 0 and 1000 ppm for the CO<sub>2</sub> experiments, but upon adding 1000 ppm of free acetic acid to the solution, a persistent H<sub>2</sub> bubble would form on the RDE tip as a result of the H<sup>+</sup> reduction reaction. This H<sub>2</sub> bubble that formed made data collection incredibly difficult due to the constant monitoring that is needed for long term exposure experiments. After analyzing all the collected data for this set of experiments, it was determined that the data from CO<sub>2</sub> corrosion with the presence of acetic acid over time was not necessary in thoroughly testing the articulated hypothesis, investigating the formation of a detectable sulfide layer, or verifying the short term exposure work at longer exposure times when 0.1 mbar of H<sub>2</sub>S is present. For that reason, this set of experiments was not completed for a CO<sub>2</sub> corrosion environment with the presence of acetic acid.

Table 10. Text matrix for investigating how acetic acid influences H<sub>2</sub>S/CO<sub>2</sub> corrosion rates over time and if a detectable sulfide layer will form during a prolonged exposure.

Experimental Conditions	
Temperature	30 °C
рН	4.0
[HAc]free	0, 1000 ppm <sub>m</sub> / 0, 16.7 mM
WE	X65 RDE
Electrolyte	1 wt.% NaCl
<b>Total Pressure</b>	1 bar
<b>Rotation Velocity</b>	1000 rpm
Sparge Gas	0, 0.1 mbar / 0, 100 ppm <sub>v</sub> H <sub>2</sub> S in CO <sub>2</sub>
Exposure Time	72 hours
Analytical Techniques	LPR, EIS SEM/EDS, Raman Spectroscopy, Profilometry
	SENTEDS, Ruman Spectroscopy, Promometry

## 5.2.3 Procedure

The experimental procedure pertaining to the preparation of the 1 L glass cell and RDE sample that was used for these sets of experiments was identical to the procedure defined in section 3.2.4 Procedure. The LPR corrosion rates over time were collected by conducting a polarization resistance/corrosion potential ( $R_p/E_c$ ) trend over time where the  $R_p$  and  $E_c$  was measured every hour over the course of a 72 hour period. The WE was polarized  $\pm$  5mV from the open circuit potential (OCP) at a scan rate of 0.125 mV/s. The Tafel constant ("B value") used for the LPR analysis was 13 mV/decade. The  $R_s$  was obtained by EIS so that the LPR measurements could be corrected for the solution resistance accordingly. The EIS measurements were conducted by applying an oscillating potential of  $\pm$ 5 mV around the OCP using a frequency range of 0.2 Hz to 8 kHz.

After the 72 hour experiment was completed, the sample was removed from the test solution, washed with isopropanol and dried, being careful not to damage the surface of the steel sample in the process. The sample was quickly then transferred to the Raman microscope as soon as possible to prevent an excessive amount of oxidation to the possibly formed sulfide layer during the experiments when 0.1 mbar of H<sub>2</sub>S was present. After measurements with the Raman microscope, the sample was then inserted inside of the SEM where pictures were taken of the surface condition. Once a sufficient image was taken, an EDS analysis was completed to measure the elemental composition on the surface of the sample. Before the profilometry scan was completed, any corrosion product that may have formed was removed. After the possible layer was removed, a profilometry scan was completed in order to characterize the surface topography of the sample.

### 5.3 Results and Discussion

#### 5.3.1 CO<sub>2</sub> Corrosion Without the Presence of Acetic Acid

LPR corrosion rates were collected over the course of 72 hours to observe what happened to the corrosion rate over time in a pure CO<sub>2</sub> corrosion environment at pH 4.0 and 30 °C. This plot can be seen in Figure 31. The initial corrosion rate after one hour of OCP measurements in this experiment was 2.29 mm/yr which is consistent with the 2.16  $\pm 0.02$  mm/yr that was obtained during the short term corrosion testing. Over the first 20 hours of immersion, there was a steady decrease in the corrosion potential as the corrosion rate had a spike at hour 4, but overall remained relatively constant. The spike in the corrosion rate was likely due to an H<sub>2</sub> bubble that formed at the end of the RDE within the first 4 hours of testing. The bubble was removed where the corrosion rate then returned to the initial corrosion rate value after 12 hours.

After the first 20 hours, the corrosion rate and corrosion potential steadily increased until the end of the test at 72 hours. This steady increase showed no signs of reaching a steady state value. It is expected that the corrosion rate would continue to increase if the test was conducted for longer exposure times since a protective corrosion product layer is unlikely to form in these conditions. The  $Fe^{2+}$  saturation concentration for the formation of an FeCO<sub>3</sub> layer to be favorable in these conditions was calculated to be 1.80 x10<sup>4</sup> ppm. The  $Fe^{2+}$  concentration was measured after the completion of the experiment and was found to be 5.90 ppm which is much below the saturation concentration.



Figure 31. The corrosion rate measured *via* LPR and the corrosion potential vs. time over a 72 hour exposure period for pure CO<sub>2</sub> corrosion at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

The corrosion rate continued to increase over time after 20 hours because, initially, the sample surface is very smooth being that it is polished to a mirror finish using down to a 0.25  $\mu$ m diamond suspension. The X-65 steel in this study has a ferrite-pearlite microstructure that consists of  $\alpha$ -ferrite and cementite (Fe<sub>3</sub>C).<sup>55</sup> As the sample starts to corrode, the  $\alpha$ -ferrite is consumed in the dissolution of Fe reaction (anodic reaction) where an unreacted cementite skeleton is left behind.<sup>55</sup> This causes the surface roughness and cathodic surface area of the sample to increase which will in turn increase the corrosion rate at a steady rate over time. This is also believed to be the reason behind the large decrease in the corrosion potential during the first 25 hours of the experiment.

The average overall corrosion rate was calculated from the  $Fe^{2+}$  concentration in solution at the end of the experiment and was compared to the average corrosion rate measured during this experiment. The equation used to calculate the weight loss corrosion rate can be seen in equation (13).

$$CR = \frac{K \cdot m_{loss}}{A \cdot t \cdot \rho} \tag{13}^{56}$$

Where *CR* is the corrosion rate in mm/yr, *K* is equal to  $8.76 \times 10^4$  and is the conversion factor so that *CR* is in the units of mm/yr,  $m_{loss}$  is the mass loss in *g*, *A* is the actively corroding surface area in  $cm^2$ , *t* is the total exposure time in *hr*, and  $\rho$  is the density of the metal in  $g/cm^3$ . The measured ppm concentration of Fe<sup>2+</sup> in the 1 L cell was converted to mass of Fe *via* the dissolution of Fe reaction shown in equation (1) to be used as the mass loss in equation (13)<sup>56</sup>. The calculated weight loss corrosion rate was found to be 4.65 mm/yr where the average measured corrosion rate *via* LPR over the 72 hour period was 2.63 mm/yr.

The weight loss corrosion rate was determined to be larger than the measured average corrosion rate, but this could be due to several factors. The Tafel slopes used to calculate the corrosion rate *via* LPR could not be representative of the experimental Tafel slopes, using the  $Fe^{2+}$  concentration rather than the true mass loss of the sample could have introduced inaccuracies to the weight loss concentration calculation, and the calculation of the weight loss corrosion rate only shows the average corrosion rate over a given time period where it can be seen from this experiment that the observed corrosion rate will change over time.

The pH of the solution slightly increased over time from the increase in the  $Fe^{2+}$  concentration as the corrosion reaction proceeded. At hour 31, the pH increased to 4.22 where it was adjusted back to 4.00 with HCl in order to keep the system at a constant pH. The pH was again adjusted at hour 50 from 4.10 to 4.00 with HCl. Both pH adjustments are labeled on the plot to explain the spike in the corrosion rate and corrosion potential at hour 31 and 50. The final pH at hour 72 before the sample was removed from the solution was recorded to be 4.12.

After the 72 hour exposure experiment, an SEM/EDS analysis was completed in order to characterize the sample surface after the corrosion testing was completed. The SEM and EDS analysis can be seen in Figure 32. The surface of the sample showed evidence of uniform corrosion over the entire sample. What is seen on the surface of the steel is a cementite scale that is left behind from the corrosion process where gaps in the cementite scale show the exposed steel substrate. An EDS analysis was completed on the exposed steel substrate and the cementite scale to analyze the elemental composition of the two features that were identified.

The EDS analysis of the steel substrate showed a high amount of Fe with little detection of other alloying elements known to exist in the steel matrix. This EDS analysis is consistent with the literature and further validates that this is indeed the exposed steel matrix underneath the cementite scale that covers the surface of the steel.<sup>55</sup> The EDS analysis of the cementite scale showed that in addition to Fe and C being detected, the scale showed high enrichment of alloying elements such as Mn, Mo, Ni, and Cr that are known to be present in the matrix of the steel. Both of these observations are indicative of a cementite scale and is consistent with what has been observed in the literature.<sup>55</sup>



Figure 32. SEM/EDS surface analysis of an X-65 steel sample after 72 hours of corrosion in a pure CO<sub>2</sub> environment at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub> (a) SEM image of the steel surface after 72 hours of exposure (b) EDS spectrum of the exposed steel substrate (c) EDS spectrum of the residual cementite scale left behind from the corrosion process.

Finally, a three dimensional (3-D) profilometry scan was completed on the surface of the sample after the cementite scale was removed. Because the cementite was not strongly adsorbed to the surface of the steel, no chemical removal of the scale was necessary. The removal of the scale was done with a conventional pencil eraser. The resulting profilometry scan can be seen in Figure 33. The sample was removed from the polytetrafluoroethylene (PTFE) sample holder in the interest of only analyzing the steel sample itself. The 3-D scan of the surface shows a uniform amount of metal loss across the entire surface. A measurement of 5 mm across a cross-section of the surface was done to analyze a two dimensional (2-D) profile of the surface. The cross section that was measured is labeled with a red line drawn across the surface.

The surface appears to be relatively rough compared to the mirror polished surface that was present before any corrosion occurred. An attempt to compare the corroded surface and the mirror polished surface was done, but due to the high reflectiveness of a mirror polished surface and the use of an optical microscope for the profilometry scan, an initial surface profile measurement was not possible. It can be assumed that due to the use of up to a 0.25  $\mu$ m diamond suspension in the polishing process, the surface roughness would have been significantly less than the 5  $\mu$ m surface roughness seen in the 2-D profile measurement.



Figure 33. Profilometry measurement of an X-65 steel sample after 72 hours of corrosion in a pure CO<sub>2</sub> environment at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub> (a) three dimensional scan of the steel surface after 72 hours of exposure (b) two dimensional profile measurement across of the steel surface where the path length is shown by the red line.

There was a slight parabolic nature to the surface of the sample where there was close to an 8  $\mu$ m difference between the edge of the sample and the center of the sample. This was found to be due to the polishing process of the sample. The RDE sample must be polished as flat as possible to ensure that the mass transfer regime is well defined but, in practice, this is very hard to accomplish. Despite the care taken in polishing the RDE sample, the edges can be polished slightly more than the center of the sample due to the sample being polished by hand. Due to the edge to center height difference being only 8  $\mu$ m, it is expected that it does not influence the mass transfer regime nor the corrosion process.

### 5.3.2 H<sub>2</sub>S/CO<sub>2</sub> Corrosion Without the Presence of Acetic Acid

The LPR corrosion rate and corrosion potential over a 72 hour exposure period was collected in the interest of studying the corrosion process over time in an H<sub>2</sub>S/CO<sub>2</sub> mixed environment with 0.1 mbar of H<sub>2</sub>S at pH 4.0 and 30 °C. The data collected can be seen in Figure 34. The initial corrosion potential was recorded immediately after immersion into the test solution where it was monitored over the course of the first hour before any electrochemical measurements were made. There was a large 39 mV increase of the corrosion potential over the course of this time period. This indicated that the surface changes rapidly over the course of the first hour and is likely due to the formation of a thin mackinawite layer. Revisiting research conducted by Lee and Nesic, a rapid change of the R<sub>p</sub> measured *via* EIS was measured only after 20 minutes of immersion. This was found to be because of the rapid coverage of the surface with a thin layer of mackinawite.<sup>35</sup> This is why in the short term experiments as well as the 72 hour exposure experiments, the system was given one hour to become stable enough for accurate electrochemical measurements.

The initial corrosion rate measured after 1 hour of immersion was 0.36 mm/yr which is consistent with the 0.40  $\pm$ 0.00 mm/yr that was obtained during the short term corrosion experiments. The significant decrease in the corrosion rate when compared to pure CO<sub>2</sub> corrosion happens within the first hour of immersion during the rapid formation of the thin mackinawite layer. The change in corrosion rate, corrosion potential, and surface coverage of mackinawite slows down significantly after the first hour. Over the course of the first 25 hours, the corrosion rate steadily decreased to 0.25 mm/yr while the corrosion potential reached a maximum at hour 14 and steadily decreased thereafter. This shows that

the thin mackinawite layer continues to become slightly more protective of the surface over time.

From hour 25 to hour 60, the corrosion rate increased slightly to 0.28 mm/yr where it stayed constant at that value until the test was completed at 72 hours. If the test continued to run past 72 hours, the corrosion rate was not expected to increase much past 0.30 mm/yr signifying that a steady state corrosion rate has been or is close to being reached after 72 hours.



Figure 34. The corrosion rate measured *via* LPR and the corrosion potential vs. time over a 72 hour exposure period for H<sub>2</sub>S/CO<sub>2</sub> corrosion with 0.1 mbar of H<sub>2</sub>S at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

The pH increased slightly over time due to the release of  $Fe^{2+}$  into solution during the anodic reaction but was of much lesser magnitude than the pure CO<sub>2</sub> test due to the significantly lower corrosion rate. At hour 32, the pH was decreased from 4.05 to 4.00 with HCl to keep the pH constant. The final pH recorded before the sample was removed was 4.01. The final Fe<sup>2+</sup> concentration was not recorded, but it was expected to be significantly less than the 5.90 ppm recorded during the pure  $CO_2$  corrosion 72 hour experiment. For this reason, the weight loss corrosion rate could not be compared to the average corrosion rate measured *via* LPR.

After the testing was completed, Raman spectroscopy was used in order to determine whether a detectable mackinawite layer could be found on the surface of the steel. When the Raman spectroscopy was completed, the Raman spectrum showed no peaks indicating that there was not a mackinawite layer that was thick enough to be detected. In addition to that, the possibility of the thin mackinawite layer being oxidized by the laser emitted during the Raman spectroscopy measurement is highly likely making it even more difficult to effectively detect its presence.

