EVALUATION OF THIOSULFATE AS A SUBSTITUTE FOR HYDROGEN SULFIDE IN SOUR CORROSION FATIGUE STUDIES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Mariano Alberto Kappes

Graduate Program in Materials Science and Engineering

The Ohio State University

2011

Dissertation Committee:
Professor Gerald Frankel, Advisor
Professor Rudolph Buchheit
Professor Katharine Flores
Dr. Narasi Sridhar
ABSTRACT

This work evaluates the possibility of replacing hydrogen sulfide (H$_2$S) with thiosulfate anion (S$_2$O$_3^{2-}$) in sour corrosion fatigue studies. H$_2$S increases the corrosion fatigue crack growth rate (FCGR) and can be present in carbon steel risers and flowlines used in off-shore oil production. Corrosion tests with gaseous H$_2$S require special facilities with safety features, because H$_2$S is a toxic and flammable gas. The possibility of replacing H$_2$S with S$_2$O$_3^{2-}$, a non-toxic anion, for studying stress corrosion cracking of stainless and carbon steels in H$_2$S solutions was first proposed by Tsujikawa et al. (Tsujikawa et al., Corrosion, 1993. 49(5): p. 409-419). In this dissertation, Tsujikawa work will be extended to sour corrosion fatigue of carbon steels.

H$_2$S testing is often conducted in deareated condition to avoid oxygen reaction with sulfide that yields sulfur and to mimic oil production conditions. Nitrogen deareation was also adopted in S$_2$O$_3^{2-}$ testing, and gas exiting the cell was forced through a sodium hydroxide trap. Measurements of the sulfide content of this trap were used to estimate the partial pressure of H$_2$S in nitrogen, and Henry’s law was used to estimate the content of H$_2$S in the solution in the cell. H$_2$S was produced by a redox reaction of S$_2$O$_3^{2-}$, which required electrons from carbon steel corrosion. This reaction is spontaneous at the open circuit potential of steel. Therefore, H$_2$S concentration was expected to be
maximum at the steel surface, and this concentration was estimated by a mass balance analysis.

Carbon steel specimens exposed to $S_2O_3^{2-}$ containing solutions developed a film on their surface, composed by iron sulfide and cementite. The film was not passivating and a good conductor of electrons. Hydrogen permeation experiments proved that this film controls the rate of hydrogen absorption of steels exposed to thiosulfate containing solutions. The absorption of hydrogen in $S_2O_3^{2-}$ solutions was compared with the absorption of hydrogen in solutions saturated with different H$_2$S partial pressures. The partial pressure was selected so that the concentration of H$_2$S in the solution saturated with the gas would be the same as that reached in the surface of steel freely corroding in the thiosulfate solution. For solutions obtained by bubbling H$_2$S, the rate of hydrogen absorption increased with the partial pressure of the gas, but the rate of hydrogen absorption reached a maximum at $10^{-3}$ M $S_2O_3^{2-}$, despite the surface concentration of H$_2$S increased with the concentration of $S_2O_3^{2-}$. This effect was associated with the formation of thicker films, which inhibited the absorption of hydrogen.

FCGR were evaluated at constant stress intensity factor range, $\Delta K$. Crack length was monitored in-situ by the direct current potential drop (DCPD) method. FCGR increased with the partial pressure of H$_2$S in nitrogen. FCGR was controlled not only by the amount of hydrogen present in the steel, but also by inhibiting contributions like crack closure and crack tip blunting. FCGR in dilute thiosulfate solutions was near that
measured in a solution saturated with a partial pressure of H$_2$S equal to 0.56 kPa, in accord with hydrogen permeation results.
To Flor and my parents
ACKNOWLEDGEMENTS

This work was funded by a gift from Det Norske Veritas in support of the DNV chair in corrosion at The Ohio State University, Prof. Gerald Frankel. I would like to thank Prof. Gerald Frankel for encouraging me to apply to graduate school and for his advice during those years. He also corrected this manuscript in content and style. Dr. Narasi Sridhar, from DNV Inc., was closely involved in this project and helped to inspire the research detailed here. I would also like to acknowledge discussions and suggestions from the rest of the committee members.

I would like to thank my colleagues at the Fontana Corrosion Center for the continuous support, especially Dr. Federico Gambina, Leonel Chiacharelli, Anusha Chilukuri, Dr. Kevin Ralston, Brendy Rincon-Troconis, Liu Cao, Xiaoji Li, Huang Lin and Dr. Belinda Hurley. The assistance of Christine Putnam with purchases is also greatly acknowledged.

I thank Hedrick Colijn for support with the X-ray diffractometer, Cameron Begg for help with the scanning electron microscope, and Dr. Lisa Hommel, for support during the use of the X-ray photoelectron spectrometer.
Part of the experimental work presented here was performed at the “Instituto de Tecnología Prof. J. Sabato” in San Martín, Argentina. I would like to specially thank Prof. Ricardo Carranza not only for providing laboratory space and equipment for electrochemistry tests, but also for his advice during my stays in Argentina and for his valuable comments on this manuscript. I also acknowledge the technical support from Mabel Giordano with potentiostats and electrochemical cells. I thank Dr. Pablo Bruzzoni for discussions about hydrogen permeation experiments.

The hydrogen permeation and corrosion fatigue tests were performed in the hydrogen sulfide laboratories of DNV Inc. Dr. Ramgopal Thodla provided invaluable support for those tests, and helped to define the details of the experimental approach. Brandon Gerst and Scott Harrods are deeply acknowledged for their technical support for the corrosion fatigue tests and safe handling of hydrogen sulfide cylinders. Without their help, Chapter 5 of this dissertation would not have been completed. I also acknowledge the assistance of Ken Evans, Steven Waters, Martin Mueller and the rest of the hydrogen sulfide team at DNV Inc., who assured that all the tests in chapter 5 involving H₂S could be performed in a safe working environment.

Finally, I would like to thank my wife, Florencia Viceconte, for being on my side since the beginning and for encouraging me to finish my thesis. I also thank to my parents, Irma and José, and family and friends for the continuous support.
VITA

2006 ................................................. Materials Engineer, Instituto de Tecnologia "Prof J. Sabato", Argentina

2009 ................................................. M.S. Materials Science and Engineering, The Ohio State University

June 2007 to present .......................... Graduate Research Associate, Materials Science and Engineering, The Ohio State University

Publications


“The Usefulness of Ultra-High Resolution Microstructural Studies for Understanding Localized Corrosion Behavior of Al Alloys”, M. Kappes, L. Kovarik, M. J. Mills, G. S.

**Fields of Study**

Major Field: Materials Science and Engineering
# TABLE OF CONTENTS

Abstract ........................................................................................................................................ ii

Acknowledgements ......................................................................................................................... vi

Vita ................................................................................................................................................ viii

Table of Contents .......................................................................................................................... x

List of Tables ................................................................................................................................ xv

List of Figures ............................................................................................................................... xvii

Chapter 1. Introduction .................................................................................................................. 1

1.1. References .............................................................................................................................. 4

Chapter 2. Literature review ......................................................................................................... 6

2.1. Corrosion fatigue of carbon steels in sour environments ................................................. 7

2.1.1. Effect of mechanical variables ......................................................................................... 7

2.1.2. Effect of environmental variables .................................................................................. 10

2.1.3. Experimental approaches .............................................................................................. 14

2.2. Electrochemistry of hydrogen sulfide vs. thiosulfate solutions ....................................... 16

x
2.2.1. Surface films formed on iron and steel in H$_2$S solutions .......... 17
2.2.2. Chemistry of thiosulfate solutions ........................................... 19
2.2.3. Hydrogen absorption................................................................. 22
2.2.4. Degradation of steels in thiosulfate solutions ......................... 32
2.3. Unsolved issues ........................................................................... 38
2.4. Figures ......................................................................................... 41
2.5. References .................................................................................... 45

Chapter 3. Reaction paths of thiosulfate during corrosion of carbon steel in substituted NACE TM0177-96 solutions ................................................. 58

3.1. Introduction .................................................................................. 58
3.2. Experimental.................................................................................. 63
  3.2.1. Hydrogen sulfide generation tests............................................. 64
  3.2.2. Quantification of sulfide film.................................................... 67
  3.2.3. Quantification of sulfur in the bulk of the solution.................... 70
3.3. Results .......................................................................................... 71
  3.3.1. Hydrogen sulfide generation tests.......................................... 71
  3.3.2. Quantification of sulfur content in the film and in the bulk solution
<table>
<thead>
<tr>
<th>3.4.</th>
<th>Discussion .................................................................................................................. 79</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5.</td>
<td>Conclusions .............................................................................................................. 88</td>
</tr>
<tr>
<td>3.6.</td>
<td>Tables ....................................................................................................................... 91</td>
</tr>
<tr>
<td>3.7.</td>
<td>Figures ..................................................................................................................... 94</td>
</tr>
<tr>
<td>3.8.</td>
<td>References ............................................................................................................... 104</td>
</tr>
</tbody>
</table>

Chapter 4. Corrosion behavior of carbon steel in acidified thiosulfate-containing brines ......................................................................................................................................... 108

<table>
<thead>
<tr>
<th>4.1.</th>
<th>Introduction ............................................................................................................. 108</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.</td>
<td>Experimental ......................................................................................................... 111</td>
</tr>
<tr>
<td>4.2.1.</td>
<td>Electrochemical tests .......................................................................................... 111</td>
</tr>
<tr>
<td>4.2.2.</td>
<td>Characterization of film structure ..................................................................... 116</td>
</tr>
<tr>
<td>4.3.</td>
<td>Results ................................................................................................................... 118</td>
</tr>
<tr>
<td>4.3.1.</td>
<td>Electrochemical tests .......................................................................................... 118</td>
</tr>
<tr>
<td>4.3.2.</td>
<td>Characterization of film structure ..................................................................... 122</td>
</tr>
<tr>
<td>4.4.</td>
<td>Discussion ............................................................................................................. 124</td>
</tr>
<tr>
<td>4.5.</td>
<td>Conclusions ......................................................................................................... 137</td>
</tr>
<tr>
<td>4.6.</td>
<td>Tables ................................................................................................................... 139</td>
</tr>
</tbody>
</table>
Chapter 6. Conclusions and recommendations for future work

6.1. Conclusions

6.2. Recommendations for future work

6.3. References

Bibliography
LIST OF TABLES

Table 3.1. Results of the H$_2$S generation test experiments. Slope is the slope of the fitting line in Figure 3.1, $\chi_{H_2S_{gas}}$ is the molar fraction of H$_2$S in the gas, $S_{2-\text{trap}}$ (end of test) is the number of mols in the trap at the end of the test, $\chi_{H_2S_{solution}}$ is the molar fraction of H$_2$S in the solution at steady state, $H_2S_{cell}$ is the number of mols in the cell at steady state, $[H_2S]_{cell}$ is the concentration of H$_2$S in the cell at steady state, $[H_2S]_{steel~surface}$ is the concentration of H$_2$S close to the steel surface and $f_{\text{trap}}$ is the fraction of thiosulfate that ended up as sulfide in the trap................................................................. 91

Table 3.2. Estimations of amount of sulfide in the film and $S^0$ in the bulk of the solution...................................................................................................................................................... 92

Table 3.3. Molar fraction ($\chi_{H_2S_{gas}}$), weight percentages, and partial pressure of H$_2$S (pH$_2$S) in an H$_2$S + N$_2$ gas mixture at 101.3 kPa (1 atm) that will yield a bulk H$_2$S concentration in a 5wt% NaCl + 0.5 wt% HAc solution equivalent to the concentration obtained at the surface of a steel electrode immersed in each thiosulfate solution ........ 93

Table 4.1. Corrosion rates measured with weight loss technique and average of polarization resistance measurements, for a total exposure time of 72h. ....................... 139

Table 5.1. Apparent diffusion coefficients calculated with the time lag method, from hydrogen permeation experiments measured in X65 pipeline steel immersed in 0.5
wt% HAc + 5wt% NaCl containing sulfide species as indicated in the table. Data for 100% H$_2$S solution was measured from [9], for a 9.6 mm X65 pipeline steel sample...