An SEM/EDS analysis was completed in order to characterize the surface of the steel after 72 hours of immersion. The SEM image and corresponding EDS spectrum is shown in Figure 35. The SEM image shows a uniform surface without many features. Two small morphological deformations on the left of the image traveling down towards the bottom left corner of the image can still be seen. These are micro scratches on the steel surface left over from polishing signifying that the metal has not undergone a significant amount of corrosion. The thin mackinawite layer that formed significantly decreased the observed corrosion rate thus protecting the surface from excessive amounts of corrosion.

An EDS analysis of the surface shows detection of Fe as well as some other alloying elements known to be present in the steel matrix. Sulfur was also detected by the EDS analysis where it was not detected on the sample that underwent pure CO<sub>2</sub> corrosion. This signifies that there were sulfur species present on the surface of the steel, but the type of sulfur species is unable to be determined with this analytical method. From what is known in literature, the thin sulfide layer that would be expected to have formed is mackinawite. 27,35



Figure 35. SEM/EDS surface analysis of an X-65 steel sample after 72 hours of corrosion in an H<sub>2</sub>S/CO<sub>2</sub> mixed environment with 0.1 mbar of H<sub>2</sub>S at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub> (a) SEM image of the steel surface after 72 hours of exposure (b) EDS spectrum of the corroded surface.

A 3-D profilometry measurement was completed to characterize the topography of the steel surface. Because there was no corrosion product layer other than the undetectable thin sulfide layer, it was deemed acceptable to complete the scan without the removal of any species on the surface of the steel. The sample was again removed from the PTFE sample holder in the interest of only analyzing the steel sample itself. The resulting 3-D scan and supplementary 2-D cross sectional surface measurement can be seen in Figure 36. It can be seen that the 3-D scan shows a uniformly smooth surface that decreases in elevation from the center to the edge of the sample. The 2-D cross-sectional scan that follows the path length indicated by the red line confirms the smoothness of the surface. The average variation in elevation across the surface was about 0.2 µm which is significantly less than the 5  $\mu$ m variation that was seen in pure CO<sub>2</sub> corrosion and coincides with the surface roughness that polishing with a 0.25 diamond suspension would achieve. The surface has a much more noticeable parabolic nature because of the decreased surface roughness where the difference in elevation from the edge to the center of the sample is about 10 µm. This again is due to the process of polishing the RDE samples by hand where it is difficult to ensure a perfectly flat surface. Being that the difference in elevation is only  $10 \,\mu\text{m}$ , it is not expected to influence the mass transfer regime or the corrosion process.



Figure 36. Profilometry measurement of an X-65 steel sample after 72 hours of corrosion in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment with 0.1 mbar of H<sub>2</sub>S at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub> (a) three dimensional scan of the steel surface after 72 hours of exposure (b) two dimensional profile measurement across of the steel surface where the path length is shown by the red line.

### 5.3.3 H<sub>2</sub>S/CO<sub>2</sub> Corrosion in the Presence of Acetic Acid

The LPR corrosion rate in addition to the corrosion potential was measured over a 72 hour immersion period in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at pH 4.0 and 30 °C. For this experiment, glacial acetic acid was added to the test solution to achieve 1000 ppm of free acetic acid in order to study its influence on the corrosion rate over time. The corrosion rate and corrosion potential over time can be seen in Figure 37. Within the first hour of immersion, a large increase of 47 mV was again seen in the OCP. This is due to the rapid formation of a thin mackinawite layer that will still occur when acetic acid is present. After the first hour, the initial corrosion rate was measured to be 0.49 mm/yr which is slightly

lower than the  $0.67 \pm 0.02$  mm/yr that was obtained during the short term corrosion testing. The corrosion rate as well as the corrosion potential steadily decreased until hour 25 where the corrosion rate stabilized at 0.30 as the corrosion potential slowly continued to decrease. The continued decrease in the corrosion rate signifies that the thin mackinawite layer is continuing to form and becoming more protective.

From hour 25 to the end of the test at hour 72, the corrosion rate remained steady with the final corrosion rate at hour 72 being 0.28 mm/yr. Due to such a small change in the corrosion rate over a significant amount of time, the corrosion rate was not expected to significantly change if the testing were to continue. For that reason, it can be said that the system reached or is close to reaching a steady state value.



Figure 37. The corrosion rate measured *via* LPR and the corrosion potential vs. time over a 72 hour exposure period for H<sub>2</sub>S/CO<sub>2</sub> corrosion with 0.1 mbar of H<sub>2</sub>S and 1000 ppm of free acetic acid at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

When comparing the test completed with and without the presence of 1000 ppm of free acetic acid, a few observations can be made. The system with 1000 ppm of free acetic acid had a higher initial corrosion rate than the system without it which is consistent with what was observed in the short term exposure experiments for the same conditions. Both systems were deemed to have almost reached a steady state value after 72 hours of immersion with the final corrosion rate being 0.28 mm/yr for both experiments. This shows that acetic acid will have an influence on the initial corrosion rate that the system will reach. Also, the corrosion rate and corrosion potential over time data with 1000 ppm of free acetic acid was much more stable over the course of the 72 hour immersion than it was without the acetic acid. This could be due to the increased buffering capacity of the bulk solution resulting from the addition of the acetic acid that better mitigates any changes in the pH over time.

Over the course of the 72 hour immersion, there was no significant change in the pH over time. This could have been due to both the low corrosion rate causing only a small amount of  $Fe^{2+}$  to be released into the solution and the increased buffering capacity of the solution as mentioned previously. Because of this, no pH adjustments were needed to be made with 4.01 being the final pH at the end of the test. The  $Fe^{2+}$  concentration at the end of this experiment was measured to be 1.02 ppm where the weight loss corrosion rate was calculated using equation (13)<sup>56</sup>. The weight loss corrosion rate was then compared to the average measured LPR corrosion rate during the experiment. The weight loss corrosion rate was found to be 0.39 mm/yr. Once again, the weight loss corrosion rate was greater than the

average measured LPR corrosion rate for reasons mentioned in section 5.3.1 CO2 Corrosion Without the Presence of Acetic Acid.

After the sample was removed from the test solution, Raman spectroscopy measurements were made in order to determine whether a detectable mackinawite layer had formed on the surface. After the measurement was taken, the Raman spectrum showed no peaks signifying that there was not a layer thick enough to be picked up by the Raman analysis. This shows that whether acetic acid is present, 72 hours is not an ample amount of time for a thick enough mackinawite layer to form and be detectable *via* Raman spectroscopy.

An SEM/EDS analysis was completed in order to better characterize the surface of the corroded sample. The SEM image and EDS spectrum can be seen in Figure 38. The SEM image once again shows a smooth homogeneous surface without many features. Micro scratches from the polishing process can also be seen in the bottom right quadrant of the image traveling from left to right at a downward angle signifying that the surface has not undergone a significant amount if corrosion. Comparing the SEM image from the system with and without the presence of acetic acid, there seems to be no difference between the two images. This means that acetic will not change the condition of the surface after 72 hours of immersion.

An EDS analysis revealed the presence of Fe as well as other alloying elements that are known to be present in the steel matrix. In addition to those elements, sulfur was also detected on the surface signifying that a sulfide species had formed, but the determination of the specific sulfide species could not be done with this analytical method. This was also observed in an environment where no acetic acid was present.



Figure 38. SEM/EDS surface analysis of an X-65 steel sample after 72 hours of corrosion in an H<sub>2</sub>S/CO<sub>2</sub> mixed environment with 0.1 mbar of H<sub>2</sub>S and 1000 ppm of free acetic acid at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub> (a) SEM image of the steel surface after 72 hours of exposure (b) EDS spectrum of the corroded surface.

A 3-D profilometry measurement was completed to characterize the topography of the steel surface. Because there was no corrosion product layer other than the undetectable thin sulfide layer, it was deemed acceptable to complete the scan without the removal of
any species on the surface of the steel. For this scan, the sample was not removed from the PTFE sample holder in order to determine if there had been enough metal loss to create a height difference between the PTFE sample holder's inner edge and the outer edge of the steel sample where the two are in contact with each other. If so, assuming the two edges were initially at the same elevation, a weight loss corrosion rate could be calculated from taking the difference in height and calculating the amount of metal that was lost in solution. The resulting 3-D scan and supplementary 2-D cross sectional surface measurement can be seen in Figure 39.

After the sample was removed from the test solution, the surface was seen to not have experienced a significant amount of corrosion and no detectable corrosion product had formed. This means that the surface was still significantly reflective. The difference in reflectiveness of the steel surface and the PTFE holder made it difficult to collect a complete scan of both materials with the optical microscope. Though this does not influence the accuracy of the scan, it is for this reason why holes in the PTFE scan data can be seen. The exposure was much too dark for the measurement to be made on some of the PTFE surfaces. The edge of the RDE is outlined by the labeled red circle on the 3-D scan.

Studying the 3-D scan of the steel surface and surrounding PTFE sample holder, a smooth homogeneous surface that decreases in elevation from the center to the edges of the sample was observed. This was no different than the analysis that was done without the presence of acetic acid. A 2-D cross sectional measurement of the surface was done while also encompassing the inner edge of the PTFE holder. The blue and black "x" on the 3-D scan denotes where the transition between the sample and PTFE holder is located. Their

location correlates with their respective vertical line on the 2-D cross sectional measurement. The surface profile is found to be very smooth, the variation in elevation along the sample surface stays around 0.2  $\mu$ m. The sample also has a parabolic shape to it which was found to be due to the process of polishing the sample by hand. Being that the difference in elevation is only 11  $\mu$ m, it is not expected to influence the mass transfer regime or the corrosion process.

Looking at the interface between the steel sample and the PTFE holder, there is a significant decrease in the elevation when going from the steel surface to the PTFE holder. This is more apparent on the left (blue) side more so than the right (black) side. This can be explained by the difference in hardness of the two materials. The PTFE is significantly softer than the steel that it is holding, thus, when the RDE sample is being polished as a whole, more PTFE will be removed than there will be steel. The additional removal of PTFE is likely to occur at the fine SiC polishing paper or diamond suspension polishing cloth due to the steel being much harder such that little to no material is removed while the soft PTFE could still be polished away. Because of this observation that was made with the additional PTFE holder material removal and the lack of significant corrosion on the sample to generate enough of an elevation difference at the steel and PTFE interface, a weight loss corrosion rate was not able to be collected during this analysis.



Figure 39. Profilometry measurement of an X-65 steel sample after 72 hours of corrosion in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment with 0.1 mbar of H<sub>2</sub>S and 1000 ppm of free acetic acid at pH 4.0, 30 °C, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub> (a) three dimensional scan of the steel surface after 72 hours of exposure (b) two dimensional profile measurement across of the steel surface where the path length is shown by the red line.

### **5.4 Conclusions**

When the steel sample was exposed to a pure CO<sub>2</sub> corrosion environment at pH 4.0 and 30 °C for 72 hours of total exposure time, the corrosion rate was seen to stay relatively constant over the first 20 hours. After the initial 20 hour period, the corrosion rate continued to increase until the test was completed at 72 hours where it was likely to keep increasing if the test were to persist past 72 hours. This steady increase in corrosion rate was due to the increase in the cathodic surface area as the sample continued to corrode. An SEM/EDS analysis revealed that a cementite scale covered the surface after 72 hour exposure where the steel substrate beneath could be seen in some locations. Finally, after the removal of the cementite scale, a profilometry scan revealed that the surface roughness had increased significantly which further supports the reasoning behind the increase in corrosion rate over time. The sample was also seen to have a slight parabolic nature that was explained by the difficulty of polishing the RDE sample perfectly flat by hand. Despite the parabolic shape, it is not believed to have influenced the mass transfer or corrosion process.

When the steel sample was exposed to a mixed  $H_2S/CO_2$  environment with 0.1 mbar of  $H_2S$  at pH 4.0 and 30 °C during a 72 hour exposure test, the initial hour of the test experienced a very large increase in the corrosion potential that correlates with the rapid formation of a thin mackinawite layer on the surface of the steel. After the initial hour, the corrosion rate steadily decreased during the first 25 hours of the test signifying that the mackinawite layer continued to become protective over time. The corrosion rate then steadily increased until hour 60 where it then remained constant until the end of the test at 72 hours. The Raman spectroscopy was unable to detect the presence of any mackinawite on the surface due to how thin the formed layer was. The SEM/EDS analysis revealed that the sample did not undergo a significant amount of corrosion given that the polishing lines were still visible on the surface. The EDS spectrum detected sulfur on the surface of the steel which provided evidence of the presence of sulfide species, but the specific type could not be determined through this analysis technique. A profilometry scan showed a homogenous surface that was very smooth compared to the test completed in pure  $CO_2$ corrosion further implying that the surface did not undergo a significant amount of corrosion.

The same test was completed with the exception of adding 1000 ppm of free acetic acid to investigate its influence on the system during the course of a 72 hour corrosion test. The initial hour OCP collection still experienced a large increase in the corrosion potential where the thin mackinawite layer was forming rapidly on the surface. The initial corrosion rate was higher than that of the test completed with 0 ppm of free acetic acid which is consistent with the experimental data. The corrosion rate then steadily decreased over time until hour 25 where thereafter, the corrosion rate remained constant until the end of the test at 72 hours. The thin mackinawite layer still continued to become increasingly protective during the first 25 hours of testing. A Raman spectroscopy analysis was still not able to detect any significant amount of mackinawite on the surface due to how thin the layer that formed was. The SEM/EDS analysis yielded similar results to the analysis without the presence of acetic acid. Polishing lines were still visible on the surface and sulfur was detected on the EDS spectrum, but the species of sulfide that was detected was not able to be determined via this method. Finally, the profilometry scan showed a smooth homogeneous surface that was not significantly different from the scan that was completed on the sample that was not exposed to any acetic acid.

Revisiting the hypotheses and research questions stated in section 5.1 Research Hypothesis and Questions, 1000 ppm of free acetic acid was found to not increase the steady state corrosion rates in a mixed  $H_2S/CO_2$  environment at 30 °C and pH 4.0. The final recorded corrosion rate for both experiments was 0.28 mm/yr. For this reason, the proposed hypothesis was rejected for the conditions that were tested. Even after 72 hours of exposure for both experiments containing 0.1 mbar of  $H_2S$ , a Raman spectroscopy

analysis was not able to detect any significant amount of sulfide species namely mackinawite. The EDS spectrum for both experiments did detect sulfur on the surface of the steel, but the specific sulfide species was not able to be determined. The initial corrosion rates after one hour of exposure were consistent with the corrosion rates collected during short term testing. For the purposes of modeling of these systems, which will be completed in the next section, it is assumed that the system being studied is bare steel corrosion. This set of long term experiments confirmed that even after 72 hours of exposure, there is no detectable layer that forms on the surface of the steel therefore validating that the system still exhibits what is considered to be bare steel corrosion at longer exposure times. This means that the short exposure time experiments completed in the potentiodynamic study are valid at longer exposure times as confirmed in the experiments conducted in this section for the conditions that were tested.