Table 5.2. High frequency slope and plateau values, obtained from the graphs of corrosion fatigue knock down factors vs. frequency for each solution, Figure 5.6, Figure 5.7 and Figure 5.8. Coated specimens were painted with epoxy in all faces except the crack and notch faces.

Table 5.3. Fitting parameters of the hydrogen flux measured in 100% H$_2$S solution [9], considering a time independent and a time dependent diffusion coefficient, and a concentration of hydrogen given by equation 5.12.

Table 5.4. Concentration of hydrogen at steady state at the input side of the sample, CHSS.
LIST OF FIGURES

Figure 2.1. a) Pourbaix diagram for sulfur in aqueous solution at 25°C, for a dissolved sulfur activity of 0.01 [39]. b) Metastable potential/pH diagram of sulfur-water system at 25 °C, constructed via exclusion of S(IV) species [39]. Adapted with permission from Springer. ................................................................. 41

Figure 2.2. a) Pourbaix diagram for iron in water and b) in presence of H₂S at unit activity and at 25ºC. Reproduced from [19] with permission from John Wiley and Sons. ................................................................................................................... 42

Figure 2.3. Relative surface coverage of sulfur (θ_S), oxygen (θ_O) and water (θ_H2O), considering that thiosulfate is the only oxidized sulfur specie of the sulfur/water diagram (--------), superimposed on a potential-pH diagram for S-Fe-H2O (-----), in presence of 10⁻⁴ mol sulfur species/kg of solution at 25°C. Reproduced from [57] with permission from Elsevier................................................................. 43

Figure 2.4. Correlation between surface concentration of hydrogen and sulfide film formation process. Adapted from [78] by permission of The Electrochemical Society................................................................. 44

Figure 3.1. Time evolution of the content of sulfide in the trap as a function of thiosulfate concentration, as indicated in the graph. Results for the 10⁻⁴ M S₂O₃²⁻ solution
were multiplied by 10 so that they could be resolved in the same scale. Slopes of the lines are given in Table 3.1.

Figure 3.2. Dependence of equilibrium concentration of hydrogen sulfide in an aqueous 0.5wt% HAc + 5wt% NaCl solution vs. partial pressure of hydrogen sulfide.

Figure 3.3. Evolution of the surface pH of a corroding steel electrode in deareated 5 wt% NaCl acidified with 0.5 wt % acetic acid and with additions of thiosulfate as indicated in the legend.

Figure 3.4. Current density vs. platinum potential, a), and limiting current density vs. concentration of Fe(CN)$_6^{4-}$, b).

Figure 3.5. XRD spectrum of the filtrand of the solution originally containing 10$^{-1}$ M S$_2$O$_3^{2-}$ at the end of a 12 h exposure of pipeline steel at OCP, suggesting bulk disproportionation of thiosulfate with generation of elemental sulfur. Red peaks indicate theoretical diffraction maximums of S$_8$ phase.

Figure 3.6. Secondary electron images of the surface of a carbon steel specimen immersed at OCP to NACE substituted solution containing a) 10$^{-4}$, b) 10$^{-3}$, c) 10$^{-2}$ and d) 10$^{-1}$ M S$_2$O$_3^{2-}$.

Figure 3.7. Back scattered electron images of cross sections of pipeline steel coupons exposed to NACE substituted solutions for 72 h at OCP, containing a)10$^{-4}$, b) 10$^{-3}$, c) 10$^{-2}$ and d) 10$^{-1}$ M S$_2$O$_3^{2-}$. An energy dispersive spectroscopy (EDS) spectrum obtained at the film is presented at the right of each picture.
Figure 3.8. Surface concentration of hydrogen sulfide, obtained by mass conservation analysis at steady state and comparison of moles of sulfide per unit area in film and in trap vs. thiosulfate concentration. Content of sulfur in the film for the sample tested in $10^{-1} \text{ M} \ S_2\text{O}_3^{2-}$ was linearly extrapolated to 72h, so that it could be compared in the same graph.

Figure 4.1. Equivalent circuit used to fit the impedance spectra obtained for pipeline steel freely corroding in a deaerated solution containing 5wt% NaCl and 0.5 wt% HAc with and without thiosulfate additions.

Figure 4.2. Potentiodynamic cathodic polarization curves of pipeline steel in base $\text{N}_2$ deaerated NACE TM0177-90 solution A and with varying additions of thiosulfate after 1 h (black lines) and after 24 h (light grey line) of OCP exposure. The effect of time on the cathodic polarization curves measured in the rest of the thiosulfate containing solutions was similar to the one presented in the graph for $[\text{S}_2\text{O}_3^{2-}] = 10^{-2} \text{ M}$, but were excluded for clarity in the presentation.

Figure 4.3. Potentiodynamic anodic polarization curves of pipeline steel in $\text{N}_2$ deaerated base NACE TM0177-90 solution, with and without additions of thiosulfate after 1 h (black lines) and after 24 h (light grey line) of OCP exposure.

Figure 4.4. Polarization curves, a), obtained in $\text{N}_2$ deaerated base NACE TM0177-96 solution A with a rotating disc electrode, operated at the angular speeds indicated in the graph. Dependence of the limiting current with angular speed, b). The
limiting current was measured from the polarization curves at the potential indicated by the dashed line. Figure 4.5. Evolution of OCP with time for various thiosulfate additions to a N₂ deaerated solution containing 0.5 wt% HAc and 5 wt% NaCl. Figure 4.6. Nyquist plots for impedance data obtained after ca. 24 h of immersion in base NACE TM0177-90 solution A, a), and with different additions of thiosulfate shown by the legends, a) and b). Scatter corresponds to measurements and lines to fitted impedance of the equivalent circuit. Notice the different scales for the two plots. Figure 4.7. Time evolution of parameters obtained after fitting EIS results for each solution, a) $R_p$, b) $C_{eq}$, c) $Y_0$, d) $\alpha$. Figure 4.8. Secondary electron images of the corroded steel, after chemically stripping the film formed after 72 h OCP immersion in substituted NACE TM0177 solution A substituted with a) $10^{-4}$ M $S_2O_3^{2-}$, b) $10^{-3}$ M $S_2O_3^{2-}$, c) $10^{-2}$ M $S_2O_3^{2-}$ and d) $10^{-1}$ M $S_2O_3^{2-}$. Figure 4.9. XRD diffraction scans of (from top to bottom) a polished iron steel sample, and the same steel specimen after OCP immersion for 143 h in $10^{-4}$ M $S_2O_3^{2-}$, 96 h in $10^{-3}$ M $S_2O_3^{2-}$, 72 h in $10^{-2}$ M $S_2O_3^{2-}$ and 24 h in $10^{-1}$ M $S_2O_3^{2-}$ substituted NACE TM0177 solutions. Peak labels are F: Ferrite ($\alpha$ Fe), C: Cementite (Fe₃C), M: Mackinawite (Fe₃(1+x)S).
Figure 4.10. XPS survey spectra, a), and XPS spectra of the S 2p region, b), for the sample exposed to $10^{-4}$ M $S_2O_3^{2-}$ substituted NACE TM0177 solution at OCP for 48 h. ..................................................................................................................... 151

Figure 4.11. XPS survey spectra, a), and XPS spectra of the S 2p region, b), for the sample exposed to $10^{-3}$ M $S_2O_3^{2-}$ substituted NACE TM0177 solution at OCP for 24h. ..................................................................................................................... 152

Figure 4.12. Comparison of average corrosion current and $H_2S$ evolution current vs. thiosulfate concentration. $H_2S$ evolution current was calculated assuming a 4 e$^-$ reduction path. ................................................................. 153

Figure 4.13. Current density, corrected by the Koutecky-Levich equation, vs. potential, for a carbon steel sample in NACE TM0177-96 base solution A after 24h of OCP immersion. The cathodic Tafel slope was $b_c=133$ mV/decade. ........................................... 154

Figure 5.1. Dimensions of the compact tension specimen, adapted from [36]. Dimensions are in mm, and numbers in brackets are the dimensions in inches. Crack length is measured from plane X-X, shown in picture. ......................................................... 205

Figure 5.2. Transients of the hydrogen flux vs. time obtained in NACE TM0177-96 solution A saturated with an $H_2S$ partial pressure of 0.56 kPa in nitrogen. The 1$^{st}$ transient was obtained with a non-charged 3mm thick X65 carbon steel sample, and the second was obtained after polishing to 600 grit and annealing at 50 °C the hydrogen graph.
charged sample, in order to remove the diffusible hydrogen. Data shown for the first 20 h.

Figure 5.3. Transients of hydrogen permeation obtained for the X65 pipeline steel sample in NACE TM0177-96 solution A saturated with pure H₂S and H₂S containing mixtures with partial pressures as indicated in the figure. The sample had a thickness near 3 mm and had irreversible traps saturated with hydrogen in all cases. Data shown for the first 42 h, for all solutions except the one saturated with H₂S. Data for the pure H₂S solution was adapted from [9], and was obtained with a 9.6 mm thick sample, for about 107 h of OCP exposure.

Figure 5.4. Transients of hydrogen permeation obtained for the X65 pipeline steel sample in NACE TM0177-96 solution A substituted with amounts of thiosulfate as indicated in the figure. The sample had irreversible traps saturated with hydrogen in all cases. The transient obtained in NACE TM0177-96 solution A saturated with an H₂S partial pressure of 0.56 kPa is drawn for comparison. Data shown for the first 72 h, except for the transient obtained in the solution containing 10⁻² M S₂O₃²⁻, where it is 20 h. Sample thickness was near 3 mm in all cases.