# Chapter 6. Electrochemical Modeling of H<sub>2</sub>S and H<sub>2</sub>S/CO<sub>2</sub> Corrosion 6.1 Modeling of H<sub>2</sub>S and H<sub>2</sub>S/CO<sub>2</sub> Corrosion in the Presence of Acetic Acid

# 6.1.1 Introduction and Methodology

In this section, an electrochemical model was created in order to predict the potentiodynamic sweeps and corrosion rates that were collected during the experimental work involved in Chapter 3: Mechanistic Study of H<sub>2</sub>S Corrosion of Mild Steel and Chapter 4. Mechanistic Study of H<sub>2</sub>S/CO<sub>2</sub> Corrosion of Mild Steel. This model was created using the methodology developed by Madani Sani for strong acid, CO<sub>2</sub>, and H<sub>2</sub>S corrosion.<sup>57</sup> In this model, only 3 electrochemical reactions were considered to be relevant in the environmental conditions tested in this study and are outlined in electrochemical equations (1) - (3). This implies that the buffering effect mechanism will be assumed for H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>S, and acetic acid as they are weak acids that only contribute to the electrochemical reactions through donating additional H<sup>+</sup> ions as they are consumed by the H<sup>+</sup> reduction reaction. By doing this, they act as a buffering species for the surface pH as it increases when H<sup>+</sup> is consumed and not as a species that is directly reduced on the surface of the steel.

The model developed by Madani Sani was derived to predict how low and high salt concentrations influence the corrosion process in strong acid, CO<sub>2</sub>, and H<sub>2</sub>S corrosion.<sup>57</sup> This means that the model had to consider the non-idealities that exist in the liquid phase as the salt concentration increased to significant amounts. For this reason, activities of the relevant species were used in this model. Because every system that was tested in this study was assumed to be ideal solutions, due to the relatively low electrolyte concentration, the activities were replaced with the bulk solution concentrations.

All the relevant parameters for the electrochemical model involving strong acid, CO<sub>2</sub>, and H<sub>2</sub>S corrosion were used from the work published by Madani Sani where modifications were made to incorporate the influence of acetic acid on the mechanisms involved.<sup>57</sup> Because the mixed system of H<sub>2</sub>S/CO<sub>2</sub> corrosion was not studied in the published work, new parameters were developed *via* the methodology outlined in the publication in order to develop a model for the mixed system where the influence of acetic acid was also incorporated. The details of the model and the modifications that were made are explained in the following sections. After the methodology is elaborated upon, the electrochemical model will then be compared to the experimental results in order to validate the accuracy of the model.

#### 6.1.2 Hydrogen Ion Reduction Reaction

To establish the effect of charge transfer and mass transfer on the reduction of H<sup>+</sup> reaction, two modes of transfer need to be accounted for. This can be done by calculating the total current density using the following equation:

$$\frac{1}{i_{H^+}} = \frac{1}{i_{\alpha,H^+}} + \frac{1}{i_{lim}} \tag{14}^{54}$$

Where  $i_{H^+}$  is the total current density for the H<sup>+</sup> reduction reaction in  $A/m^2$ ,  $i_{\alpha,H^+}$  is the charge transfer current density in  $A/m^2$ , and  $i_{lim}$  is the mass transfer limiting current density in  $A/m^2$ . The charge transfer current density component can be found using the Tafel equation shown below:

$$i_{\alpha,H^+} = i_{o,H^+} * 10^{-\left(\frac{E - E_{rev}}{\beta_{c,H^+}}\right)}$$
(15)<sup>54</sup>

Where  $i_{\alpha,H^+}$  is the charge transfer current density in  $A/m^2$ ,  $i_{o,H^+}$  is the exchange current density in  $A/m^2$ , E is the potential of the system at a certain point in V,  $E_{rev}$  is the reversible potential for the H<sup>+</sup> reduction reaction in V, and  $\beta_{c,H^+}$  is the Tafel slope for the H<sup>+</sup> reduction reaction in V/decade. The  $E - E_{rev}$  term in the Tafel equation is often referred to as the overpotential and is commonly denoted by the  $\eta$  symbol and in the units of V. The Tafel slope for a given cathodic reaction can be calculated using the following equation:

$$\beta_c = \frac{2.303RT}{\alpha_c F} \tag{16}^{54}$$

Where  $\beta_c$  is the cathodic Tafel slope in *V*/decade, *R* is the universal gas constant that is equal to 8.314 *J*/mol · *K*, T is the temperature in *K*,  $\alpha_c$  is the cathodic electron transfer coefficient, and F is Faraday's constant that is equal to 96485 *C*/mol. The  $E_{rev}$  is used in the calculation of the charge transfer current density but, in practice, this can be very difficult to use because it can vary based on the concentration of the reacting species in the system. For this reaction, the  $E_{rev}$  depends on the concentration of H<sup>+</sup> species present as well as the partial pressure of H<sub>2</sub> dissolved in the solution, which is particularly difficult to measure. For this reason, an arbitrary reversible potential,  $E_{rev}^{ref}$ , is used in this model. The choice of this arbitrary potential will not influence the results as long as this chosen  $E_{rev}^{ref}$  is held constant with its respective reference exchange current density ( $i_o^{ref}$ ) and activation energy ( $E_a$ ) for all environments that are modeled. The reversible potential chosen in the model developed by Madani Sani was -0.685 V vs. sat. Ag/AgCl which is the reversible potential of X65 steel at standard conditions.<sup>57</sup>

The exchange current density,  $i_{o,H^+}$ , cannot be measured for a given reaction so an equation has been derived to be able to calculate this parameter. The equation that is used is shown below.

$$i_{o,H^+} = i_{o,H^+}^{ref} \left(\frac{c_{H^+}}{c_{H^+}^{ref}}\right)^{n_{H^+}^{H^+}} \left(\frac{c_{Cl^-}}{c_{Cl^-}^{ref}}\right)^{n_{H^+}^{Cl^-}} \left(\frac{c_{HAc}}{c_{HAc}^{ref}}\right)^{n_{H^+}^{HAc}} e^{-\frac{E_{a,H^+}}{R} \left(\frac{1}{T} - \frac{1}{T^{ref}}\right)}$$
(17)

Where  $i_{o,H^+}$  is the exchange current density in  $A/m^2$ ,  $i_{o,H^+}^{ref}$  is the reference exchange current density in  $A/m^2$ ,  $c_{H^+}$  is the molar concentration of H<sup>+</sup> in the bulk in M,  $c_{H^+}^{ref}$  is the reference molar concentration of H<sup>+</sup> in the bulk that is equal to  $1 \times 10^{-4} M$ ,  $n_{H^+}^{H^+}$  is the reaction rate order for H<sup>+</sup>,  $c_{Cl^-}$  is the molar concentration of Cl<sup>-</sup> in the bulk in M,  $c_{Cl^-}^{ref}$  is the reference molar concentration of Cl<sup>-</sup> in the bulk that is equal to 1.00 M,  $n_{H^+}^{Cl^-}$  is the reaction rate order for Cl<sup>-</sup>,  $c_{HAc}$  is the molar concentration of free acetic acid in the bulk in M,  $c_{HAc}^{ref}$  is the reference molar concentration of free acetic acid in the bulk in M,  $c_{HAc}^{ref}$  is the reference molar concentration of free acetic acid in the bulk in  $H^+$  is equal to 1.67 \times 10^{-8} M,  $n_{H^+}^{HAc}$  is the reaction order for acetic acid,  $E_{a,H^+}$  is the activation energy for the H<sup>+</sup> reduction reaction in J/mol, R is the universal gas constant, T is the temperature of the system in K, and  $T^{ref}$  is the reference temperature that is equal to 293.15 K.

During this study, the addition of acetic acid to the system was seen to influence the H<sup>+</sup> reduction reaction. In order to incorporate this influence into the electrochemical model, a term was added to the equation used to calculate  $i_{o,H^+}$ . For each acetic acid containing corrosion system that was tested (strong acid, CO<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>S/CO<sub>2</sub>) a fitting exercise was done by varying the  $n_{H^+}^{HAc}$  and  $i_{o,H^+}^{ref}$  until a good fit was achieved. If the results from the experimental data showed that free acetic acid had no influence on the H<sup>+</sup> reduction reaction,  $n_{H^+}^{HAC}$  was set to zero which reduces the added term to 1 thus having no influence on the calculated  $i_{o,H^+}$ .

For this model, the reference concentration for free acetic acid was intended to be zero, but because of the nature of the term included to account for the influence of free acetic acid, the use of zero is not possible for the reference. To solve this complication, the reference concentration of free acetic acid was set to  $1.67 \times 10^{-8} M$ , which is equal to a ppb concentration of 1.0 in the bulk which was determined to be sufficiently small to be used as the "zero" free acetic acid reference point.

The parameters for the H<sup>+</sup> ion reduction reaction used in the electrochemical model can be found in Table 11.

Parameter	Strong Acid Corrosion <sup>57</sup>	H <sub>2</sub> S Corrosion <sup>57</sup>	CO <sub>2</sub> Corrosion <sup>57</sup>	H2S/CO2 Corrosion
$E_{rev,H^+}^{ref}(V)$	-0.685	-0.685	-0.685	-0.685*
$E_{a,H^+}(J/mol)$	59860	59860	59860	23141*
$i_{o,H^+}^{ref} (A/m^2)$	5.20	0.38	4.70	1.18*
$n_{H^+}^{H^+}$	0.50	0.50	0.50	0.50
$n_{H^+}^{Cl^-}$	-0.20	-0.25	-0.37	-0.25
$n_{H^+}^{HAc}$	-0.03*	0*	-0.08*	0*
$\alpha_{c,H^+}$	0.50	0.50	0.50	0.50

Table 11. The parameters for the  $H^+$  ion reduction reaction for each environment that was modeled.

\*Parameters determined in this study; all other parameters were determined by Madani Sani<sup>57</sup>

The model for H<sub>2</sub>S/CO<sub>2</sub> corrosion in the presence of acetic acid was adapted from the original H<sub>2</sub>S model to incorporate the presence of both CO<sub>2</sub> and acetic acid.<sup>57</sup> The parameters  $E_{rev,H^+}^{ref}$ ,  $n_{H^+}^{H^+}$ ,  $n_{H^+}^{Cl^-}$ , and  $\alpha_c$  were found to work well for the H<sub>2</sub>S/CO<sub>2</sub> corrosion model where the parameters  $E_{rev,H^+}^{ref}$ ,  $E_{a,H^+}$ , and  $i_{o,H^+}^{ref}$  did not fit the model well. For that reason, new parameters for  $E_{rev,H^+}^{ref}$ ,  $E_{a,H^+}$ , and  $i_{o,H^+}^{ref}$  needed to be found from the experimental data collected in this study in order to accurately model changes in the solution temperature. A new  $E_{a,H^+}$  and  $i_{o,H^+}^{ref}$  was calculated to be 23141 *J/mol* and 1.18  $A/m^2$  respectively from the same  $E_{rev,H^+}^{ref}$  of -0.685 *V* that was used previously. The details of this calculation can be found in Appendix B: Determination of the Activation Energy for the H<sup>+</sup> Ion Reduction Reaction in an H<sub>2</sub>S/CO<sub>2</sub> Corrosion Environment.

## 6.1.3 Mass Transfer Limiting Current from Hydrogen Ions

The mass transfer limitation that exists in the  $H^+$  reduction reaction occurs because of the relatively slow mass transfer process that involves the movement of reactive species across the diffusion boundary layer to the metal surface. In CO<sub>2</sub> corrosion, the slow hydration of the CO<sub>2</sub> chemical reaction also plays a role in this mass transfer limitation. In order to mathematically describe this mass transfer limitation, an equation has been derived that aims to quantify the magnitude of this limitation while also assuming the buffering effect mechanism for all the weak acids involved in the corrosion process (H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>S, and HAc). This equation is shown in the following equation:

$$i_{lim,H^{+}}^{buff} = 1000nF \sqrt{D_{H^{+}}^{eff} k_{f,CO_2} c_{b,CO_2}^{eq} c_{b,H^{+}}^{eq} coth\left(\frac{\delta_{m,H^{+}}}{\delta_r}\right)}$$
(18)<sup>58</sup>

Where  $i_{lim,H^+}^{buff}$  is the limiting current involving the buffering of the weak acids in  $A/m^2$ , n is the charge number of the H<sup>+</sup> reduction reaction which is equal to 1, F is Faraday's constant,  $D_{H^+}^{eff}$  is the effective diffusivity in  $m^2/s$ ,  $k_{f,CO_2}$  is the forward reaction rate constant for the CO<sub>2</sub> hydration reaction in 1/M/s,  $c_{b,CO_2}^{eq}$  and  $c_{b,H^+}^{eq}$  are the equilibrium concentrations of CO<sub>2</sub> and H<sup>+</sup> in the bulk phase in M,  $\delta_{m,H^+}$  is the thickness of the mass transfer boundary layer for H<sup>+</sup> in m, and  $\delta_{r,H^+}$  is the thickness of the chemical reaction boundary layer in m. This equation for the mass transfer limiting current is an analytical solution that was solved from what is referred to as the "co-diffusion" equations which involves a steady-state one-dimensional Nernst-Planck equation for H<sup>+</sup> and H<sub>2</sub>CO<sub>3</sub>.<sup>58</sup> Through this derivation, the effective diffusivity,  $D_{H^+}^{eff}$ , is defined as the effective diffusivity of H<sup>+</sup> in the presence of CO<sub>2</sub> which accounts for the co-diffusion present in the system. This equation for the effective diffusivity can be seen in the equation below.

$$D_{H^+}^{eff} = D_{H^+} + \frac{c_{b,H_2CO_3}^{eq}}{c_{b,H^+}^{eq}} D_{H_2CO_3}$$
(19)<sup>58</sup>

Where  $D_{H^+}$  is the diffusion coefficient for H<sup>+</sup> in  $m^2/s$ ,  $c_{b,H_2CO_3}^{eq}$  is the equilibrium concentration of H<sub>2</sub>CO<sub>3</sub> in the bulk in *M*, and  $D_{H_2CO_3}$  is the diffusion coefficient for H<sub>2</sub>CO<sub>3</sub> in  $m^2/s$ . In this model specifically, there exists more than just H<sup>+</sup> and H<sub>2</sub>CO<sub>3</sub>. The codiffusion of H<sub>2</sub>S and acetic acid is also present in the system and needs to be considered in this model. In order to circumvent the need to complicate the solution with two more steady-state one-dimensional Nernst-Planck equations for H<sub>2</sub>S and acetic acid, a method has been developed to account for these additional diffusing species.<sup>59</sup> Also, the addition of these two extra equations would make a meaningful analytical solution likely impossible. The method is included in the modified  $D_{H^+}^{eff}$  equation below.

$$D_{H^{+}}^{eff} = D_{H^{+}} + \frac{c_{b,H_2CO_3}^{eq}}{c_{b,H^{+}}^{eq}} D_{H_2CO_3} + \frac{c_{b,HAC}^{eq}}{c_{b,H^{+}}^{eq}} D_{HAC} + \frac{c_{b,H_2S}^{eq}}{c_{b,H^{+}}^{eq}} D_{H_2S}$$
(20)<sup>59</sup>

Where  $c_{b,HAc}^{eq}$  and  $c_{b,H_2S}^{eq}$  are the equilibrium concentrations of acetic acid and H<sub>2</sub>S in the bulk in *M*, and  $D_{HAc}$  and  $D_{H_2S}$  are the diffusion coefficients for acetic acid and H<sub>2</sub>S in  $m^2/s$ . The incorporation of H<sub>2</sub>S and acetic acid into the  $D_{H^+}^{eff}$  term allows for the relative concentration of each species in relation to the H<sup>+</sup> concentration to influence the overall limiting current that is calculated. The forward reaction rate constant for the CO<sub>2</sub> hydration reaction,  $k_{f,hyd}$ , can be calculated using the equation below.

$$k_{f,hyd} = \frac{5.796 \, x \, 10^{10} \cdot e^{\left(\frac{-69335}{RT}\right)}}{a_{H_20,b}^{eq}} \tag{21}^{57}$$

Where  $a_{H_2O,b}$  is the activity of H<sub>2</sub>O in the bulk which is equal to 1 for pure water. The mass transfer boundary layer thickness,  $\delta_{m,H^+}$ , for H<sup>+</sup> assuming RDE hydrodynamics can be calculated using the equation below.

$$\delta_{m,H^+} = 1.61 D_{H^+}^{\frac{1}{3}} \nu^{\frac{1}{6}} \omega^{-\frac{1}{2}}$$
(22)<sup>60</sup>

Where  $\nu$  is the kinematic viscosity of the solution in  $m^2/s$  and  $\omega$  is the rotational velocity of the RDE in *rad/s*. The chemical reaction boundary layer thickness,  $\delta_r$ , regardless of the type of hydrodynamics is calculated using the following equation:

$$\delta_r = \sqrt{\frac{D_{H^+}^{eff} c_{b,H^+}^{eq}}{k_{f,hyd} c_{b,CO_2}^{eq}}}$$
(23)<sup>58</sup>

It has been verified that the weak acids studied in this research will partially dissociate in the solution producing additional H<sup>+</sup> ions that contribute to the cathodic reaction *via* the reduction of H<sup>+</sup>. This is what is referred to as the buffering effect mechanism.<sup>4,5,43</sup> It is this buffering that happens within the mass transfer boundary layer that needs to be accounted for in the calculation of the limiting current. This essentially is what including the chemical reaction boundary layer is doing in the limiting current equation. The chemical reaction boundary layer is defined by the region very close to the reacting surface where chemical reactions occur and, in this case, contribute to the cathodic reaction occurring at the surface of the steel. This reaction boundary layer relating to the concentration profile.<sup>58</sup>

The equation for the limiting current uses both the thickness of the mass transfer boundary layer as well and the thickness of the chemical reaction boundary layer but, in reality, there only exists one boundary layer involving the concentration profile that the participating species must diffuse through.<sup>58</sup> The partial dissociation of weak acids close to the surface decreases the overall thickness of the boundary layer that would have been observed had there been no dissociation present at all. Typically, the chemical reaction boundary layer thickness in aqueous CO<sub>2</sub> solutions is one order of magnitude smaller than the thickness of the mass transfer boundary layer.<sup>58</sup> The limiting current equation that is used to calculate the limiting current in this model, through derived to be used in  $CO_2$  corrosion, can be used for all systems that were tested in this study. This includes the experiments conducted in a strong acid and H<sub>2</sub>S environment that lacks the presence of  $CO_2$ . If the partial pressure of  $CO_2$  is set to zero, the equation will be reduced to normal Fick's diffusion where the magnitude of the limiting current, among the other environmental factors, will be influenced by only the H<sub>2</sub>S and free acetic acid concentration, and no longer the concentration of  $CO_2$ .<sup>59</sup>

#### 6.1.4 Water Reduction Reaction

The reduction of  $H_2O$  reaction becomes relevant at high negative overpotentials where the effect of charge transfer on the reaction can be calculated with the following equation:

$$i_{H_2O} = i_{o,H_2O} * 10^{-\left(\frac{E - E_{rev}}{\beta_{c,H_2O}}\right)}$$
(24)<sup>54</sup>

Where  $i_{H_2O}$  is the total current density of the H<sub>2</sub>O reduction reaction in  $A/m^2$ ,  $i_{o,H_2O}$  is the exchange current density for the H<sub>2</sub>O reduction reaction in  $A/m^2$ , E is the potential of the system at a certain point in V,  $E_{rev}$  is the reversible potential for the H<sub>2</sub>O reduction reaction in V, and  $\beta_{c,H_2O}$  is the Tafel slope for the H<sub>2</sub>O reduction reaction in V/decade. The  $\beta_{c,H_2O}$  can be calculated using equation (16)<sup>54</sup>. Much like with the H<sup>+</sup> reduction reaction, an arbitrary  $E_{rev}^{ref}$  was chosen rather than using the thermodynamic  $E_{rev}$  in the interest of making the calculation of the total current density of the H<sub>2</sub>O reduction reaction simpler.

The exchange current density once again cannot be measured for a given reaction, so an equation has been derived to be able to calculate this parameter. The equation that was used is shown below.

$$i_{o,H_2O} = i_{o,H_2O}^{ref} \left(\frac{c_{H^+}}{c_{H^+}^{ref}}\right)^{n_{H_2O}^{H^+}} \left(\frac{c_{Cl^-}}{c_{Cl^-}^{ref}}\right)^{n_{H_2O}^{Cl^-}} \left(\frac{c_{H_2O}}{c_{H_2O}^{ref}}\right)^{n_{H_2O}^{H_2O}} e^{-\frac{E_{a,H_2O}}{R} \left(\frac{1}{T} - \frac{1}{T^{ref}}\right)}$$
(25)<sup>57</sup>

Where  $i_{o,H_2O}$  is the exchange current density in  $A/m^2$ ,  $i_{o,H_2O}^{ref}$  is the reference exchange current density in  $A/m^2$ ,  $c_{H^+}$  is the molar concentration of H<sup>+</sup> in the bulk in M,  $c_{H^+}^{ref}$  is the reference molar concentration of H<sup>+</sup> in the bulk that is equal to  $1 \times 10^{-4} M$ ,  $n_{H_2O}^{H^+}$  is the reaction rate order for H<sup>+</sup>,  $c_{Cl^-}$  is the molar concentration of Cl<sup>-</sup> in the bulk in M,  $c_{Cl^-}^{ref}$  is the reference molar concentration of Cl<sup>-</sup> in the bulk that is equal to 1.00 M,  $n_{H_2O}^{Cl^-}$  is the reaction rate order for Cl<sup>-</sup>,  $E_{a,H_2O}$  is the activation energy for the H<sub>2</sub>O reduction reaction in J/mol, R is the universal gas constant, T is the temperature of the system in K, and  $T^{ref}$ is the reference temperature that is equal to 293.15 K. Acetic acid was not seen to influence the H<sub>2</sub>O reduction reaction, so it was not accounted for in the calculation of the exchange current density.

The parameters for the  $H_2O$  reduction reaction used in the electrochemical model can be found in Table 12.

Parameter*	Strong Acid Corrosion <sup>57</sup>	H <sub>2</sub> S Corrosion <sup>57</sup>	CO <sub>2</sub> Corrosion <sup>57</sup>	H <sub>2</sub> S/CO <sub>2</sub> Corrosion
$E_{rev,H_20}^{ref}(V)$	-0.685	-0.685	-0.685	-0.685
$E_{a,H_20}$ (J/mol)	24809	24809	24809	24809
$i_{o,H_20}^{ref} (A/m^2)$	0.20	$5.0 \mathrm{x} 10^{-4}$	$5.10 \times 10^{-2}$	$5.0 \mathrm{x} 10^{-4}$
$n_{H_20}^{H^+}$	-0.50	-0.50	-0.50	-0.50
$n_{H_2O}^{Cl^-}$	1.35	0.50	0.60	0.50
$n_{H_20}^{H_20}$	2	2	2	2
$\alpha_{c,H_20}$	0.50	0.50	0.50	0.50

Table 12. The parameters for the H<sub>2</sub>O reduction reaction for each environment that was modeled.

\*All other parameters were determined by Madani Sani<sup>57</sup>

The model for  $H_2S/CO_2$  corrosion in the presence of acetic acid was adapted from the original  $H_2S$  model to incorporate the presence of both  $CO_2$  and acetic acid.<sup>57</sup> All parameters that were used in the  $H_2S$  model for the reduction of  $H_2O$  reaction worked well for the  $H_2S/CO_2$  model, so no changes were made to the parameters.

# 6.1.5 Iron Oxidation Reaction

The effect of charge transfer on the Fe oxidation reaction can be calculated using the following equation:

$$i_{Fe} = i_{o,Fe} * 10^{\left(\frac{E - E_{rev}}{\beta_{a,Fe}}\right)}$$
(26)<sup>54</sup>

Where  $i_{Fe}$  is the total current density for the Fe oxidation reaction in  $A/m^2$ ,  $i_{o,Fe}$  is the exchange current density for the Fe oxidation reaction in  $A/m^2$ , E is the potential of the system at a certain point in V,  $E_{rev}$  is the reversible potential for the Fe oxidation reaction

in *V*, and  $\beta_{a,Fe}$  is the Tafel slope for the Fe oxidation reaction in *V*/*decade*. The  $\beta_{a,Fe}$  can be calculated using the equation below.

$$\beta_a = \frac{2.303RT}{\alpha_a F} \tag{27}^{54}$$

Where  $\beta_a$  is the anodic Tafel slope in *V*/decade, *R* is the universal gas constant that is equal to 8.314 *J*/mol · *K*, T is the temperature in *K*,  $\alpha_a$  is the anodic electron transfer coefficient, and F is Faraday's constant that is equal to 96485 *C*/mol. Just as in the previous two reactions, an arbitrary reference reversible potential,  $E_{rev}^{ref}$ , was chosen to simplify the modeling and was kept constant for each environment that was modeled. The exchange current density can be calculated using the following equation:

$$i_{o,Fe} = i_{o,Fe}^{ref} \left(\frac{c_{OH^{-}}}{c_{OH^{-}}^{ref}}\right)^{n_{Fe}^{OH^{-}}} \left(\frac{c_{Cl^{-}}}{c_{Cl^{-}}^{ref}}\right)^{n_{Fe}^{Cl^{-}}} \left(\frac{c_{H_{2}O}}{c_{H_{2}O}^{ref}}\right)^{n_{Fe}^{H_{2}O}} \left(\frac{c_{HAC}}{c_{HAC}^{ref}}\right)^{n_{Fe}^{HAC}} e^{-\frac{E_{a,Fe}(\frac{1}{T} - \frac{1}{T^{ref}})}{R}}$$
(28)

Where  $i_{o,Fe}$  is the exchange current density in  $A/m^2$ ,  $i_{o,Fe}^{ref}$  is the reference exchange current density in  $A/m^2$ ,  $c_{OH^-}$  is the molar concentration of OH<sup>-</sup> in the bulk in M,  $c_{OH^-}^{ref}$  is the reference molar concentration of OH<sup>-</sup> in the bulk that is equal to  $1 \times 10^{-10} M$ ,  $n_{Fe}^{OH^-}$  is the reaction rate order for OH<sup>-</sup>,  $c_{Cl^-}$  is the molar concentration of Cl<sup>-</sup> in the bulk in M,  $c_{Cl^-}^{ref}$  is the reaction rate order for OH<sup>-</sup>,  $c_{Cl^-}$  is the molar concentration of Cl<sup>-</sup> in the bulk in M,  $c_{Re}^{ref}$  is the reaction rate order for Cl<sup>-</sup>,  $c_{H_2O}$  is the molar concentration of H<sub>2</sub>O in the bulk in M,  $c_{H_2O}^{ref}$ is the reference molar concentration of H<sub>2</sub>O in the bulk that is equal to 55.4 M,  $n_{Fe}^{H_2O}$  is the reaction rate order for H<sub>2</sub>O,  $c_{HAC}$  is the molar concentration of free acetic acid in the bulk in M,  $c_{HAC}^{ref}$  is the reference molar concentration of free acetic acid in the bulk to  $1.67 \times 10^{-8} M$ ,  $n_{Fe}^{HAc}$  is the reaction order for acetic acid,  $E_{a,Fe}$  is the activation energy for the Fe oxidation reaction J/mol, R is the universal gas constant, T is the temperature of the system in K, and  $T^{ref}$  is the reference temperature that is equal to 293.15 K.

During this study, the addition of acetic acid to strong acid, CO<sub>2</sub>, and H<sub>2</sub>S environments was seen to influence the Fe oxidation reaction as well. In order to incorporate this influence into the electrochemical model, a term was added to the equation used to calculate  $i_{o,Fe}$ . Once again, for each corrosion system that showed evidence of being influenced by the presence of free acetic acid, a fitting exercise was done by varying the  $n_{Fe}^{HAc}$  and  $i_{o,Fe}^{ref}$  until a good fit was achieved. If the results from the experimental data showed that free acetic acid had no influence on the Fe oxidation reaction,  $n_{Fe}^{HAc}$  was set to zero which reduces the added term to 1 thus having no influence on the calculated  $i_{o,Fe}$ .