Figure 5.5. Corrosion fatigue crack length vs. time during a frequency scan experiment, performed in coated X65 pipeline steel exposed to NACE TM0177-96 solution A saturated with an H₂S partial pressure of 0.56 kPa, at a ΔK of 19.1 MPa·m¹/² (17.4 ksi·in¹/²) and R of 0.13. Each segment was fitted with a straight line to obtain crack propagation rates as a function of frequency.
length increase vs. time, and the slope was divided by frequency to obtain crack length increase vs. number of cycles.

Figure 5.6. Corrosion fatigue crack growth rates of coated X65 pipeline steel measured in NACE TM0177-96 solution A saturated with N₂, H₂S and N₂ + H₂S mixtures with partial pressure of H₂S as indicated in the legend, at a ΔK of 19.1 MPa·m¹/² (17.4 ksi·in¹/²) and R of 0.13. Left scale shows FCGR normalized by values measured in air [39].

Figure 5.7. Corrosion fatigue crack growth rates of coated X65 pipeline steel measured in NACE TM0177-96 solution A with additions of thiosulfate as indicated in the legend, at a ΔK of 19.1 MPa·m¹/² (17.4 ksi·in¹/²) and R of 0.13. The curve measured in the solution saturated with an H₂S partial pressure of 0.56 kPa is shown for comparison purposes. Left scale shows FCGR normalized by values measured in air [39].

Figure 5.8. Corrosion fatigue crack growth rates vs. frequency, at a ΔK of 19.1 MPa·m¹/² (17.4 ksi·in¹/²) and R of 0.13. Left scale show FCGR normalized by air measured FCGR [39]. Filled squares correspond to FCGR obtained for a X65 pipeline steel immersed in 100 % H₂S saturated NACE TM0177-96 solution A. Sample was uncoated, except for the points where it was spot welded. Hollow circles correspond to an air fatigue test, re-drawn from [9], performed after 3 days exposure to the same solution at OCP of an X65 compact tensile specimen extracted from the same pipe, with the crack
tip region coated with epoxy. At the end of this fatigue experiment, sample was placed in an oven at 60°C for 4 days and then FCGR vs. frequency were measured, hollow triangles [9].

Figure 5.9. Flux of hydrogen measured at the exit side of a 9.6 mm X65 pipeline steel sample exposed to NACE TM0177-96 solution A saturated H₂S [9]. One of every 5 experimental data points is shown for clarity in the presentation. The black fitting line was obtained considering a single diffusion coefficient, $D_{\text{lag}}$. The grey fitting line was obtained considering a diffusion coefficient given by $D_{\text{bt}}$ for $t<4.3$ h and by $D_{\text{lat}}$ for longer times. Fitting parameters are given in Table 5.3.

Figure 5.10. Geometry used in modeling. a) Schematic of the compact tension specimen, indicating presence of symmetry planes in bold dash and dotted lines. Cuboid used to approximate this geometry for b) coated and c) uncoated specimens. At each symmetry plane the boundary condition was zero flux of hydrogen. The boundary conditions in the rest of the surfaces are indicated.

Figure 5.11. Concentration profiles of hydrogen in the plane containing the crack, obtained with the finite difference program after a) 3.6 h, b) 72 h of OCP exposure in NACE TM0177-96 solution A saturated with H₂S, for the un-coated specimen. Notice the difference in the $C_{\text{H}}$ scale in the two graphs. The concentration profile is shown in half the plane, and it has a symmetry plane that contains the points situated at half thickness,
Figure 5.10c. The region of constant concentration of hydrogen in each picture corresponds to the notch.

Figure 5.12. Concentration profile of hydrogen vs. distance, at the line that is contained in the crack plane at the mid-section, obtained with finite difference program, for a) the un-coated and b) coated specimen. Exposure time at OCP in NACE TM0177-96 solution A saturated with H₂S is shown in the figure.

Figure 5.13. Normalized FCGR at the low frequency plateau measured for coated specimens, vs. the surface concentration of hydrogen at steady state for all solutions studied, CHSS. Pressures are the partial pressures of H₂S in the different H₂S/N₂ mixtures. The point for the solution saturated in H₂S corresponds to the maximum value of the FCGR vs. frequency curve.
CHAPTER 1. INTRODUCTION

Corrosion fatigue affects the integrity of carbon steel pipes used in deepwater oil extraction. Waves, tidal motion, and operational vibrations control the periodic stresses [1-3], which are usually superimposed on static tension stresses arising from the internal pressure of the pipe, or residual stresses near welds. Externally, sea water corrosion can be minimized by cathodic protection (CP) [1], but it is not practical to use CP to protect the internal surface of the pipe. Internal corrosion fatigue can be aggravated by the presence of sour (i.e. H₂S containing) brines, which cause a decrease in fatigue life with respect to air performance [2, 4, 5]. Hydrogen sulfide increases corrosion and hydrogen absorption [6], causing embrittlement [7]. Therefore, standards like NACE MR0175 [8] establish limits for use of carbon steels in sour service. For static loads applied on parts designed with conventional elastic design criteria, sulfide stress cracking (SSC) is not a problem for partial pressures of H₂S lower that 0.3 kPa (0.05 psi) [8]. At higher partial pressures, SSC-resistant carbon and low alloy steels are required. The aggressiveness of the environment is specified by pH and H₂S partial pressure [8]. Required composition, heat treatment, hardness and manufacturing procedures are detailed in the standard [8] for the different regimes of pH and H₂S partial pressure. However, with cyclic loads applied at low frequency, SSC-resistant steels can exhibit sour corrosion fatigue even in the regime of pH and partial pressure of H₂S of SSC immunity [9].
Sour corrosion fatigue tests can provide design data such as maximum acceptable service loads or flaw sizes for a given life of the component. Sour corrosion fatigue studies require the use of gaseous hydrogen sulfide, which can be bubbled pure or mixed in nitrogen throughout the test. This proceeds after an initial deareation with pure nitrogen where oxygen is removed to minimize hydrogen sulfide oxidation and to mimic well environments [10]. Those tests are challenging because hydrogen sulfide is lethal if inhaled above a certain level, flammable and corrosive for materials. Therefore, handling of this gas requires expensive facilities with special safety features. An interesting alternative is to simulate the sour conditions by the use of substances that generate H2S in-situ. Tsujikawa [11, 12] proposed the possibility of replacing H2S with thiosulfate (S2O32−) for studying pitting and stress corrosion cracking susceptibility of steels in sour environments. Sodium and potassium thiosulfate salts are non-toxic and water soluble. Therefore, if it can be proved that corrosion fatigue in thiosulfate solutions mimics behavior in hydrogen sulfide solutions, tests would be simpler because handling of hydrogen sulfide cylinders would not be required.

This dissertation is divided in 6 chapters, including this one. Chapter 2 is a review of the literature on sour corrosion fatigue and presents evidence that supports the use of thiosulfate solutions for simulating hydrogen sulfide solutions in stress corrosion cracking of carbon and stainless steels. Similarities between corrosion behavior of carbon steel in thiosulfate vs. hydrogen sulfide solutions are pointed out and unsolved issues are exposed, which inspired the research detailed in the next chapters.
Chapter 3, 4 and 5 detail the research performed for this dissertation and are written in the style of a stand-alone publication. Chapter 3 contains an overview of the reaction paths of thiosulfate in acid brines. Concentrated thiosulfate solutions can undergo a disproportionation reaction, which yields elemental sulfur. At the corrosion potential of carbon steel, thiosulfate undergoes a cathodic reaction that yields hydrogen sulfide. This cathodic reaction is the basis for thiosulfate solutions ability to simulate hydrogen sulfide solutions, and its kinetics was studied as a function of thiosulfate concentration. Carbon steel exposed to acid thiosulfate solutions becomes covered by a black film, which contains sulfur. The amount of hydrogen sulfide produced was compared to the amount of sulfide lost in the film and in the disproportionation of thiosulfate.

Chapter 4 contains structural characterization of the film formed on carbon steel exposed to acid thiosulfate containing brines. The corrosion rate of carbon steel was studied as a function of the amount of thiosulfate in solution. The role of films in corrosion was assessed by contrasting anodic and cathodic polarization curves obtained after short and long exposure times. Those films could affect fatigue crack growth by a crack closure mechanism or by blocking hydrogen permeation.

Chapter 5 compares hydrogen permeation in thiosulfate solutions and hydrogen sulfide solutions. Hydrogen sulfide was bubbled pure and mixed with nitrogen, at concentrations that matched the levels of hydrogen sulfide present on the surface of carbon steel freely corroding in thiosulfate solutions. Corrosion fatigue tests were performed at constant stress intensity factor range and constant ratio of maximum over
minimum loads. Crack growth rate was measured as a function of frequency for hydrogen sulfide and thiosulfate solutions, and interpreted with aid of the hydrogen permeation transients and electrochemical results from chapter 3 and 4.

Chapter 6 summarizes the main findings and conclusions of this dissertation, and contains suggestions for further work.

1.1. References


CHAPTER 2. LITERATURE REVIEW

In this review, the effect of mechanical and environmental variables on the fatigue life of carbon steels exposed to sour environments will be discussed. Experimental approaches used to study corrosion fatigue will be reviewed. The environment can enhance crack growth by anodic dissolution or hydrogen embrittlement [1]. Therefore, the influence of hydrogen sulfide on corrosion and hydrogen absorption of carbon steels will be discussed. Corrosion in sour environments usually proceeds with formation of iron sulfide films. Films can affect fatigue crack growth due to crack closure mechanisms, but they can also hinder hydrogen absorption. This literature data on the behavior of carbon steels in hydrogen sulfide is critical for the understanding of sour corrosion fatigue and will be compared to available data in thiosulfate solutions. The chemistry of thiosulfate solutions will be discussed and thermodynamic evidence in favor of the use of thiosulfate as a replacement for H₂S will be presented. No literature results are available about corrosion fatigue of carbon steels in thiosulfate solutions, but studies about pitting of stainless steel and stress corrosion cracking of carbon and stainless steels in thiosulfate solutions will be discussed because they might be relevant to understand corrosion fatigue in thiosulfate solutions.
2.1. Corrosion fatigue of carbon steels in sour environments

Fatigue cracking involves cyclic plastic deformation, microcrack initiation and coalescence and crack propagation [2]. Corrosion fatigue refers to the acceleration of one or more of those stages due to the action of a deleterious environment. Cracks and defects are usually present in engineering structures. Crack-tip stress intensity factor range, $\Delta K$, is defined as the difference between maximum, $K_{\text{max}}$, and minimum, $K_{\text{min}}$, stress intensity factors and is useful for describing the mechanical driving force for crack propagation [1, 3]. $R$, the ratio of minimum to maximum applied stress intensity factor, can also affect crack growth rate in sour environments [2]. Unlike fatigue in inert environments, the frequency of the time fluctuating stresses can affect crack growth rate during corrosion fatigue [2]. This is associated with mass transport and electrochemical reaction limitations. Environmental variables of interest here include the concentration of hydrogen sulfide, salts, pH and temperature. Sour corrosion fatigue tests are usually performed at the free corrosion potential [4-8] in an effort to simulate internal pipeline service conditions. Experimental approaches to study corrosion fatigue include endurance based and crack growth rate based tests, which will be contrasted below.

2.1.1. Effect of mechanical variables

Crack growth rate in air and inert environments often follows the Paris law,

$$\frac{da}{dN} = A(\Delta K)^m$$  \hspace{1cm} (2.1)

where $da/dN$ is the change of crack length per cycle, and $A$ and $m$ are material dependent constants [9]. Crack growth rate is not observed below a minimum or threshold value of
stress intensity range, $\Delta K_{\text{threshold}}$. The upper bound of the Paris law is reached when $K_{\text{max}}$ approaches the fracture toughness of the material, $K_c$ [9].

A usual way of characterizing corrosion fatigue involves the use of acceleration factors, which is the ratio of crack growth rates in the corrosive environment over that in air. Reported values for acceleration factors for $\text{H}_2\text{S}$ saturated seawater range between 20 and 100, depending on $\Delta K$ [4, 7, 8, 10]. A typical corrosion fatigue da/dN curve vs. $\Delta K$ has three stages. Stage 1 is characterized by increasing da/dN with increasing $\Delta K$ and can be described by the Paris law [4]. Stage 2 corresponds to the plateau beyond this region, where da/dN becomes independent of $\Delta K$. This plateau is associated with limitations of the environment to sustain crack growth above a critical rate [8]. Crack growth rate might be controlled by transport of reactive species to the crack tip, charge transfer reactions at the crack tip, absorption and diffusion of hydrogen into the metal lattice or transport of reaction products away from the crack tip [1]. Stage 3 starts at the end of the plateau region at high stress intensity factors, where $K_{\text{max}}$ approaches the fracture toughness of the material in the environment. This latter value can be lower than the air measured value [4].

$\Delta K_{\text{threshold}}$ values in sour conditions were similar to values in air when $R$ was 0.6 [10]. However, a decrease in stress ratio $R$ can increase the $\Delta K_{\text{threshold}}$ in the corrosive environment [1, 4]. Such effect is related to beneficial crack closure effects [1, 7]. Crack closure is associated with the presence of oxides, scales or deposits, that wedge open the crack during the unloading cycle, therefore diminishing the range of stress intensity factor seen by the crack tip [1, 6, 8]. This premature contact of crack surfaces is
prevented at high R values. On the other hand, the crack propagation rate value at the plateau and the $K_{\text{max}}$ value required for onset of stage 3 measured in sour brine were independent of R [4].

It is widely accepted that a decrease in frequency enhances sour corrosion fatigue [4, 7, 11, 12]. The main affected zone of the crack propagation rate vs. $\Delta K$ curve is the value of the plateau and slope of the Paris law [4]. Such effect is common in the corrosion fatigue literature [13], and contrasts with the independence of crack propagation rates with frequency of samples tested in air [4, 11]. This dependence with frequency provides a challenge to corrosion fatigue studies, because measurements performed at higher frequency aimed to reduce test time might not reflect the actual degradation kinetics encountered in service. Buitrago [11] studied the crack propagation rate in sour brines for a broader range of frequencies at fixed $\Delta K$ and found a limit in crack propagation rates with decreasing frequency, between values of 0.1 and 1 Hz. Such a limit in crack growth rate was also reported by Thodla et al., working in sour conditions [14]. The dependence of crack growth rate on frequency can correspond to increased times for transport of reactants and surface reactions at the crack tip and hydrogen diffusion through the plastic zone [3]. It should also be mentioned that in the limit of very low frequencies, crack growth rate can slow down due to crack tip blunting by anodic dissolution, especially in aggressive electrolytes [5]. Likewise, when R is low and $\Delta K$ is near the threshold value, low frequencies can exacerbate crack closure effects [6], leading to an increase in the threshold stress intensity factor range required for crack propagation.
2.1.2. Effect of environmental variables

The concentrations of CO$_2$, H$_2$S, O$_2$, salts, pH, and temperature define the service environment and are controlled during sour corrosion fatigue testing. In sour corrosion studies, oxygen is often displaced from the solution by purging with nitrogen or argon [15] before addition of H$_2$S. This practice prevents the oxidation of H$_2$S to elemental sulfur or polysulfides [16] and mimics well environments. The pH is often adjusted by additions of acetic acid and sodium acetate [15]. Control of pH is critical because it has been reported that a change of one unit of pH is equivalent to a tenfold increase in H$_2$S partial pressure in terms of hydrogen embrittlement and sulfide stress cracking [17, 18]. A possible cause for this dependence is related to the fact that at higher pH, OH$^-$ competes with H$^+$ for adsorption sites on metal surface, a prerequisite for hydrogen embrittlement [19]. Chlorides, bicarbonates, carbonates and sulfates are common in service and are added to the base electrolyte during corrosion fatigue testing to simulate pipeline service conditions. Service temperature can range from 5°C in the North Sea [7] to values near 30°C.

2.1.2.1. Carbon dioxide

Service in sweet environment or CO$_2$-containing solutions reduces fatigue life, might eliminate the endurance limit [8, 20], and increases the low frequency crack growth rate limit, probably due to crack tip dissolution [21]. The CO$_2$ concentration affects the pH of the solution, and some authors speculated about the possibility that an increase in CO$_2$ concentration would favor the buildup of corrosion products at the crack tip, which could inhibit crack growth for lower values of $\Delta K$ [7], due to crack closure.
effects. Films of siderite, FeCO$_3$, are able to form on iron in presence of carbon dioxide, but they are not completely protective [22]. On the other hand, in corrosive solutions saturated with CO$_2$ and at 60°C crack tip blunting due to anodic dissolution was so strong that the measured crack growth rate was smaller than in air, for the lower values of $\Delta K$ [23]. Therefore, selecting the worst case scenario for studying fatigue crack growth in sweet fluids might be difficult because it does not necessarily correspond directly with the most corrosive environment.

2.1.2.2. Hydrogen sulfide

Hydrogen sulfide promotes hydrogen embrittlement and corrosion of carbon steels [24]. The harsh effect of hydrogen sulfide on steel under static applied stresses is well documented [25-28]. Sources for this gas are not limited to sour produced fluids, but can also include reactions with manganese sulfide inclusions in steel, or the action of sulfate reducing bacteria [2, 29]. SCC in H$_2$S environments is better known as sulfide stress cracking (SSC). Other related failure mode in sour environments include hydrogen induced cracking (HIC), where cracks nucleate usually at MnS inclusions and then propagate along inhomogenities such as segregations or pearlite bands [26, 28]. Unlike SSC, external stresses are not necessary for occurrence of HIC. For SSC, the degree of embrittlement or loss in ductility is maximum at low strain rates, under applied cathodic potentials, at low pH and temperatures near ambient [25, 27, 30], supporting a hydrogen embrittlement mechanism. Such mechanism is in accord with the well known fact that sulfur compounds, like arsenic, phosphorus, antimony, tin and arsenic inhibit the formation of molecular hydrogen in the hydrogen evolution reaction, thus favoring the
absorption of this element into the metal lattice [31]. Berkowitz [32] suggested that the effect of hydrogen sulfide is related to its outstanding capabilities in increasing the rate of hydrogen permeation. The author performed in situ permeation experiments during straining of a low alloy steel sample in H$_2$S- and NaAsO$_2$-containing environments at different applied cathodic currents. The currents were selected to yield equal values of hydrogen permeation current. When NaAsO$_2$ was the hydrogen ingress promoting substance, a higher cathodic current was required to yield the same value of hydrogen permeation current than in H$_2$S environments, due to the outstanding capabilities of H$_2$S to promote hydrogen absorption. Despite the expected differences in iron dissolution rates, the two tests showed similar levels of reduction in area, loss of ductility and failure mode. Similar results were presented by Turn et al. [30], who found that values of reduction in area in different environments containing H$_2$S or As$_2$O$_3$, either freely corroding or under applied cathodic potential, fall in the same curve if plotted vs. the input hydrogen fugacity. Both papers [30, 32] concluded that the increase in corrosion associated with presence of H$_2$S in service conditions is important but only as it increases the rate of the hydrogen reduction reaction.

During dynamic loading, hydrogen sulfide affects crack growth rate, especially at lower frequencies [5] and moderate to high applied stresses [7, 8]. Crack growth rates more than two orders of magnitude higher than air measured values were reported in sour brines [7]. The plot of crack growth rate vs. $\Delta K$ in H$_2$S environments exhibits the common form with three stages [4, 7]. An applied cathodic potential can increase significantly the crack growth rates and decrease the fracture toughness in the
environment, thus producing the absence of the plateau region [7]. In support of those observations, a hydrogen embrittlement mechanism is often assumed [4, 7, 33, 34]. On the other hand, $\Delta K_{\text{threshold}}$ values seem to be similar or slightly higher than air measured values [7, 21, 34]. Such increase in $\Delta K_{\text{threshold}}$ is greater at higher temperatures, low frequencies and low R, suggesting crack closure effects by scales [4, 6]. The increase in crack growth rate is dependent on the external partial pressure of H$_2$S [4, 7], but contents as low as 1% were reported to accelerate crack growth rates [5], and the real threshold concentration could be lower than this value.

2.1.2.3. Temperature

An increase in temperature from 30 to 90°C does not affect fatigue crack growth rates in H$_2$S containing environments [7], and some authors actually reported lower degradation kinetics and the absence of the stage 2 plateau at 90°C [4]. On the other hand, crack growth rates in sea water doubled when test temperature was increased from 5°C to 20°C [7]. Those observations are in accord with a hydrogen embrittlement based mechanism, where maximum embrittlement is seen at ambient temperature. A decrease in temperature would diminish hydrogen mobility, whereas an increase in temperature would increase H mobility but decrease trapping [31]. Moreover, the crack growth rate independence with increasing temperature could be explained in terms of the formation of protective scales that hinder the ingress of hydrogen [4], or accelerated crack tip dissolution that blunts the crack tip at high temperature [21]. This scenario would mask any increase in crack growth kinetics related to faster diffusion of hydrogen or corrosive
species. Finally, crack closure effects also seem to be more important at higher temperature [6].