For systems where  $H_2S$  was present, the influence of  $H_2S$  on the anodic reaction was accounted for in this model by using a term that involves its relative concentration of  $H_2S$  in the bulk in relation to the reference concentration which is the molar concentration of  $H_2S$  when 1 bar of  $H_2S$  is present (pure  $H_2S$ ) and its respective reaction rate. The exchange current density equation that was used when  $H_2S$  was present in the system is shown below.

i<sub>o,Fe</sub>

$$= i_{o,Fe}^{ref} \left(\frac{c_{OH^{-}}}{c_{OH^{-}}^{ref}}\right)^{n_{Fe}^{OH^{-}}} \left(\frac{c_{Cl^{-}}}{c_{Cl^{-}}^{ref}}\right)^{n_{Fe}^{Cl^{-}}} \left(\frac{c_{H_2O}}{c_{H_2O}^{ref}}\right)^{n_{Fe}^{H_2O}} \left(\frac{c_{H_2S}}{c_{H_2S}^{ref}}\right)^{n_{Fe}^{H_2S}} \left(\frac{c_{HAC}}{c_{HAC}^{ref}}\right)^{n_{Fe}^{HAC}} e^{-\frac{E_{a,Fe}(\frac{1}{T} - \frac{1}{T^{ref}})}{R}}$$
(29)

Where  $c_{H_2S}$  is the molar concentration of H<sub>2</sub>S in the bulk in *M*,  $c_{H_2S}^{ref}$  is the reference molar concentration of H<sub>2</sub>S in the bulk that is equal to 0.104 *M*, and  $n_{Fe}^{H_2S}$  is the reaction rate order for H<sub>2</sub>S.

The parameters for the  $H^+$  ion reduction reaction used in the electrochemical model are listed in Table 13.

Parameter	Strong Acid Corrosion <sup>57</sup>	H <sub>2</sub> S Corrosion <sup>57</sup>	CO <sub>2</sub> Corrosion <sup>57</sup>	H2S/CO2 Corrosion
$E_{rev,Fe}^{ref}(V)$	-0.685	-0.685	-0.685	-0.685
$E_{a,Fe}(J/mol)$	25398	25398	25398	25398
$i_{o,Fe}^{ref} \left( A/m^2 \right)$	0.20	0.16	0.23	0.25*
$n_{Fe}^{OH^-}$	1.00	1.00	1.00	0.40*
$n_{Fe}^{H_2O}$	0	0	0	0
$n_{Fe}^{H_2S}$	N/A	0.30	N/A	0.25
$n_{Fe}^{Cl^-}$	0.48	-0.40	0.14	-0.40
$n_{Fe}^{HAc}$	-0.11*	0*	-0.08*	0*
$\alpha_{c,H^+}$	1.20	1.05	1.10	1.05

Table 13. The parameters for the Fe oxidation reaction for each environment that was modeled.

# \*Parameters determined in this study; all other parameters were determined by Madani Sani<sup>57</sup>

The model for H<sub>2</sub>S/CO<sub>2</sub> corrosion in the presence of acetic acid was adapted from the original H<sub>2</sub>S model to incorporate the presence of both CO<sub>2</sub> and acetic acid.<sup>57</sup> The parameters  $E_{rev,Fe}^{ref}$ ,  $E_{a,Fe}$ ,  $n_{Fe}^{H_2O}$ ,  $n_{Fe}^{H_2S}$ ,  $n_{H^+}^{Cl^-}$ , and  $\alpha_c$  were found to work well for the H<sub>2</sub>S/CO<sub>2</sub> corrosion model where the parameters  $n_{Fe}^{OH^-}$  and  $i_{o,Fe}^{ref}$  did not fit the model well. For that reason, new parameters for  $n_{Fe}^{OH^-}$  and  $i_{o,Fe}^{ref}$  needed to be found using the experimental data collected in this study in order to accurately model changes in the solution pH. A new value for  $n_{Fe}^{OH^-}$  and  $i_{o,Fe}^{ref}$  was found by conducting a fitting exercise by varying both  $n_{Fe}^{OH^-}$  and  $i_{o,Fe}^{ref}$  until a good fit was achieved. The resulting values for  $n_{Fe}^{OH^-}$  and  $i_{o,Fe}^{ref}$  was 0.40 and 0.25  $A/m^2$  respectively.

A summary of all the parameters used in this electrochemical model can be seen in Table 14.

Parameter	Strong Acid Corrosion <sup>57</sup>	H <sub>2</sub> S Corrosion <sup>57</sup>	*CO <sub>2</sub> Corrosion <sup>57</sup>	H <sub>2</sub> S/CO <sub>2</sub> Corrosion
$E_{rev,H^+}^{ref}(V)$	-0.685	-0.685	-0.685	-0.685*
$E_{rev,H_20}^{ref}(V)$	-0.685	-0.685	-0.685	-0.685
$E_{rev,Fe}^{ref}(V)$	-0.685	-0.685	-0.685	-0.685
$E_{a,H^+}(J/mol)$	59860	59860	59860	23141*
$E_{a,H_20} (J/mol)$	24809	24809	24809	24809
$E_{a,Fe}$ (J/mol)	25398	25398	25398	25398
$i_{o,H^+}^{ref} \left( A/m^2 \right)$	5.20	0.38	4.70	1.18*
$oldsymbol{n}_{H^+}^{H^+}$	0.50	0.50	0.50	0.50
$n_{H^+}^{Cl^-}$	-0.20	-0.25	-0.37	-0.25
$n_{H^+}^{HAc}$	0*	0*	-0.08*	0*
$\alpha_{c,H^+}$	0.50	0.50	0.50	0.50
$i_{o,H_20}^{ref} (A/m^2)$	0.20	$5.0 \mathrm{x} 10^{-4}$	$5.10 \mathrm{x} 10^{-2}$	$5.0 \mathrm{x} 10^{-4}$
$n_{H_20}^{H^+}$	-0.50	-0.50	-0.50	-0.50
$n_{H_2O}^{Cl^-}$	1.35	0.50	0.60	0.50
$n_{H_20}^{H_20}$	2	2	2	2
$\alpha_{c,H_20}$	0.50	0.50	0.50	0.50
$i_{o,Fe}^{ref}$ (A/m <sup>2</sup> )	0.20	0.16	0.23	0.25
$n_{Fe}^{OH^-}$	1.00	1.00	1.00	0.40*
$n_{Fe}^{H_2O}$	0	0	0	0
$n_{Fe}^{H_2S}$	N/A	0.30	N/A	0.25
$n_{Fe}^{Cl^-}$	0.48	-0.40	0.14	-0.40
$n_{Fe}^{HAc}$	-0.11*	0*	-0.08*	0*
$lpha_{c,H^+}$	1.20	1.05	1.10	1.05

Table 14. A summary of the parameters used in the electrochemical model.

\*Parameters determined in this study; all other parameters were determined by Madani Sani<sup>57</sup>

# 6.1.6 Mixed Potential Theory

According to mixed potential theory, the overall corrosion potential,  $E_{corr}$ , can be calculated by writing a charge balance for the system that takes the form of the equation written below.

$$\sum i_a = \sum i_c \tag{30}^{54}$$

Substituting in the total currents for each respective cathodic and anodic reaction the equation becomes:

$$i_{Fe} = i_{H^+} + i_{H_2O} \tag{31}$$

This equation is then solved for  $E_{corr}$ . Because every involved electrochemical reaction must proceed at the same exact rate, the  $i_{corr}$  can be calculated by using any of the total current equations. Throughout the open literature, it is most conventional to use the anodic current to calculate the  $i_{corr}$ , so equation (26)<sup>54</sup> was used to complete this calculation. The corrosion rate can then be calculated from the  $i_{corr}$  using the following equation:

$$CR = \frac{i_{corr} \cdot MW}{\rho \cdot n \cdot F} \tag{32}^{61}$$

Where *CR* is the corrosion rate in m/s,  $i_{corr}$  is the corrosion current in  $A/m^2$ , *MW* is the molecular weight of the metal in g/mol,  $\rho$  is the density of the metal in  $g/m^3$ , n is the number of electrons involved in the overall electrochemical reaction which is equal to 2 e<sup>-</sup> in this system, and *F* is Faraday's constant that is equal to 96485 *C/mol*.

#### 6.2 Implication of the Model and Comparison to Experimental Data

This model requires the total pressure, solution temperature, bulk pH, partial pressure of CO<sub>2</sub>, concentration of H<sub>2</sub>S, weight percent NaCl, total solution volume, concentration of free acetic acid, and the RDE rotational velocity as inputs for the calculations of the potentiodynamic sweeps and corrosion rate. The model will output the net potentiodynamic sweep as well as the calculated  $E_{corr}$ ,  $i_{corr}$ , and corrosion rate. In order to validate the accuracy of the model, the results were compared to the experimental data that was collected for every environmental condition that was tested in this study. The results are shown and analyzed in this section.

#### 6.2.1 Modeling of H<sub>2</sub>S Corrosion of Mild Steel in the Presence of Acetic Acid

This section will evaluate the accuracy of the developed electrochemical model for strong acid and H<sub>2</sub>S corrosion in the presence of acetic acid at 30 °C, pH 4.0, and a 1000 rpm RDE. The first environment that was modeled involved varying the pH<sub>2</sub>S between 0 and 10 mbar without the presence of acetic acid. The modeled sweep can be seen in Figure 40. It should be noted that the H<sub>2</sub>S model developed by Madani Sani is only valid for partial pressures of H<sub>2</sub>S between 0.0001 and 1 bar.<sup>57</sup> This means that the 0.00005 bar (0.05 mbar) of H<sub>2</sub>S that was tested in this study is outside of the limits set by this model. From experimental data collected in this study, a decrease in the corrosion rate was seen when increasing the partial pressure of H<sub>2</sub>S from 0 to 0.05 to 0.1 mbar where after increasing pH<sub>2</sub>S to 10 mbar, an increase was observed. This maximum retardation that was seen at 0.1 mbar cannot be predicted using this model. Looking at the modeled sweep for 0.05 mbar compared to the modeled sweep at 0.1 mbar, a further decrease in the anodic reaction

rate and corrosion rate was observed at 0.05 mbar. This is different than the increase in the anodic reaction rate and corrosion rate that was observed in the experimental data. This model does not account for the maximum retardation of the anodic reaction that is seen at 0.1 mbar of  $H_2S$ . This should be kept in mind when studying the data with 0.05 mbar of  $H_2S$ .

Looking that the modeled sweep for 0 mbar of  $H_2S$ , this was modeled using the strong acid model where the fit for the anodic and cathodic reaction was good. The corrosion current was overpredicted, but this could have been due to the difference in the  $\beta_a$  value that was used to calculate the corrosion current via LPR and the  $\beta_a$  value used in the electrochemical model. The LPR  $\beta_a$  was 0.040 V/decade whereas the model  $\beta_a$  was 0.050 V/decade which will cause the LPR corrosion rate to be smaller than the modeled corrosion rate. Studying the sweeps for 0.1 and 10 mbar of H<sub>2</sub>S, they were generated using the  $H_2S$  model where the fit for the anodic and cathodic sweep was also good whereas the fit for the sweeps at 0.05 mbar was not as good. The experimental data at 10 mbar of  $H_2S$ exhibited two mass transfer limiting currents that were not predicted by the model. This is because equation  $(18)^{58}$  that was used to calculate the limiting current and equation  $(15)^{54}$ that was used to calculate the charge transfer currents used bulk concentration of species rather than surface concentrations. For this reason, only the overall limiting current is predicted by the model. Overall, the limiting current for all sweeps modeled in Figure 40 matched the experimental data relatively well.



Figure 40. Modeled potentiodynamic sweeps for experiments containing 0 - 10 mbar of H<sub>2</sub>S without the presence of acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.

The next set of modeled sweeps involved adding 1000 ppm of free acetic acid to a strong acid environment without the presence of H<sub>2</sub>S. The resulting sweep can be seen in Figure 41. The anodic and cathodic sweep agree with the experimental data that was collected. The  $n_{Fe}^{HAc}$  and  $n_{H^+}^{HAc}$  that resulted in the best fit was determined to be -0.11 and 0 respectively. This signifies a retardation in the anodic reaction as the concentration of free acetic acid increases in relation to the reference while the free acetic acid has no influence on the rate of the cathodic reaction. This is consistent with the data collected in this study as well as data collected by others.<sup>48</sup>



Figure 41. Modeled potentiodynamic sweeps for experiments containing 0 mbar of H<sub>2</sub>S with 0 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.

The next modeled sweeps involved adding 1000 ppm of free acetic acid to environments containing 0.05 - 10 mbar of H<sub>2</sub>S. The partial pressure of 0.05 mbar is outside the limits set by the original H<sub>2</sub>S model, but the potentiodynamic sweep was still modeled in the interest of testing its accuracy outside its limits.<sup>57</sup> For each partial pressure of H<sub>2</sub>S, upon adding 1000 ppm of free acetic acid, the experimental data showed a variety of increases and decreases in the anodic and cathodic reaction rate for the three partial pressures of H<sub>2</sub>S that were tested. These increases and decreases in the reaction rate were captured in the  $n^{HAc}$  reaction order for each reaction by conducting a fitting exercise to the data. These reaction orders are summarized in Table 15.

<b>Reaction Order</b>	Value	pH2S (mbar)
$n_{Fe}^{HAc}$	-0.05	0.05
$n_{H^+}^{HAc}$	0.02	0.05
$n_{Fe}^{HAc}$	0.04	0.1
$n_{H^+}^{HAc}$	0.02	0.1
$n_{Fe}^{HAc}$	0.04	10
$n_{H^+}^{HAc}$	0	10

Table 15. Reaction orders for acetic acid in H<sub>2</sub>S corrosion with 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.

As one can observe, there was much variation in the reaction order for each reaction in the three partial pressures of H<sub>2</sub>S that were tested. For example, the rate of the anodic reaction was retarded with 0.05 mbar of H<sub>2</sub>S but then accelerated with 0.1 mbar of H<sub>2</sub>S when the same amount of free acetic acid was added to the system. Because the reaction orders were found to be of such small magnitude and there being much variation in the reaction order without any concrete evidence as to why, the reaction orders were assumed to be zero for all H<sub>2</sub>S environments containing acetic acid that were modeled. The resulting sweeps assuming  $n_{Fe}^{HAc}$  and  $n_{H^+}^{HAc}$  to be zero can be seen in Figure 42 - Figure 44.

Due to  $n_{Fe}^{HAc}$  and  $n_{H^+}^{HAc}$  being equal to zero, there was no change in the anodic and cathodic reaction rate in the model when the free acetic acid concentration was increased to 1000 ppm. Despite this being the case, the model still performed relatively well with the best fit occurring at 10 mbar of H<sub>2</sub>S shown in Figure 44. The limiting currents in these conditions were slightly underpredicted when compared to the experimental value, but

considering the oversimplification that was done involving the effective diffusivity, the accuracy of the prediction model is sufficient.



Figure 42. Modeled potentiodynamic sweeps for experiments containing 0.05 mbar of H<sub>2</sub>S with 0 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.



Figure 43. Modeled potentiodynamic sweeps for experiments containing 0.1 mbar of H<sub>2</sub>S with 0 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.



Figure 44. Modeled potentiodynamic sweeps for experiments containing 10 mbar of H<sub>2</sub>S with 0 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.

The calculated corrosion rates from the strong acid and H<sub>2</sub>S models were compared to the experimental LPR corrosion rates in order to determine the accuracy of each model's corrosion rate prediction. The resulting corrosion rate comparison can be seen in Figure 45. The strong acid corrosion model (0 ppm HAc and 0 mbar H<sub>2</sub>S) overpredicted the corrosion rates that were determined experimentally. This was found to be partially due to the usage of a different  $\beta_c$  value for the corrosion rate prediction model and the calculation of the corrosion rate *via* LPR. The corrosion rate prediction for the H<sub>2</sub>S corrosion model was relatively close to the corrosion rates that were determined experimentally with the best prediction occurring at 10 mbar of H<sub>2</sub>S. Despite 0.05 mbar being outside the limits of the H<sub>2</sub>S model, the corrosion rate prediction was good, but caution should be taken as this may not always be the case as environmental conditions change.



Figure 45. Comparison between the corrosion rates calculated from the strong acid and H<sub>2</sub>S models and the LPR corrosion rates determined experimentally at 30 °C, pH 4.0, 1000 rpm RDE, and N<sub>2</sub> as the sparge gas.

# 6.2.2 Modeling of H<sub>2</sub>S/CO<sub>2</sub> Corrosion of Mild Steel in the Presence of Acetic Acid

This section will evaluate the accuracy of the developed electrochemical model for  $CO_2$  and  $H_2S/CO_2$  corrosion in the presence of acetic acid at 30 °C, pH 4.0, and a 1000 rpm RDE. Environmental parameters such as pH, temperature, and the mass transfer coefficient were also be varied with 0.1 mbar of  $H_2S$  to further test the accuracy of the  $H_2S/CO_2$  model. The first environment that was modeled involved varying the pH<sub>2</sub>S between 0 and 10 mbar without the presence of acetic acid. The modeled sweep can be seen in Figure 46. The potentiodynamic sweep that was modeled with 0 mbar of  $H_2S$  was done using the  $CO_2$  model. The anodic and cathodic sweep fit the experimental data very well while the corrosion current was overpredicted. This could have been due to the difference in the  $\beta_a$ 

value that was used to calculate the corrosion current *via* LPR and the  $\beta_a$  value used in the electrochemical model. The LPR  $\beta_a$  was 0.040 *V/decade* whereas the model  $\beta_a$  was 0.055 *V/decade* which will cause the LPR corrosion rate to be smaller than the modeled corrosion rate.

The sweeps modeled with 0.1 and 10 mbar of  $H_2S$  were done using the newly modified  $H_2S/CO_2$  model where the fit for the anodic and cathodic sweep was found to be good. The acceleration of the anodic reaction seen when the pH<sub>2</sub>S is increased from 0.1 to 10 mbar was modeled well. The experimental data at 10 mbar of H<sub>2</sub>S exhibited two mass transfer limiting currents that were not predicted by the model. This is found to be because of the use of bulk concentrations of species rather than the surface concentration when calculating the total current density for the H<sup>+</sup> reduction reaction. For this reason, only the overall limiting current is predicted by the model. Despite using the bulk concentrations for species, the limiting currents were predicted with a sufficient amount of accuracy.



Figure 46. Modeled potentiodynamic sweeps for experiments containing 0 - 10 mbar of H<sub>2</sub>S in a H<sub>2</sub>S/CO<sub>2</sub> mixed environment without the presence of acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

The next set of potentiodynamic sweeps that were modeled involved adding 100 and 1000 ppm of free acetic acid to a pure CO<sub>2</sub> environment in order test the accuracy of the CO<sub>2</sub> model in the presence of acetic acid. In order to achieve the best for the model, the  $n_{Fe}^{HAc}$  and  $n_{H^+}^{HAc}$  were varied until the best fit to the experimental data was found. The resulting reaction orders can be seen in Table 16.

<b>Reaction Order</b>	Value	[HAc]free (ppm)
$n_{Fe}^{HAc}$	-0.05	100
$n_{H^+}^{HAc}$	-0.05	100
$n_{Fe}^{HAc}$	-0.12	1000
$n_{H^+}^{HAc}$	-0.08	1000

Table 16. Reaction orders for acetic acid in CO<sub>2</sub> corrosion with 100 and 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and CO<sub>2</sub> as the sparge gas.

The magnitude of the reaction orders is of a significant quantity, but they change depending on the concentration of free acetic acid. In reality, the reaction order should not change with the concentration of the species. Because of this, a singular reaction order of bet fit was chosen to take into account the retardation of the reaction rates caused by the presence of acetic acid. The reaction order that resulted in the best fit for  $n_{Fe}^{HAC}$  and  $n_{H^+}^{HAC}$  was determined to be -0.08 for both the Fe oxidation and H<sup>+</sup> reduction reaction. The modeled sweep using this reaction order for acetic acid can be found in Figure 47.

Retardation of the anodic reaction has been reported in previous research as well as the research conducted in this study, but no literature has been found that supports the retardation of the cathodic reaction that is evident from the fitting exercise completed for this model.<sup>3,42</sup> The reaction orders  $n_{Fe}^{HAc}$  and  $n_{H^+}^{HAc}$  were determined to be negative which signifies a retardation of the calculated current density as the concentration of free acetic acid is increased. This phenomenon could be explained by how acetic behaves when it comes in contact with the steel.

It has been reported in literature that acetic will adsorb onto the surface of the steel and interfere with charge transfer rates of reactions.<sup>3,42,48</sup> For reasons not studied in this
research, the surface coverage achieved during the adsorption of acetic acid onto the surface of the metal will retard the charge transfer rates for both the Fe oxidation reaction and H<sup>+</sup> reduction reaction with the Fe oxidation experiencing more of the retardation than the H<sup>+</sup> reduction. When studying the potentiodynamic sweeps, the H<sup>+</sup> reduction reaction will experience a significant increase in the limiting current which can overshadow any evidence of a slight decrease in the reaction rate resulting from the adsorption of acetic acid. This implies that the decrease in the cathodic reaction rate is due to the surface coverage of the steel by acetic acid and likely has nothing to do with the direct reduction of acetic acid. Taking this into consideration, it is concluded that acetic acid will still follow the buffering effect mechanism in these conditions.



Figure 47. Modeled potentiodynamic sweeps for experiments in CO<sub>2</sub> corrosion containing 0 – 1000 ppm of free acetic acid at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

The anodic reaction with 0 and 100 ppm of free acetic acid was modeled well, but upon increasing the concentration to 1000, the model did not predict a significant further retardation of the anodic reaction. The term intended to account for the influence of acetic acid in equation (28) assumes that the trend will follow a basic power law. Being that the model does not predict the retardation of the anodic reaction with 1000 ppm of free acetic acid as well as it does at 100 ppm, the phenomenon is observed to not follow the power law. Aside from that conclusion, the cathodic reaction as well as the limiting current was modeled well in these conditions.

The next modeled sweeps involved adding 100 and 1000 ppm of free acetic acid to environments containing 0.1 and 10 mbar of H<sub>2</sub>S in a H<sub>2</sub>S/CO<sub>2</sub> mixed environment using the model for H<sub>2</sub>S/CO<sub>2</sub> corrosion. The experimental data showed that acetic acid did not have any influence on the rate of the anodic or cathodic reaction for both partial pressures of H<sub>2</sub>S that were tested. For this reason, the reaction orders  $n_{Fe}^{HAc}$  and  $n_{H^+}^{HAc}$  were set to zero in the H<sub>2</sub>S/CO<sub>2</sub> model. The modeled sweeps can be seen in Figure 48 and Figure 49. The anodic and cathodic reactions are predicted with good accuracy. Being that the model showed good accuracy with  $n_{Fe}^{HAc}$  and  $n_{H^+}^{HAc}$  set to zero, it can be concluded that acetic has no influence on the anodic or cathodic reactions in the H<sub>2</sub>S/CO<sub>2</sub> corrosion environments that were tested thus further validating that acetic acid will follow the buffering effect mechanism in these conditions. The limiting currents in these conditions were slightly underpredicted when compared to the experimental value, but considering the oversimplification that was done involving the effective diffusivity, the accuracy of the prediction model is sufficient.



Figure 48. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 0 – 1000 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.



Figure 49. Modeled potentiodynamic sweeps for experiments in containing 10 mbar of H<sub>2</sub>S and 0 – 1000 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

The calculated corrosion rates from the CO<sub>2</sub> and H<sub>2</sub>S/CO<sub>2</sub> models were compared to the experimental LPR corrosion rates in order to determine the accuracy of each model's corrosion rate prediction. The resulting corrosion rate comparison can be seen in Figure 50. The CO<sub>2</sub> corrosion model (0 - 1000 ppm HAc and 0 mbar H<sub>2</sub>S) overpredicted the corrosion rate at 0 ppm of free acetic acid compared to the corrosion rate that was determined experimentally. This was found to be partially due to the use of a different  $\beta_c$ value for the corrosion rate prediction model and the calculation of the corrosion rate *via* LPR. The corrosion rate prediction was good with 100 ppm of free acetic acid, but overpredicted with 1000 ppm of free acetic acid. This was found to be due to the poor prediction of the increased retardation of the anodic reaction that was observed with 1000 ppm of free acetic acid when compared to the system with only 100 ppm. The corrosion rate prediction for the  $H_2S/CO_2$  corrosion model was overpredicted by only a small amount with the best prediction being at 0.1 mbar of  $H_2S$ .



Figure 50. Comparison between the corrosion rates calculated from the CO<sub>2</sub> and H<sub>2</sub>S/CO<sub>2</sub> models and the LPR corrosion rates determined experimentally at 30 °C, pH 4.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

The next set of modeled potentiodynamic sweeps involves increasing the pH from 4.0 to 5.0 with 0 – 1000 ppm of free acetic acid in the presence of 0.1 mbar of H<sub>2</sub>S at 30 °C and a 1000 rpm RDE. During the modeling of this environment, the parameters  $n_{Fe}^{OH^-}$  and  $i_{o,Fe}^{ref}$  did not fit the model well. For that reason, new parameters for  $n_{Fe}^{OH^-}$  and  $i_{o,Fe}^{ref}$  needed to be found. Through the fitting exercise mentioned in section 6.1.5 Iron Oxidation Reaction, the values for  $n_{Fe}^{OH^-}$  and  $i_{o,Fe}^{ref}$  was determined to be 0.40 and 0.25  $A/m^2$  respectively. The resulting sweeps can be seen in Figure 51 - Figure 53.

Increasing the pH to 5.0 with 0 ppm of free acetic acid shown in Figure 51 resulted in the modeled sweep exhibiting more definitive transition from charge transfer controlled to mass transfer controlled corrosion than what was observed in the experimental data. At 100 and 1000 ppm of free acetic acid shown in Figure 52 - Figure 53, the fit for the anodic and cathodic sweep was better with the best fit being with 1000 ppm of free acetic acid. The limiting current was again underpredicted but is still predicted relatively close to the experimental value.



Figure 51. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 0 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0 and 5.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.



Figure 52. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 100 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0 and 5.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.



Figure 53. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 1000 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0 and 5.0, 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>.

Next set of modeled potentiodynamic sweeps involved increasing the solution temperature from 30 °C to 50 °C with 0 – 1000 ppm of free acetic acid in the presence of 0.1 mbar of H<sub>2</sub>S at pH 4.0 and a 1000 rpm RDE. During the modeling of this environment, the parameters  $E_{rev,H^+}^{ref}$ ,  $E_{a,H^+}$ , and  $i_{o,H^+}^{ref}$  were found to not fit the model well. For that reason, new parameters for  $E_{rev,H^+}^{ref}$ ,  $E_{a,H^+}$ , and  $i_{o,H^+}^{ref}$  needed to be found. The methodology behind the calculation of these new values for  $E_{a,H^+}$  and  $i_{o,H^+}^{ref}$  can be found in Appendix B: Determination of the Activation Energy for the H+ Ion Reduction Reaction in an H2S/CO2 Corrosion Environment. The resulting sweeps can be seen in Figure 54 - Figure 56. The model showed a good fit for the anodic and cathodic sweep with 0 mbar of free acetic acid shown in Figure 54. Increasing the free acetic concentration to 100 and 1000 ppm shown in Figure 55 and Figure 56, the Fe oxidation and H<sup>+</sup> reduction sweep continued to be modeled well with the exception of the H<sup>+</sup> reduction reaction in 1000 ppm of free acetic acid far away from the corrosion potential. The increase in the limiting current with 1000 ppm of free acid present predicted by equation (18)<sup>58</sup> was not as large as the increase seen in the experimental data when the temperature was increased resulting in it being significantly underpredicted.



Figure 54. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 0 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of CO<sub>2</sub>.



Figure 55. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 100 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of CO<sub>2</sub>.



Figure 56. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 1000 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 and 50 °C, pH 4.0, 1000 rpm RDE, and 0.88 bar of CO<sub>2</sub>.

The last set of potentiodynamic sweeps that were modeled involved varying the mass transfer coefficient *via* the RDE rotation rate at 500, 1000, and 2000 rpm with 0 - 1000 ppm of free acetic acid in the presence of 0.1 mbar of H<sub>2</sub>S at 30 °C and pH 4.0. The modeled sweeps can be seen in Figure 57 - Figure 59. It can be seen for all concentrations of free acetic acid, the anodic and cathodic sweeps were modeled well. The increase in the limiting current when the rotation rate was increased was adequately modeled as well. When the rotation rate is increased, the change in corrosion current predicted by the model was almost insignificant for concentrations up to 1000 ppm of free acetic acid. This further validates that the system in these conditions has become primarily charge transfer controlled where the corrosion rate has become nearly independent from the flow.



Figure 57. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 0 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0, 500 - 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>. ( $k_{RDE}$  is equal to 2.06x10<sup>-4</sup>, 2.91x10<sup>-4</sup>, and 4.12x10<sup>-4</sup> m/s, respectively).