2.1.3. Experimental approaches

Common approaches used to study corrosion fatigue include endurance testing of polished specimens and crack growth rate measurements of notched specimens with mode I compact tension or three or four point bend geometries [2]. Recirculation of electrolyte from a large storage tank is advised [2, 21] to minimize the buildup of corrosion products at the crack tip region, which can decelerate crack growth rate due to crack closure effects. Since it cannot be guaranteed that such effect will occur in service, recirculation of electrolyte allows the study of the worst case scenario.

Maximum and minimum applied loads are controlled in endurance tests, and converted to stresses using the nominal area of the calibrated section. The result of such a test is the alternating stress vs. number of cycles curve (S-N curve). A main limitation of this approach is that, unlike studies of fatigue in air, an increase in frequency will reduce crack propagation rate, which makes it difficult to study the service degradation kinetics in reasonable times. Buitrago recommends testing at the highest frequency of any plateau in crack growth rate vs. frequency to reduce testing time [11], but the existence of such plateau needs to be assessed a priori for the particular environment and material combination. Moreover, this approach assumes that crack growth dominates fatigue life. That is not the case for high cycle fatigue, where crack initiation represents a big fraction of the total life of the component. During endurance tests, the number of cycles required to failure is monitored, but crack area is not commonly measured [2]. Therefore, a second
limitation of this approach is that little is understood in terms of the contributions of the
different stages of fatigue damage to the total fatigue life. The effect of the environment
on each stage of the degradation failure is difficult to discern if only the number of cycles
to failure is monitored. Lastly, real structures tend to have shorter life than that predicted
by S-N data, because there is a higher probability to find larger defects than in the small
probes used during testing [35].

Measuring corrosion fatigue kinetics with crack growth rate approaches requires
more complex equipment. Crack area is measured in situ and used to adjust the applied
load with a feedback loop, in order to maintain the applied $\Delta K$ constant [2]. The method
is appropriate to study the effect of external environmental and mechanical variables on
corrosion fatigue crack growth kinetics, but no insight is provided on the very early
stages of corrosion fatigue damage, where pitting and generalized corrosion can generate
defects or blunt existing crack tips [21]. Moreover, the S-N curve can be obtained
theoretically by fracture mechanics based calculations if the size of the initial defects is
known [21]. The main limitation of this approach is that compact tension and bending
specimens usually have crack lengths that can exceed the length of cracks encountered in
practice, and some authors [36, 37] found that for a given $\Delta K$, short cracks might grow
faster than longer ones, which can lead to overestimations in the service life of the
component. Microscopically, the situation can correspond to decreased influence of bulk
hydrogen charging, increased crack closure phenomena or differences in crack tip
chemistry [37]. One last objection related to the use of fracture mechanics specimens is
associated with the fact that they allow through thickness transport because the crack
sides are open [38], a situation seldom observed in real specimens. A final unaccomplished goal of corrosion fatigue testing involves understanding the information acquired during endurance and crack growth rate tests to predict the life of a component with microscopic defects in sour environments [2].

### 2.2. Electrochemistry of hydrogen sulfide vs. thiosulfate solutions

Sulfur has a complex chemistry, but at 25°C, ambient pressure and in presence of water, it exhibits only 3 thermodynamically stable oxidation states, 0, -2 and +6 [39]. The stable species corresponding to those valences are presented in a potential-pH diagram in Figure 2.1a. H₂S is a weak acid that dominates in the low potential region, and remains protonated in a fairly wide region of pH. The activation energy for oxidation of hydrosulfide, HS⁻, to sulfate, SO₄²⁻ is extremely large, which results in the existence of metastable products like sulfite, SO₃²⁻, thiosulfate, S₂O₃²⁻, dithionate, S₂O₆²⁻ and tetrathionate, S₄O₆²⁻. Thiosulfate can be used as a substitute of H₂S because it can reduce to H₂S [29] when in contact with carbon steel. On the other hand, dithionate can reduce to sulfite or disproportionate in concentrated solutions to give sulfite and sulfate [29]. Tetrathionate can reduce to sulfur or thiosulfate [29]. The predominance of these species is depicted in Figure 2.1b, which was constructed by elimination of sulfate compounds from the calculation [39]. Other metastable species resulting from oxidation of hydrogen sulfide solutions include polysulfide ions, like Sn²⁻, where n=2,3,4,5 [39].

Carbon steel in contact with hydrogen sulfide and sulfur compounds develops a film of iron sulfide, which can affect corrosion fatigue by crack closure or by hydrogen ingress blocking. On the other hand, since thiosulfate solutions are metastable, the ion
tends to react yielding stable compounds, like H₂S and S. Some evidence about formation of sulfide films in thiosulfate solutions will be presented below.

2.2.1. Surface films formed on iron and steel in H₂S solutions

The Pourbaix diagram for iron in the presence of H₂S is compared to the iron-air water diagram in Figure 2.2 [19]. Hydrogen sulfide reduces the region of immunity of iron, and increases the electromotive force for oxidation of iron in the whole range of pH, in presence or absence of oxygen. A direct complication associated with this observation is that lower cathodic protection potentials are required, which might increase the rate of reduction of hydrogen and its diffusion into the metal lattice. Stable iron sulfides form in a large pH-potential window but, unlike iron oxides formed in water, they tend to be non-passivating. The main reasons for this fact include their good electronic conductivity due to the high density of defects [40] and their discontinuity and tendency to crack [41]. Perturbations such as stirring affect considerably the anodic behavior of steel in H₂S solutions, due to the faster transport of the reactive species to the steel surface and the removal of films [42].

Troillite, mackinawite, and cubic ferrous sulfide are the sulfides commonly found in aqueous environments, in decreasing order of stability [41]. The corrosion potential of iron in sulfide solutions tends to range between -0.38 to -0.60 V\text{SHE}, for solutions of pH values between 4 and 12 [19]. This corresponds to the iron sulfide stable zone of the potential-pH diagram, Figure 2.2b, which explains why sulfides occur naturally in sour conditions. Experimentally, it is usually found that sulfide films depart from the expected FeS₂ composition, appearing as monosulfides [19] or mixtures of FeS and FeS₂ [43]. Iron
sulfides encountered in carbon steel corrosion are often non-stoichiometric [40], with a structure rich in defects that contributes to their good electron conductivity.

In aqueous solutions of hydrogen sulfide, two mechanisms were proposed for the formation of iron sulfide films, namely, dissolution of iron followed by precipitation of iron sulfide and sulfide ion adsorption followed by direct film formation [19]. Shoesmith [16, 41] studied the structure and mechanism of formation of sulfide films in H₂S-containing solutions as a function of pH. For the pH range between 4.0 and 7.0, a solid state grown layer of mackinawite was observed, which follows adsorption of SH⁻ ions. Adsorption of this ion inhibits oxide formation due to the competition with hydroxide ion [16]. On the other hand, a clean and roughened surface was observed for pH values of 1.7, with no precipitates due to their high solubility at this level of acidity. The layer formed at values of pH between 4.0 and 6.0 tended to crack and spall, allowing further metal dissolution. Metal dissolution effects were more important at lower values of pH. On the other hand, the solubility of iron sulfides decreases with increasing pH. Therefore, the amount of precipitated sulfides was measured to be maximum at pH near 4, which is the natural pH of H₂S-saturated water [41]. Upper layers of troilite, mackinawite and cubic ferrous sulfide precipitated from the solution with their relative quantities varying with pH. The amounts of mackinawite and troilite increased with time at the expense of cubic ferrous sulfide, due to their higher stability.

Sulfides offer a minimum amount of protection when H₂S is dissolved in deionized water [43], but the protective character is dependent on pH and is minimum between intermediate values of 6.0 and 9.5. Foroulis found a correlation between
crystallographic structure of the film and the level of protection offered [43]. When chlorides are present, sulfides are non-protective and also corrosive [19, 40, 43]. A possible reason is that, since they are more noble than iron and favor hydrogen evolution, a galvanic corrosion mechanism might be operating in their presence [40, 44]. An etched, bright surface was observed after exposure of mild steel to sulfide suspensions, which supports the idea that iron might act as the anode of a galvanic cell [45]. However, corrosion kinetics tended to decrease with time, but to increase with shaking and if fresh sulfide was produced and allowed to contact the metallic surface [22]. Those findings suggested that sulfides experienced a chemical or saturation reaction during corrosion of iron, which might inhibit the capacity to act as a cathode. Since iron does not form hydrides, hydrogen absorption with concurrent saturation of the solid solution was proposed to explain the reduction in cathodic kinetics, but the quantitative aspects of this theory were not verified [45].

2.2.2. Chemistry of thiosulfate solutions

The thiosulfate ion can be formed when oxygen ingresses in an originally deareated H₂S environment [46]. Reported values for the corrosion potential of carbon steel in thiosulfate solutions with pH near 2.7 situated it near -400 mV_{SHE} [47-49], which corresponds to the H₂S stable region in a sulfur-water diagram at room temperature, Figure 2.1 [39]. This provides a thermodynamic basis for the use of thiosulfate solutions as a replacement of conventional H₂S solutions in carbon steels degradation studies.
Due to thiosulfate metastability, it might undergo disproportionation and reduction reactions [29, 47]. Disproportionation reactions can occur in the bulk solution because the same element undergoes both a reduction and oxidation reaction [29, 47]:

\[
S_2O_3^{2-} + H^+ = S^0 + HSO_3^- \quad \Delta G^0 = -3.1 \text{ kJ/mol} \tag{2.2}
\]

Thiosulfate can also reduce to yield elemental sulfur [29, 50]

\[
S_2O_3^{2-} + 6H^+ + 4e^- = 2S^0 + 3H_2O \quad E_0 = 0.465 \text{ V}_{\text{SHE}} \tag{2.3}
\]

and sulfur can further reduce to yield H\textsubscript{2}S gas, via a disproportionation reaction or a reduction reaction [29, 47]

\[
4S^0 + 4H_2O + H^+ = 3H_2S + SO_4^{2-} + 3H^+ \quad \Delta G^0 = 124 \text{ kJ/mol} \tag{2.4}
\]

\[
S + 2H^+ + 2e^- = H_2S \quad E_0 = 0.142 \text{ V}_{\text{SHE}} \tag{2.5}
\]

where the standard Gibbs free energy change and reversible potential was calculated based on electrochemical data [29]. The tendency to react yielding H\textsubscript{2}S, and the fact that ferrous salts of thiosulfate are highly soluble [51], make it a viable alternative for H\textsubscript{2}S replacement. H\textsubscript{2}S generation was detected in the bulk of thiosulfate containing acid brine, when carbon steels were immersed in the environment [47, 48]. For stainless steels at 80°C, H\textsubscript{2}S gas was detected only after scratching the steel surface [47]. Scratching caused the corrosion potential to decrease to values inside the H\textsubscript{2}S stability domain [47]. This suggests that hydrogen sulfide is dependent on the occurrence of an anodic reaction, which provides the necessary electrons for thiosulfate reduction, equations 2.3 and 2.5. While disproportionation of sulfur to H\textsubscript{2}S and sulfate, equation 2.4, could be possible at concentrations different than standard state, the kinetics of this reaction are very low [52].
2.2.2.1. Surface films formed on iron and steel in $\text{S}_2\text{O}_3^{2-}$ solutions

Little is known about the film formation process in thiosulfate solutions. Hörlund proposed that a film formation process in thiosulfate solutions might affect hydrogen entry, but his proof was limited to visual observation of a black tarnish [53]. It is curious that such film formation process did not affect the corrosion potential, corrosion current or any other feature of the polarization curves recorded in 5% NaCl with $10^{-3}$ M $\text{Na}_2\text{S}_2\text{O}_3$ acidified with 0.5% acetic acid (CH$_3$COOH) to a pH of 2.7 after 1 and 24 h of exposure [54]. On the other hand, for concentrations of thiosulfate between $10^{-2}$ and $10^{-1}$ M at neutral pH, the corrosion rate was lower after 28 than after 14 days, and presence of a film containing sulfur was detected with Energy Dispersive Spectroscopy (EDS) [55]. After monitoring the corrosion process in a $10^{-2}$ M $\text{S}_2\text{O}_3^{2-}$ solution with a video camera, a grey scale analysis of the images was performed and it was concluded that denser films form at higher pH [56]. Moreover, the corrosion rate decreased with pH increase for thiosulfate solutions, whereas the opposite trend was found for a sulfide solution, between pH 3 and 9. In summary, films formed in basic solutions of thiosulfate seem to be more protective, but the dependence of film structure with pH and thiosulfate concentration requires further study.

Formation of sulfur monolayers after reduction of thiosulfate anions were predicted by Marcus [57]. Thermodynamic calculations have shown that sulfur/water or sulfur/oxygen adsorption quotients are high in a broad region of potential and pH, Figure 2.3. Similar results were reported considering H$_2$S solutions [58]. Whereas conventional Pourbaix diagrams are constructed considering the stability of bulk solids, such diagrams
consider as well the occurrence of two dimensional films adsorbed on metals [57, 58]. Langmuir adsorption is assumed [58] and it is observed that adsorption of S atoms is possible in a domain larger than that corresponding to iron sulfides. Therefore, detrimental effects based on structural changes in the passive layer and enhanced anodic dissolution and hydrogen absorption are expected [57].

2.2.3. Hydrogen absorption

One of the aggressive effects of hydrogen sulfide in corrosion fatigue is related to the fact that it favors the ingress of hydrogen into the metallic lattice. Therefore, as a prior step in the use of thiosulfate solutions to predict mechanical resistance of steels in sour environment, it is of interest to compare the hydrogen absorption kinetics in both environments. Since a basic knowledge of hydrogen trapping is required to understand hydrogen absorption characteristics in different environments, a brief introduction to this subject will be presented. One of the well-established electrochemical techniques to characterize hydrogen absorption was proposed by Devanathan and Stachurski [59], and is based on the measurement of hydrogen permeation through metallic membranes. This section will end with a summary of the current knowledge about hydrogen absorption in H₂S and thiosulfate environments.

2.2.3.1. Hydrogen trapping and lattice and apparent diffusion coefficients

Traps are special sites in the metal lattice where the enthalpy of dissolution for hydrogen is energetically favorable relative to ordinary sites [60]. Trapping sites for steels include dislocations, carbides, inclusions and second phase interfaces and
microcracks, which can develop during cold work [60, 61]. Their fraction of occupation is controlled by the lattice concentration of hydrogen, the number of traps per unit volume and the trapping equilibrium constant. Depending on the depth of the trapping well and for a given temperature and time scale, traps can be further characterized as either reversible or non-reversible [62]. McNabb and Foster [62] modified Fick’s second law to include the effect of traps

\[
\frac{\partial C}{\partial t} + N \frac{\partial f}{\partial t} = \nabla \cdot (D_{\text{lat}} \nabla C)
\]

where \(C\) is the concentration of diffusible hydrogen, \(D_{\text{lat}}\) is the lattice diffusion coefficient, \(N\) the number of traps per unit volume and \(f\) the fraction of occupation of traps. The change in \(f\) per unit time can be related to \(k\) and \(p\), the mean probabilities of absorption and releasing a hydrogen atom from a trap [62]:

\[
\frac{\partial f}{\partial t} = kC(1-f) - pf
\]

The absorption and release probabilities, k and p, are a function of temperature and the enthalpy of dissolution of hydrogen in traps. Eventually, the trapped hydrogen will equilibrate with the diffusing hydrogen and the right side term in equation 2.7 will be zero. Under this condition, and in the absence of plastic deformation which can affect \(N\) by an increase in dislocation density, equation 2.6 reduces to Fick’s first law, relating the flux of hydrogen to the concentration of diffusible hydrogen with \(D\) equal to the lattice diffusion coefficient.

An apparent or effective diffusion coefficient was defined, which is a function not only of temperature like the conventional or lattice diffusion coefficient, but also of
hydrogen concentration in normal and trapping sites [60]. The effective diffusion coefficient, which is smaller than the lattice diffusion coefficient, when inserted in Fick’s first law relates the observed flux with the total concentration of hydrogen, defined as the sum of contributions from lattice and trapping sites [60]. The effective diffusivity becomes concentration independent in the limit of low concentration of trapped hydrogen [60].

2.2.3.2. Measurement of hydrogen permeation through membranes

In the Devanathan and Stachurski approach [59], a split cell is used where one side of the membrane is polarized cathodically or left at open circuit while the other side is polarized anodically. The surface concentration of hydrogen on the cathodic side reaches an environment- and potential-dependent value, but is fixed to zero on the anodic side. Part of the hydrogen produced cathodically absorbs into the metal lattice and diffuses down the concentration gradient to the anodically polarized side, where it is oxidized to $H^+$. “Poisons” like $As_2O_3$ [63] or $H_2S$ [64] might be added to the cathodic side to increase the fraction of hydrogen that diffuses into the metal or to characterize hydrogen absorption in particular environments. Ideally, the current measured on the anodic side of the membrane increases until it reaches a steady state, $i^\infty$

$$i^\infty = F \frac{D_{lat} C_0}{L} \tag{2.8}$$

where $C_0$ is the surface concentration of diffusible hydrogen on the cathodic side, controlled by the environment and potential, L is the thickness of the membrane, and F is Faraday’s constant. This equation assumes the diffusion coefficient is not dependent on
hydrogen concentration, and can be used to estimate the surface concentration of hydrogen attained in the environment [65]. At steady state, hydrogen in traps is in equilibrium with the hydrogen in the lattice, so transport of diffusible hydrogen is controlled by the lattice diffusion coefficient.

A number of techniques exist for estimating the value of the diffusion coefficient from the sigmoidal current transient measured at the anodic side of the membrane [59, 61, 66]. The time lag, \( t_{lag} \), is defined by the extrapolation of the time integral of hydrogen flux, which represents the amount of absorbed hydrogen, to the time axis [59]. It is also equal to the time required for the hydrogen oxidation current to attain 63\% of the steady state value [59]. A value of the hydrogen diffusion coefficient, \( D_{tlag} \), can be calculated by the following equation [59, 61]:

\[
D_{tlag} = \frac{L^2}{6t_{lag}}
\]  

where \( L \) is the thickness of the membrane.

The breakthrough time, \( t_b \), is obtained from extrapolation of the tangent at the inflexion point in the raising transient of the flux to the time axis. A value of hydrogen diffusion coefficient can be determined from \( t_b \) using [66]:

\[
D_{tb} = \frac{L^2}{2\pi^2t_b}
\]  

\( D_{lat} \), \( D_{tb} \), and \( D_{tlag} \), are all equal when transport is controlled by Fick’s laws. Traps are active during the increasing transient of the flux so transport of hydrogen is described by equations 2.6 and 2.7. Attempt to use equations 2.9 and 2.10, which are based on
Fick’s laws, to a system where traps are active result in apparent or phenomenological values of the diffusion coefficient, which are different than the lattice diffusion coefficient. On the other hand, it has been shown that, in the limit of low occupation of traps, $D_{\text{lag}}$ is equal to the effective diffusivity [60], defined in the previous section. Reported values of the phenomenological diffusion coefficient of hydrogen in steel vary by over three orders of magnitude between different experimentalists [65] because of the presence of traps and differences in trap nature and density between different steels. On the other hand, the lattice diffusion coefficient, required for calculation of concentration of hydrogen at the surface by equation 2.8, can be calculated from the initial decay in steady state flux [67], after decreasing the cathodic charging current on the input side of the Devanathan and Stachurski cell [59], because diffusible hydrogen leaves the sample first [68]. Another technique is to extrapolate the phenomenological diffusion coefficient vs. temperature curve to room temperature [68], because trapping disappears at high temperature. Typical values of the lattice diffusion coefficient for carbon steels are on the order of $10^{-6}$ cm$^2$/s [67, 69], varying with microstructure and direction of flux with respect to the parent plate.