Figure 58. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 100 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0, 500 - 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>. ( $k_{RDE}$  is equal to 2.06x10<sup>-4</sup>, 2.91x10<sup>-4</sup>, and 4.12x10<sup>-4</sup> *m/s*, respectively).



Figure 59. Modeled potentiodynamic sweeps for experiments in containing 0.1 mbar of H<sub>2</sub>S and 1000 ppm of free acetic acid in a mixed H<sub>2</sub>S/CO<sub>2</sub> environment at 30 °C, pH 4.0, 500 - 1000 rpm RDE, and 0.96 bar of CO<sub>2</sub>. ( $k_{RDE}$  is equal to 2.06x10<sup>-4</sup>, 2.91x10<sup>-4</sup>, and 4.12x10<sup>-4</sup> *m/s*, respectively).

### **6.3 Conclusions**

An electrochemical model developed by Madani Sani for strong acid,  $CO_2$ , and  $H_2S$  corrosion was modified to incorporate the influence acetic acid has on the involved corrosion mechanisms.<sup>57</sup> The model developed for  $H_2S$  corrosion was also modified for use as a prediction model for  $H_2S/CO_2$  corrosion in the presence of acetic acid. Overall, the model showed good performance in modeling the anodic sweeps, cathodic sweeps, limiting current, and corrosion rate when acetic acid was introduced to the system for the conditions that were tested; the exception being  $CO_2$  corrosion where the retardation of the anodic reaction at 1000 ppm of free acetic acid was not predicted well. This was because

the term inserted into the model for the purpose of accounting for this retardation was assumed to follow a simple power law which was found not to be true.

The simplification of the limiting current equation by simply including the additional H<sub>2</sub>S and HAc species in the effective diffusivity resulted in limiting currents that were consistently underpredicted when compared to the experimental data. These underpredictions were of relatively small magnitude, so it was concluded that they were predicted with a sufficient amount of accuracy considering the oversimplification of the complex buffering of weak acids happening inside of the diffusion boundary layer.

## **Chapter 7. Conclusions and Future Work**

#### 7.1 Final Conclusions

To summarize the work that has been completed in this research, select results from investigating the hypotheses and research questions that were proposed will be summarized in this section. When studying H<sub>2</sub>S corrosion mechanisms at 30 °C and pH 4.0, it was of interest to investigate whether acetic acid would follow the buffering effect mechanism. In this study, acetic acid was found to follow the buffering effect mechanism when 0.05 and 10 mbar of H<sub>2</sub>S was present whereas the experiments conducted with 0.1 mbar of H<sub>2</sub>S require further investigation into whether the buffering effect mechanism is followed.

When studying H<sub>2</sub>S/CO<sub>2</sub> corrosion mechanisms at 30 °C and pH 4.0, a retardation of the anodic reaction was observed without the presence of H<sub>2</sub>S (CO<sub>2</sub> corrosion) when acetic acid was added to the system. Upon introducing 0.1 and 10 mbar of H<sub>2</sub>S to the system, acetic acid no longer will retard the rate of the anodic reaction. This was postulated to be due to the presence of a thin mackinawite layer that will form quickly on the surface of the steel that will interfere with the adsorption process of acetic acid. It was also concluded that acetic acid does in fact follow the buffering effect mechanism when 0 - 10mbar of H<sub>2</sub>S was present with up to 1000 ppm of free acetic acid.

Long term experiments in a H<sub>2</sub>S/CO<sub>2</sub> corrosion environment lasting 72 hours at 30 °C and pH 4.0 were conducted in order to study the effect acetic acid would have on corrosion rates over time and if a detectable sulfide layer will form given an extended amount of time. It was found that 1000 ppm of free acetic did not increase the steady state corrosion rates in the conditions that were tested. The final recorded corrosion rate for both

experiments was 0.28 mm/yr. Even after 72 hours of exposure with and without 1000 ppm of free acetic acid and 0.1 mbar of  $H_2S$ , a Raman spectroscopy analysis was not able to detect any significant amount of sulfide species, namely surface mackinawite. The EDS spectrum for both experiments did detect sulfur on the surface of the steel, but the specific sulfide species was not able to be determined. This section of the study confirmed that even after 72 hours of exposure, there is no detectable layer that forms on the surface of the steel therefore validating that the system still exhibits bare steel corrosion even at longer exposure times in the conditions that were tested.

An electrochemical model was created that predicts the potentiodynamic sweeps and corrosion rates in strong acid, H<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>S/CO<sub>2</sub> corrosion in the presence of acetic acid with sufficient accuracy. The retardation of the anodic reaction due to the presence of acetic acid in CO<sub>2</sub> corrosion was not modeled well with 1000 ppm of free acetic acid due to the model using a power law to incorporate this retardation which was found to not be the case. Incorporation of the additional H<sub>2</sub>S and HAc species in the effective diffusivity term in the limiting current equation resulted in limiting current predictions with a sufficient amount of accuracy considering the oversimplification of the complex buffering of weak acids happening inside of the diffusion boundary layer. All of these conclusions are neatly summarized in Table 17 and Table 18.

RESEARCH HYPOTHESES						
Hypothesis	Hypothesis Testing Result	Explanation				
Like in $CO_2$ environments, acetic acid in $H_2S$ environments is not directly reduced, it only increases the limiting current associated with the cathodic reaction.	<ul> <li>Hypothesis was accepted for 0.05 and 10 mbar of H<sub>2</sub>S.</li> <li>Hypothesis was inconclusive for 0.1 mbar of H<sub>2</sub>S.</li> </ul>	Acetic acid was found to only increase the limiting current associated with the cathodic reaction when 0.05 and 10 mbar of H <sub>2</sub> S was present whereas the experiments conducted with 0.1 mbar of H <sub>2</sub> S require further investigation.				
Like in $CO_2$ environments, acetic acid in $H_2S/CO_2$ mixed environments will retard the anodic dissolution rate at low temperatures.	Hypothesis was rejected for all conditions tested	A retardation of the anodic reaction was observed without the presence of $H_2S$ (CO <sub>2</sub> corrosion) when acetic acid was added to the system. Upon introducing 0.1 and 10 mbar of $H_2S$ to the system, acetic acid no longer will retard the rate of the anodic reaction.				
Acetic acid will increase the steady state corrosion rate in $H_2S/CO_2$ mixed environments.	Hypothesis was rejected for all conditions tested	1000 ppm of free acetic did not increase the steady state corrosion rates in the conditions that were tested.				

Table 17. Summary of the important research hypotheses that were proposed in this research and their results.

RESEARCH QUESTIONS				
Research Question	Explanation			
How does the concentration of free acetic acid influence the anodic and cathodic reactions in H <sub>2</sub> S environments?	Acetic acid will only increase the limiting current associated with the cathodic reaction when 0.05 and 10 mbar of $H_2S$ was present whereas the experiments conducted with 0.1 mbar, in addition to the increase in the limiting current, a possible increase in the rate of the cathodic reaction was observed.			
Considering that acetic acid follows the buffering effect mechanism in strong acid and $CO_2$ environments, will the same be true in a $H_2S/CO_2$ mixed environment?	This was found to be true through the experimental data and the modeling, acetic acid will follow the buffering effect mechanism in a $H_2S/CO_2$ mixed environment.			
Will exposing mild steel to low partial pressure $H_2S$ environment for an extended period of time allow for a detectable sulfide layer to form?	Through the use of EDS and Raman spectroscopy, EDS was able to detect sulfur on the surface of the steel, but the identity of the sulfide species was not able to be determined by Raman spectroscopy.			
Are the experiments conducted previously involving short term testing still valid at longer exposure times when small amounts of H <sub>2</sub> S are present?	This study confirmed that even after 72 hours of exposure, there is no detectable layer that forms on the surface of the steel therefore validating that the system still exhibits bare steel corrosion even at longer exposure times in the conditions that were tested.			

Table 18. Summary of the important research questions that were proposed in this research and their results.

# 7.2 Future Work

During the progress of this research, topics that would further enhance the quality of the current research or provide direction to meaningful future research have been included in the list below.

- Design experiments to better investigate the influence of acetic acid on pitting corrosion in the environments studied in this work.
- Taking the current work and extending it beyond bare steel corrosion. Much work has been done on how acetic acid will influence the formation of FeCO<sub>3</sub> in CO<sub>2</sub> corrosion, but little work has investigated how it would influence the formation of iron sulfide layers in H<sub>2</sub>S corrosion or layer formation in a H<sub>2</sub>S/CO<sub>2</sub> mixed environment.
- The usage of X-ray photoelectron spectra (XPS) would likely be able to better detect the presence of a thin mackinawite layer than the surface analysis techniques that were used in this study. This method was used by Lee in their research and was successful in identifying the thin layer of mackinawite that had formed in conditions similar to this study.<sup>39</sup>
- More data from experiments must be collected with more concentrations of free acetic acid in order to more accurately account for the retardation of the anodic reaction from acetic acid in the strong acid and CO<sub>2</sub> corrosion model.
- Extend the H<sub>2</sub>S and H<sub>2</sub>S/CO<sub>2</sub> corrosion models developed in this work to partial pressures of H<sub>2</sub>S higher than 10 mbar, temperatures higher than 50 °C, and pH values higher than 5.0.
- The experimental data collected and model that was developed in this work can be used to test the accuracy and be incorporated into a corrosion prediction software such as MULTICORP<sup>™</sup> to better improve its performance in high organic acid concentration environments.

#### References

- Sankata, P. Corrosion Control in the Oil and Gas Industry. In *Corrosion Control in the Oil and Gas Industry*; Elsevier: Amsterdam, Netherlands, 2014; p xxi.
- (2) Robertson, T.; DeCola, E.; Pearson, L. Final Report on North Slope Spills Analysis and Expert Panel Recommendations and Mitigation Measures; Final Report; 2010; p 268.
- (3) Crolet, J.-L.; Thevenot, N.; Dugstad, A. Role of Free Acetic Acid on the CO<sub>2</sub> Corrosion of Steels; Paper No. 24; NACE International, 1999; p 16.
- (4) Kahyarian, A.; Brown, B.; Nešić, S. Mechanism of Cathodic Reactions in Acetic Acid Corrosion of Iron and Mild Steel. *Corrosion* 2016, 72 (12), 1539–1546.
- (5) Tran, T.; Brown, B.; Nesic, S.; Tribollet, B. Investigation of the Mechanism for Acetic Acid Corrosion of Mild Steel; Paper No. 2487; NACE International, 2013; p 12.
- (6) Oddo, J. E.; Tomson, M. B. Simplified Calculation of CaCO<sub>3</sub> Saturation at High Temperatures and Pressures in Brine Solutions. *J. Pet. Technol.* 1982, *34* (07), 1583– 1590.
- (7) Marshall, W. L.; Franck, E. U. Ion Product of Water Substance, 0–1000 °C, 1–10,000
   Bar New International Formulation and Its Background. J. Phys. Chem. Ref. Data 1981, 10 (2).
- (8) Palmer, D. A.; Van Eldik, R. The Chemistry of Metal Carbonato and Carbon Dioxide Complexes. *Chem. Rev.* 1983, *83* (6), 651–731.
- (9) Ma, Z.; Brown, B.; Nesic, S.; Singer, M. Precipitation Kinetics of FeCO<sub>3</sub> in Non-Ideal Solutions; Paper No. 14987; NACE International, 2020; p 13.

- (10) Sun, W.; Nesic, S. Basics Revisited: Kinetics of Iron Carbonate Scale Precipitation in CO<sub>2</sub> Corrosion; Paper No. 06365; NACE International, 2006; p 21.
- (11) Fajardo, V.; Eslami, M.; Choi, Y.-S.; Brown, B.; Nesic, S. Influence of Acetic Acid on the Integrity and Protectiveness by an Iron Carbonate (FeCO<sub>3</sub>) Layer. *Corros. J.* 2021, 77 (1), 15.
- (12) Nafday, O. A.; Nesic, S. Iron Carbonate Scale Formation and CO<sub>2</sub> Corrosion in the Presence of Acetic Acid; Paper No. 05295; NACE International, 2005; p 27.
- (13) Kermani, M. B.; Morshed, A. Carbon Dioxide Corrosion in Oil and Gas Production
   A Compendium. *Corrosion* 2003, *59* (8), 659–683.
- (14) Farelas, F.; Brown, B.; Nesic, S. Iron Carbide and Its Influence on the Formation of Protective Iron Carbonate in CO<sub>2</sub> Corrosion of Mild Steel; Paper No. 2219; NACE International, 2013; p 15.
- (15) Ayyagari, S.; Brown, B.; Nesic, S. Effect of Acetic Acid on Corrosion Product Layer Formation in Aqueous CO<sub>2</sub> Environments; Paper No. 19306; Association for Materials Protection and Performance, 2023; p 13.
- (16) Tran, T.; Brown, B.; Nesic, S. Corrosion of Mild Steel in an Aqueous CO<sub>2</sub> Environment - Basic Electrochemical Mechanisms Revisited; Paper No. 5671; NACE International, 2015; p 11.
- (17) Kahyarian, A.; Nesic, S. Mechanisms of CO<sub>2</sub> Corrosion of Mild Steel: A New Narrative; Paper No. 11232; NACE International, 2018; p 16.

- (18) Gray, L.; Anderson, B.; Danysh, M.; Tremaine, P. Mechanisms of Carbon Steel Corrosion in Brines Containing Dissolved Carbon Dioxide at pH 4; Paper No. 464; NACE, 1989; p 20.
- (19) Nesic, S.; Postlethwaite, J.; Olsen, S. An Electrochemical Model for Prediction of Corrosion of Mild Steel in Aqueous Carbon Dioxide Solutions. *Corrosion* 1996, *52* (4), 280–294.
- (20) Schmitt, G.; Rothman, B. Studies on the Corrosion Mechanism of Unalloyed Steel on Oxygen-Free Carbon Dioxide Solutions Part 1. Kinetics of the Liberation of Hydrogen Part 2. Kinetics of Iron Dissolution. In *Werkstoffe und Korrosion*; 1977; Vol. 28, pp 154–166.
- (21) de Waard, C.; Lotz, U. Prediction of CO<sub>2</sub> Corrosion of Carbon Steel; Paper No. 69;
   NACE, 1993; p 17.
- (22) Pots, B. F. M. Mechanistic Models for the Prediction of CO<sub>2</sub> Corrosion Rates Under Multi-Phase Flow Conditions; Paper No. 137; NACE International, 1995; p 20.
- (23) Sardisco, J. B.; Pitts, R. E. Mechanism of Sulfide Film Formation and Kinetics of Corrosion Reaction. *Corrosion* 1965, *21* (8), 245–253.
- Ma, Z. Precipitation Kinetics of FeCO<sub>3</sub> and FeS on Steel Substrate. Dissertation, Ohio University, Athens, OH, 2021.
- (25) Migdisov, A. A.; Williams-Jones, A. E.; Lakshtanov, L. Z.; Alekhin, Y. V. Estimates of the Second Dissociation Constant of H<sub>2</sub>S from the Surface Sulfidation of Crystalline Sulfur. *Geochim. Cosmochim. Acta* 2002, *66* (10), 1713–1725.