2.2.3.3. Effect of surface films on hydrogen permeation

Films formed on the metal might interfere with the hydrogen absorption or desorption process. This is particularly the case for solutions containing sulfur compounds, because iron sulfide films can form and act as a barrier to hydrogen permeation [70]. A cathodic potential or current is often applied on the entrance side, and therefore fresh metal is expected to be exposed after a given transient. A several hours
long, uninterrupted cathodic treatment might be required to completely remove the surface films that hinder hydrogen entry, as shown by Zakroczymski [71]. However, since the point of hydrogen permeation experiments is to characterize hydrogen ingress into the metal lattice, any film developed on the anodic side that restricts hydrogen oxidation is of concern because it can lead to errors in the environment characterization. Therefore, it is recommended to cover the anodic side of the membrane with an inert coating of palladium, which does not appreciably affect the permeation rate but prevents iron oxidation or passivation [72]. The usefulness of such a coat was critically assessed by Manolatos [73]. The author studied the influence of the passive film developed on the anodic side of non-coated membranes on the permeation curves. Passive films affect the hydrogen concentration gradient in the membrane, because they induce variations in the surface concentration of hydrogen at the exit side. Therefore, they might prevent a steady state in hydrogen flux to be reached. Modifications of the models are required to interpret the results, since most of the models assume that hydrogen concentration at the exit side remains fixed at zero [59, 63, 74]. Working with no palladium coating but under careful control of the passivation conditions, Manolatos managed to obtain qualitative information about differences in trapping behavior in a carbon steel with differing microstructure, ranging from ferritic-pearlite to martensite [75]. However, because the structure of the passive film is expected to change with the alloy composition, it is difficult to extrapolate those results to other systems.
2.2.3.4. Effect of hydrogen sulfide in hydrogen absorption

Berkowitz reported that hydrogen sulfide has a double effect on hydrogen absorption [24]; it increases the rate of hydrogen reduction reaction (HRR) and poisons the hydrogen recombination reaction, thereby increasing the fraction absorbed into the steel. As a result, the hydrogen steady state permeation current of steel at open circuit in a solution containing 0.5% acetic acid and 5% NaCl was reported to be more than an order of magnitude higher when purged with $\text{H}_2\text{S}$ than when purged with $\text{N}_2$ [24]. The increase in the rate of HRR is thought to be due to an increase in anodical dissolution of iron in presence of $\text{H}_2\text{S}$, since a negative shift in potential was reported in the same work. It is seen in Figure 2.2b that sulfide films are stable near the hydrogen reduction potential and in acid environments, which contrasts the situation observed in absence of this gas, where $\text{Fe}^{++}$ is the stable species. Therefore, based on Berkowitz’s results, it can be concluded that the catalytic effects discussed above outweigh any hindering effect for hydrogen ingress presented by the sulfide. However, such effects are important since they can eventually affect the value of steady state permeation current.

The slowing down of hydrogen transport by film formation was suggested by Brickell [76]. The author showed that the hydrogen exit rate through a mechanically polished surface was considerably lower than one corroded in hydrogen sulfide. Similar effects would be expected when hydrogen ingresses the metal lattice. Foroulis proposed a correlation between the crystallographic structure of the film and hydrogen absorption rates [43]. Azevedo et al. [77] reported a correlation between hydrogen permeation at open circuit and weight loss in different $\text{H}_2\text{S}$ solutions. The author found that the greater
the protectiveness of the film in the given solution, the lower the amount of hydrogen permeating that surface.

Tsai [78] studied hydrogen permeation in a 0.5% acetic acid and 5% NaCl saturated with H₂S at open circuit potential, and found a clear maximum in the current vs. time curve measured in the anodic side of Devanathan and Stachurski cell, after which point current reached a steady state but at a lower value. Such a maximum was in accord with previously reported measurements by Petelot in the same solution [79], also obtained at open circuit potential. Scanning electron microscopy (SEM) studies conducted on samples exposed at different times showed that there exists a clear correlation between hydrogen ingress rate and surface film formation process [78, 79], which was also in agreement with loss of ductility [78]. Tsai proposed that this film acted as a barrier to hydrogen sulfide access to the metallic surface and to the exit of iron ions from metallic surface [78], therefore decreasing the surface concentration of atomic hydrogen produced by the following reaction:

\[
\text{Fe} + \text{H}_2\text{S} = \text{FeS} + 2\text{H}_{\text{ads}} \tag{2.11}
\]

Initially, FeS particles form at certain locations and a high fraction of the iron surface is available for the above reaction. After a certain period, the film is continuous and, for the particular concentrations used by Tsai [78], this time was found to be equal to 8 h, Figure 2.4. From this point, the film grows in thickness, slowing down the reaction between iron and H₂S, equation 2.11. This generates a decrease in the surface concentration of hydrogen, which decreases the steady state permeation flux of hydrogen, Figure 2.4, and causes atomic hydrogen release from reversible traps [78]. Petelot also
proposed that the sulfide film controlled the surface concentration of hydrogen on the cathodic side of the cell once it has developed. A clear dependence with pH was reported, probably due to a higher etching rate at lower pH, which favors hydrogen ingress [79]. However, once the hydrogen ingress rate passed the maximum value and reached a plateau, it was reported that the value of the plateau is independent of the pH or chloride concentration of the environment. On the other hand, Foroulis [43] showed that the protectiveness of the sulfide film, quantified by weight loss measurements, depends on the presence of chlorides and pH. A change from parabolic to linear kinetics was observed when chlorides were added to the H₂S solution. It is interesting that protective and non-protective sulfide films in the corrosion sense can provide a similar barrier to hydrogen ingress.

2.2.3.5. Effect of thiosulfate on hydrogen absorption

Elhamid et al. [80] characterized the dependence of hydrogen absorption on thiosulfate content in neutral and acid solutions using permeation experiments. The steady state current for hydrogen oxidation on the anodic side of the membrane depended strongly on thiosulfate content for a fixed cathodic current. This can be rationalized in terms of an increase in surface concentration of hydrogen (C₀) with thiosulfate content, as proposed by Hörnlund [53], and suggests that thiosulfate, or one of its decomposition products, could be acting as a poison for hydrogen recombination as observed in hydrogen sulfide solutions. Unlike galvanostatic tests [80], where the hydrogen permeation current does not seem to have a maximum with thiosulfate concentration, in open circuit conditions a maximum in the permeation current at 10⁻³ M of S₂O₃²⁻ was
reported independently by Tsujikawa [47] and Zucchi [49]. For concentrations of sulfur compound between $10^{-2}$ M and 0.1 M, Hörmund [53] found that thiosulfate ion produces a smaller increase in C$_0$ than sulfide, sulfite or dithionite at pH near 7. Horowitz [81], using a 5% sodium chloride solution and 0.5 % acetic acid solution with 0.1 M S$_2$O$_3^{2-}$ found that, although the corrosion current at the open circuit potential was considerably increased with respect to the same solution without the sulfur oxyanion, the percentage of permeated hydrogen current remained as low as 2% of the cathodic current. Such a value is negligible if compared to the 70% of cathodic current attained in the same solution with 0.1 M H$_2$S [81]. No mechanistic explanations are available in the literature for this maximum in permeation current with S$_2$O$_3^{2-}$ concentration. Such knowledge would be desirable since it is relevant to corrosion fatigue tests, where absorption of hydrogen can control fatigue crack growth rate [1].

The corrosion potential of martensitic and supermartensitic stainless steels [82] and carbon steel [49] experienced a negative shift with the increase in thiosulfate content, whereas the cathodic current increased monotonically with thiosulfate additions. Elhamid [80] reported that thiosulfate depolarizes the hydrogen evolution reaction in neutral and acid environments, but without affecting the Tafel slopes significantly. However, it is unclear whether the increase in potentiodynamically measured current reported by Zucchi [49] actually corresponds to an increase in hydrogen evolution or is related to the occurrence of reduction reactions of thiosulfate, equations 2.3 and 2.5, which are thermodynamically possible at the corrosion potential of carbon steels. Further study is needed on this topic, since this could be the cause of the lower values of hydrogen
permeation in thiosulfate compared to hydrogen sulfide solutions as reported by Horowitz [81]. For a hydrogen sulfide solution, since H$_2$S is the stable phase at the corrosion potential, electrons from iron dissolution are consumed exclusively by the reduction of protons, and part of the hydrogen produced can be absorbed into the metal. On the other hand, reduction of thiosulfate could be consuming electrons otherwise available for hydrogen evolution, therefore diminishing the amount of hydrogen reduced. While it is true that films formed in thiosulfate solutions could be blocking hydrogen ingress [53], there is not available evidence in the literature to conclude in favor of one or both mechanisms. Hydrogen permeation experiments and corrosion studies were performed in this work to clarify this.

2.2.4. Degradation of steels in thiosulfate solutions

Much of the literature of corrosion behavior of steels in thiosulfate solutions is related to pitting or stress corrosion cracking of stainless steels. Interest in thiosulfate is based on its presence in certain liquors used in paper mills, the fact that it is stored in nuclear power plants to react with iodine fission products in case of an accident, or the possibility that it is a product of sulfate reducing bacteria.

2.2.4.1. Pitting of stainless steels in thiosulfate solutions

Pitting of stainless steels in thiosulfate solutions was studied by Newman [83-85]. Remarkable findings include the fact that thiosulfate pitting occurs over a certain range of concentration [84] and potential [83]. Newman [84] rationalized his results suggesting that with higher concentrations of thiosulfate, electromigration of this ion to pit bottoms
and accumulation becomes relevant, which can decrease local acidification via equation 2.3. The presence of an additional anion of a strong acid, like chloride or sulfate, is required for pitting to occur [85]. The upper bound in potential for pitting occurrence suggested that pitting requires reduction to sulfide or sulfur [83]. It is believed that sulfide and sulfur hinder repassivation of pits by adsorbing on the bare metal surface.

A correlation between pitting of stainless steels in K$_2$S$_2$O$_3$ and in H$_2$S solutions was found by Tsujikawa [50], in terms of pitting potential, with a conversion factor equal to $10^{-1}$ M K$_2$S$_2$O$_3$/atm H$_2$S. Test temperature was 80°C and solutions contained 20% NaCl. However, open circuit potential (OCP) in the salt solution was 100 mV higher than in the gas solution, which increased its susceptibility to cause pitting. Pitting was found in alloys with OCP lower than the reversible potential indicated by equation 2.5, where hydrogen sulfide is the stable specie. On the other hand, for passivated and platinum surfaces, an increase in thiosulfate shifted the potential from that corresponding to equation 2.3 to that corresponding to equation 2.5 [47]. Tsujikawa [50] found a continuous decrease in pitting potential as a function of thiosulfate concentration for the 20% NaCl solution, which is in contrast with the situation described by Newman [84], who reported that for a solution containing 0.25 M NaCl at room temperature a large amount of thiosulfate can cause inhibition. The higher Cl$^{-}$ concentration in the solution studied by Tsujikawa might decrease the concentration of thiosulfate in pit bottoms and prevent the occurrence of the buffering effect of thiosulfate as shown in Equation 2.3.
2.2.4.2. Stress corrosion cracking of stainless steels in thiosulfate solutions

Stress corrosion cracking (SCC) in thiosulfate solutions is observed in sensitized 18Cr-8Ni stainless steels [51, 86], martensitic and supermartensitic stainless steels at room temperature [82] or unsensitized stainless steels at higher T [47, 87, 88]. For sensitized austenitic stainless steels at room temperature, intergranular cracks are observed in thiosulfate solutions [51, 89], similar to the ones observed in hydrogen sulfide solutions. Concentrations of S$_2$O$_3^{2-}$ as low as 10$^{-6}$ M [89] were reported to produce cracking, which was explained in terms of the high tendency of adsorption of the anion on steel surfaces [90].