- (26) Kahyarian, A.; Nesic, S. H<sub>2</sub>S Corrosion of Mild Steel: A Quantitative Analysis of the Mechanism of the Cathodic Reaction. *Electrochimica Acta* 2019, *297*, 676–684.
- (27) Zheng, Y.; Brown, B.; Nesic, S. Electrochemical Study and Modeling of H<sub>2</sub>S
   Corrosion of Mild Steel. *Corros. J.* 2014, *70* (4), 15.
- (28) Kittel, J.; Ropital, F.; Grosjean, F.; Sutter, E. M. M.; Tribollet, B. Corrosion Mechanisms in Aqueous Solutions Containing Dissolved H<sub>2</sub>S. Part 1: Characterization of H<sub>2</sub>S Reduction on a 316L Rotating Disc Electrode. *Corros. Sci.* 2013, *66*, 324–329.
- (29) Abdar, P. S.; Hariri, M. B.; Kahyarian, A.; Nesic, S. A Revision of Mechanistic Modeling of Mild Steel Corrosion in H<sub>2</sub>S Environments. *Electrochimica Acta* 2021, *382*, 11.
- (30) Anderko, A.; Young, R. D. Simulation of CO<sub>2</sub>/H<sub>2</sub>S Corrosion Using Thermodynamic and Electrochemical Models; Paper No. 31; NACE International, 1999; p 19.
- (31) Brown, B.; Parakala, S. R.; Nesic, S. CO<sub>2</sub> Corrosion in the Presence of Trace Amounts of H<sub>2</sub>S; Paper No. 04736; NACE International, 2004; p 28.
- (32) Singer, M.; Brown, B.; Camacho, A.; Nesic, S. Combined Effect of CO<sub>2</sub>, H<sub>2</sub>S and Acetic Acid on Bottom of the Line Corrosion; Paper No. 07661; NACE International, 2007; p 25.
- (33) Cutright, A.; Brown, B.; Nesic, S.; Singer, M.; Young, D. Onset of Corrosion Rate Retardation at Very Low Concentrations of H<sub>2</sub>S in a CO<sub>2</sub> Environment; Paper No. 16676; NACE International, 2021; p 10.

- (34) Greco, E. C.; Wright, W. B. Corrosion of Iron in an H<sub>2</sub>S-CO<sub>2</sub>-H<sub>2</sub>O System. *Corrosion* 1962, 18, 119–124.
- (35) Lee, K.-L. J.; Nesic, S. EIS Investigation of CO<sub>2</sub>/H<sub>2</sub>S Corrosion; Paper No. 04723;
   NACE International, 2004; p 13.
- (36) Smith, S. M.; Pacheco, J. L. Prediction of Corrosion in Slightly Sour Environments;Paper No. 02241; NACE International, 2002; p 16.
- (37) Sun, W.; Nesic, S. A Mechanistic Model of H<sub>2</sub>S Corrosion of Mild Steel; Paper No.
   07655; NACE International, 2007; p 26.
- (38) Ning, J.; Zheng, Y.; Young, D.; Brown, B.; Nešić, S. Thermodynamic Study of Hydrogen Sulfide Corrosion of Mild Steel. *Corrosion* 2014, *70* (4), 375–389.
- (39) Lee, K.-L. J. A Mechanistic Modeling of CO<sub>2</sub> Corrosion of Mild Steel in the Presence of H<sub>2</sub>S. Dissertation, Ohio University, Athens, OH, 2004.
- (40) Shoesmith, D. W.; Taylor, P.; Bailey, M. G.; Owen, D. G. The Formation of Ferrous Monosulfide Polymorphs during the Corrosion of Iron by Aqueous Hydrogen Sulfide at 21°C. *Electrochem. Sci. Technol.* 1980, *127*, 1007–1015.
- (41) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. pKa Prediction for Organic Acids and Bases; Chapman and Hall: London, 1981.
- (42) George, K. S.; Nesic, S. Investigation of Carbon Dioxide Corrosion of Mild Steel in the Presence of Acetic Acid - Part 1: Basic Mechanisms. *Corrosion* 2007, 178–186.
- (43) Amri, J.; Gulbrandsen, E.; Nogueira, R. P. Role of Acetic Acid in CO<sub>2</sub> Top of the Line Corrosion of Carbon Steel; Paper No. 11329; NACE International, 2011; p 22.

- (44) Garsany, Y.; Pletcher, D.; Hedges, B. The Role of Acetate in CO<sub>2</sub> Corrosion of Carbon Steel: Has the Chemistry Been Forgotten?; Paper No. 02273; NACE International, 2002; p 16.
- (45) Gulbrandsen, E.; Bilkova, K. Solution Chemistry Effects on Corrosion of Carbon Steels in the Presence of CO<sub>2</sub> and Acetic Acid; Paper No. 06364; NACE International, 2006; p 37.
- (46) Okafor, P. C.; Brown, B.; Nesic, S. CO<sub>2</sub> Corrosion of Carbon Steel in the Presence of Acetic Acid at Higher Temperatures. J. Appl. Electrochem. 2009, 39 (6), 873–877.
- (47) Kharaka, Y. K.; Gunter, W. D.; Aggarwal, P. K. Solmineq 88: A Computer Program for Geochemical Modeling of Water Rock Interactions.
- (48) Kahyarian, A.; Schumaker, A.; Brown, B.; Nesic, S. Acidic Corrosion of Mild Steel in the Presence of Acetic Acid: Mechanism and Prediction. *Electrochimica Acta* 2017, 258, 639–652.
- (49) Camacho, A. Study and Modeling of the Localized Nature of Top of the Line Corrosion. Thesis, Ohio University, Athens, OH, 2006.
- (50) Airgas USA. Hydrogen Sulfide Safety Data Sheet; SDS No. 001029; Airgas USA:
   Radnor, PA, 2021; p 12.
- (51) Kahyarian, A. Mechanism and Prediction of Mild Steel Corrosion in Aqueous Solutions Containing Carboxylic Acids, Carbon Dioxide, and Hydrogen Sulfide. Dissertation, Ohio University, Athens, OH, 2018.
- (52) Tran, T. N. B. Corrosion Mechanisms of Mild Steel in Weak Acids. Dissertation, Ohio University, Athens, OH, 2017.

- (53) Bockris, J. O.; Drazic, D.; Despic, A. R. The Electrode Kinetics of the Deposistion and Dissolution of Iron. *Electrochimica Acta* 1961, *4*, 325–361.
- (54) Nesic, S.; Thevenot, N.; Crolet, J.-L.; Drazic, D. M. Electrochemical Properties of Iron Dissolution in the Presence of CO<sub>2</sub> - Basics Revisited; Paper No. 3; NACE International, 1996; p 23.
- (55) Al-Asadi, A. A. Iron Carbide Development and Its Effect on Inhibitor Performance. Theis, Ohio University, 2014.
- (56) ASTM. Standard Guide for Laboratory Immersion Corrosion Testing of Metals, 2021.
- (57) Madani Sani, F. The Effect of Salt Concentration on Aqueous Strong Acid, Carbon Dioxide, and Hydrogen Sulfide Corrosion of Carbon Steel. Dissertation, Ohio University, Athens, OH, 2021.
- (58) Nesic, S.; Madani Sani, F. Calculation of Cathodic Limiting Current Density in Weak Acids: Part I. Aqueous CO<sub>2</sub> Solutions. *J. Electrochem. Soc.* 2023, *170* (1), p 11.
- (59) Nesic, S. Corrosion of Mild Steel in Weak Acids; in press, 2023.
- (60) Physicochemical Hydrodynamics: V. G. Levich Festschrift; Spalding, D. B., Levič,
   V. G., Imperial College of Science and Technology, Eds.; Advance Publ: London,
   1977.
- (61) ASTM. Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements, 1994.

# Appendix A: Determination of the RDE Mass Transfer Coefficient *via* the Dimensionless Sherwood, Reynolds, and Schmidt Number for RDE hydrodynamics

The mass transfer coefficient for an RDE can be found by using a mass transfer correlation what was derived by Levich in terms of dimensionless numbers.<sup>60</sup> This correlation is shown in Equation 1.

$$Sh = 0.62Re^{0.5}Sc^{0.33}$$
 1

The Sherwood number (*Sh*), Sh = kd/D, is the dimensionless equivalent of the mass transfer coefficient where k is the mass transfer coefficient in m/s, d is the RDE diameter in m, and D is the diffusion coefficient of the reacting species in  $m^2/s$ . The Reynolds number (*Re*), Re = Vd/v, is the dimensionless relationship between the inertial and viscous forces in the fluid where V is the linear flow velocity in m/s, d is the RDE diameter in m, and v is the kinematic viscosity in  $m^2/s$ . The Schmidt number (*Sc*), Sc = v/D, is the dimensionless relationship between the effectiveness of momentum and mass transfer where v is the kinematic viscosity in  $m^2/s$ , and D is the diffusion coefficient of the reacting species in  $m^2/s$ . After substituting these dimensionless relationships into Equation 1 and simplifying, one can solve for the mass transfer coefficient k. The mass transfer coefficient for an RDE is shown in Equation 2.

$$k_{RDF} = 0.62D^{2/3} v^{-1/6} \omega^{1/2}$$

Where D is the diffusion coefficient of the reacting species in  $m^2/s$ , v is the kinematic viscosity in  $m^2/s$ , and  $\omega$  is the angular velocity in radians/s.

# Appendix B: Determination of the Activation Energy for the H<sup>+</sup> Ion Reduction Reaction in an H<sub>2</sub>S/CO<sub>2</sub> Corrosion Environment<sup>59</sup>

The determination of the activation energy for the H<sup>+</sup> reduction reaction,  $E_{a,H^+}$ , can be found using the following methodology. To start the calculation, one must start with the fully expanded equation used to calculate the charge transfer current density for the H<sup>+</sup> reduction reaction with the reference reversible potential substituted in for the thermodynamic reversable potential. The expanded equation written with base 10 exponents can be seen in equation 1 below.

$$i_{\alpha,H^+} = i_{o,H^+}^{ref} \left(\frac{c_{H^+}}{c_{H^+}^{ref}}\right)^{n_{H^+}^{H^+}} \left(10^{-\frac{E_{a,H^+}}{2.303R}\left(\frac{1}{T} - \frac{1}{T^{ref}}\right)}\right) \left(10^{\left(-\frac{\alpha_{c,H^+}F\left(E - E_{rev}^{ref}\right)}{2.303RT}\right)}\right)$$
 1

In this equation, there is four variables that are unknown and need to be determined experimentally,  $i_{o,H^+}^{ref}$ ,  $n_{H^+}^{H^+}$ ,  $E_{a,H^+}$ , and  $\alpha_{c,H^+}$ . In order to determine  $i_{o,H^+}^{ref}$  and  $E_{a,H^+}$ , the variables of interest, one must vary these variables while keeping the other unknows constant at the reference point to observe what happens with  $i_{\alpha,H^+}$ . This is done in this study by varying the temperature of an experiment at the selected reference H<sup>+</sup> concentration,  $c_{H^+}^{ref}$ , while measuring the current density at the defined reference reversible potential. The following variables are kept constant at their reference point and substituted into equation 1:

$$E = E_{rev}^{ref}$$
$$c_{H^+} = c_{H^+}^{ref}$$

After substituting these variables into equation 1, the equation can be simplified to yield the following equation:

$$i_{\alpha,H^+} = i_{o,H^+}^{ref} \left( 10^{-\frac{E_{a,H^+}}{2.303R} \left(\frac{1}{T} - \frac{1}{T^{ref}}\right)} \right)$$
 2

Taking the base 10 log of both sides will result in the final equation that will be plotted in order to calculate the  $i_{o,H^+}^{ref}$  and  $E_{a,H^+}$ .

$$log(i_{\alpha,H^+}) = log(i_{o,H^+}^{ref}) - \frac{E_{a,H^+}}{2.303R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)$$
3

Where the equation takes the form of a typical liner y = mx + b formula. The  $log(i_{\alpha,H^+})$  is plotted versus the  $\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)$  where the slope will be equal to  $\frac{E_{\alpha,H^+}}{2.303R}$  and the y-intercept will be  $log(i_{\alpha,H^+}^{ref})$ . The  $i_{\alpha,H^+}$  is determined from the potentiodynamic sweep at the defined reference potential and the temperature is whatever temperature the potentiodynamic sweep was collected at in *K*. This can be done for as many temperatures as deemed necessary. From here, the  $i_{\alpha,H^+}^{ref}$  and  $E_{\alpha,H^+}$  can be back calculated from the plot itself. The data and plot that was created in this study using the methodology explained in this section can be seen in Table 1 and Figure 1.

Table 1. Data collected from potentiodynamic sweeps and plotted for determining the activation energy for the H<sup>+</sup> reduction reaction in an H<sub>2</sub>S/CO<sub>2</sub> corrosion environment.

Experimental Conditions	E (V vs. sat. Ag/AgCl)	Т (К)	$i_{\alpha,H^+}$ (A/m <sup>2</sup> )	$log\left( i_{lpha,H^{+}}^{ref} ight)$	$\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)$
0.1 mbar H <sub>2</sub> S 100 ppm HAc	-0.6850	303.15	2.019	0.305	-1.13 x10 <sup>-4</sup>
0.1 mbar H <sub>2</sub> S 100ppm HAc	-0.6849	323.15	3.564	0.552	$-3.17 \text{ x} 10^{-4}$



Figure 1. Plot of  $log(i_{\alpha,H^+}^{ref})$  vs.  $(\frac{1}{T} - \frac{1}{T_{ref}})$  for determining the activation anergy for the H<sup>+</sup> reduction reaction in an H<sub>2</sub>S/CO<sub>2</sub> corrosion environment.

From this plot,  $i_{o,H^+}^{ref}$  was determined to be 1.18  $A/m^2$  and  $E_{a,H^+}$  was determined to be 23141 *J/mol*.



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