Pitting in the thiosulfate solution and presence of chlorides seem to be necessary conditions for the occurrence of SCC [91]. However, measured crack length of a sensitized austenitic stainless steel in a thiosulfate solution was more than one order of magnitude higher than predicted by metal dissolution of chromium depleted zones [51]. It is thought that S$_2$O$_3^{2-}$ induces SCC by its propensity to transform to H$_2$S and S [47, 48, 91, 92], which can catalyze the ingress of hydrogen and inhibit repassivation. Such reaction could only be possible if the passivating film is perturbed, driving the potential to low enough values [86]. Due to the known effects of H$_2$S on hydrogen ingress, contributions from a hydrogen embrittlement mechanism were proposed [93, 94]. It was reported [93] that a net anodic current circulates from the crack tip to the external surface of a notched stainless steel sample in a thiosulfate solution, therefore aiding in the creation of a particular environment of high acidity. Maintenance of acidity at the crack tip seems to be a necessary condition for SCC, since it was shown that a decrease in pH
increases the crack nucleation rate, while the addition of a buffer in concentrations greater than thiosulfate decreased it [95]. The characteristic rotten eggs odor of H\(_2\)S and a change in the color of a thiosulfate solution from clear to yellow, probably indicating presence of colloidal S, were reported after an SCC test of a sensitized stainless steel [93]. Moreover, energy dispersive X ray analysis have shown presence of sulfur rich compounds on crack surfaces [95].

Other authors [51, 90, 95] have criticized the hydrogen embrittlement mechanism and proposed enhancement of anodic dissolution by thiosulfate anions, thiosulfate induced changes in the passive film structure [90], and contribution from embrittlement associated with the formation of strain induced martensite [51]. Isaacs [89] found that SCC is inhibited at potentials lower than -0.75 V\(_{\text{SHE}}\). It is likely that acidity cannot be sustained at the crack tip at such low values of potential, and the dissolution of iron in chromium depleted grain boundaries is inhibited. However, such a lower potential bound is inconsistent with a hydrogen embrittlement mechanism. Moreover, Wells [95] and Newman [51] reported maximum loss of ductility and maximum crack growth rate at potentials well above the reversible potential for hydrogen reduction. Horowitz [90] supported the anodic dissolution mechanism, when he reported that the species that reduce the passivation current of steel in thiosulfate solutions also inhibit SCC. The author also found that the oxyanion increases considerably the passivation current of a carbon steel [81] and of a 7% Cr steel [90], which has a concentration similar to that of sensitized grain boundaries. It was proposed that the effect is related to a strong adsorption of the sulfur compound on the steel surface.
SCC performance of several corrosion resistant alloys, including ferritic, austenitic and duplex microstructures were tested in 20% NaCl solutions with pH=4.0 and at a temperature of 80°C containing H₂S or S₂O₃²⁻ [47]. SCC in S₂O₃²⁻ correlated with SCC in H₂S environments for tests that produced fair amounts of plastic deformation, like slow strain rate testing or constant load tests performed well above the yield stress, but it could not predict SCC for tests with constant deformation, where the surface film is allowed to heal and remain undisturbed afterwards. The necessary potential perturbation is expected to occur during tests where plastic deformation is continuous, exposing fresh metal and driving the potential to low values where S and H₂S can be formed. In thiosulfate solutions, such potential perturbations were observed in a constant extension rate test of an AISI 304 sensitized stainless steel sample at room temperature after the yield point [95] and during mechanical scratching of the surface of an AISI 316 stainless steel [47]. Another effect of the continuous plastic deformation was the transport of hydrogen into the metal lattice by moving dislocations [48]. Cracks were usually found at the bottom of pits [47], which act as stress concentrators and where the potential might be low enough to allow production of H₂S. SCC experiments under potentiostatic control inside and outside the H₂S stable region could provide further proof of those statements, but they were not performed by the authors. It can be deducted from Tsujikawa’s work that 0.1 MPa of H₂S corresponds to 0.01 M of S₂O₃²⁻ in terms of occurrence/non-occurrence of SCC for different stainless steels, but the quantitative correlation in terms of loss of elongation or time to failure is less clear. The minimum in
loss of elongation occurred near $10^{-2}$ M. A minimum in pitting potential was reported at that same concentration for a 18Cr-8Ni stainless steel [88].

2.2.4.3. Stress corrosion cracking of carbon steels in thiosulfate solutions

Tsujikawa [47] studied stress corrosion cracking susceptibility of carbon steels as a function of $\text{S}_2\text{O}_3^{2-}$ concentration. Slow strain rate tests were performed, but the aggressiveness of the solution could not reach that of saturated $\text{H}_2\text{S}$ solutions in terms of loss of elongation, even though the corrosion potential and pH values corresponded clearly to the $\text{H}_2\text{S}$ stable region. The author proposed decreasing the pH of the solution to raise its severity, but Newman [51] has pointed out the difficulties to maintain a pH below 4, due to the buffer effect of sulfite and sulfurous anions. Zucchi [49] compared the hydrogen permeation flux as a function of thiosulfate additions to solutions of pH 2.7 and 1.5, but the increase in hydrogen permeation obtained due to the decrease in more than one pH unit was lower than 50%. For a solution with pH of 2.7, the maximum susceptibility to SCC [47] occurred at a concentration near $10^{-3}$ M $\text{S}_2\text{O}_3^{2-}$ coincident with a maximum in hydrogen absorption, which is in agreement with an independent study published later by Zucchi et al. [49]. For ferritic steels, including martensitic and supermartensitic stainless steels [82], and carbon steels [47, 49], there is agreement in the literature that SCC in thiosulfate solutions is the result of a hydrogen embrittlement mechanism.
2.3. Unsolved issues

Similarities between electrochemical behavior in hydrogen sulfide and thiosulfate solutions have been exposed. The most notable findings discussed in this review are that thiosulfate decomposes to hydrogen sulfide at the corrosion potential of steel in acid and neutral solutions, and that thiosulfate increases the rate of hydrogen ingress in permeation experiments. However, several aspects about the electrochemical behavior of steel in thiosulfate solutions need to be addressed to achieve an appropriate understanding of corrosion fatigue in such environments.

The kinetics of hydrogen sulfide generation needs to be assessed, because this will determine the ability of thiosulfate solutions to simulate hydrogen sulfide solutions. It has to be stated that corrosion fatigue tests usually extend over few days. If the kinetics are too slow, simulation of concentrated hydrogen sulfide environments might not be possible. However, if the kinetics are too fast, thiosulfate should be replenished during the test. The Tsujikawa mechanism indicates that hydrogen sulfide generation consumes electrons, but the relationship between this current and total corrosion current has not been explored. Hydrogen evolution reaction rate, which is closely related to hydrogen absorption, will be reduced if most electrons resulting from open circuit corrosion of steel are consumed for thiosulfate reduction. If that is the case, simulation of sour corrosion fatigue, which is influenced by hydrogen embrittlement, might not be possible. Finally, the amount of thiosulfate that is lost in the sulfide film formation process and during bulk disproportionation has not been compared to the amount of hydrogen sulfide generated.
The structure of films formed in thiosulfate solutions needs further characterization. Films may affect not only hydrogen permeation rates, as for hydrogen sulfide solutions, but also diminish crack growth rate due to crack closure effects. Current knowledge is limited to visual observation of tarnish appearing on samples exposed to thiosulfate solutions, but the dependence of film structure with thiosulfate concentration needs to be assessed. The effect of those films on corrosion rate and anodic and cathodic currents needs to be studied, which can be used to understand the hydrogen absorption experiments described in the literature. The presence of a maximum in hydrogen permeation current with thiosulfate concentration was shown independently by Tsujikawa and Zucchi [47, 49], but little is known about the microscopic causes behind such maximum. The hydrogen permeation current after long exposure times also needs to be addressed, because due to the long time extension of corrosion fatigue tests, embrittlement might be controlled not by the initial rate of hydrogen absorption, but by the rate of hydrogen absorption when the sulfide films have covered the surface. Fundamental understanding of thiosulfate effects on hydrogen permeation is required to fully understand the possibility of replacing \( \text{H}_2\text{S} \) by thiosulfate.

No studies on corrosion fatigue of steels in thiosulfate solutions have been reported in the literature, but it is known that nickel base alloys can suffer a decrease in fatigue life in such environments [96, 97], especially in the sensitized condition and at low frequencies. An anodic dissolution mechanism was proposed, due to the increase in fatigue crack growth rate with anodic potential [97]. However, based on the stress corrosion cracking studies of ferritic and martensitic steels, where there is general
agreement that hydrogen embrittlement controls SCC failure, it is expected that hydrogen embrittlement will play a significant role in corrosion fatigue of carbon steels. Although it is expected that the localized plastic deformation at the crack tip would affect the rate of ingress of hydrogen, such effects should not differ for thiosulfate or hydrogen sulfide environments, unless the films formed in each environment affects in considerably different ways the effective stress state via a crack closure mechanism. It is therefore expected that comparison of the electrochemistry of steel in thiosulfate solutions against the behavior in hydrogen sulfide solutions should provide valuable information for selecting alternative, safer solutions for the study of sour corrosion fatigue.
2.4. Figures

Figure 2.1. a) Pourbaix diagram for sulfur in aqueous solution at 25°C, for a dissolved sulfur activity of 0.01 [39]. b) Metastable potential/pH diagram of sulfur-water system at 25 °C, constructed via exclusion of S(IV) species [39]. Adapted with permission from Springer.
Figure 2.2. a) Pourbaix diagram for iron in water and b) in presence of $\text{H}_2\text{S}$ at unit activity and at 25°C. Reproduced from [19] with permission from John Wiley and Sons.
Figure 2.3. Relative surface coverage of sulfur ($\theta_S$), oxygen ($\theta_O$) and water ($\theta_{H2O}$), considering that thiosulfate is the only oxidized sulfur specie of the sulfur/water diagram (--------), superimposed on a potential-pH diagram for S-Fe-H2O (-----), in presence of $10^{-4}$ mol sulfur species/kg of solution at 25ºC. Reproduced from [57] with permission from Elsevier.
Figure 2.4. Correlation between surface concentration of hydrogen and sulfide film formation process. Adapted from [78] by permission of The Electrochemical Society.
2.5. References


CHAPTER 3. REACTION PATHS OF THIOSULFATE DURING CORROSION OF CARBON STEEL IN SUBSTITUTED NACE TM0177-96 SOLUTIONS

3.1. Introduction

Thiosulfate, S$_2$O$_3^{2-}$, is a non-toxic, metastable ion that can react to yield hydrogen sulfide, H$_2$S, in solution in a broad range of potential and pH [1]. This situation, combined with the dangers involved in the manipulation of gaseous H$_2$S, led Tsujikawa to propose it as a replacement of H$_2$S for laboratory studies of pitting corrosion [2] and stress corrosion cracking [1] in sour environments. The ion can be formed when oxygen ingresses in an originally deareated H$_2$S solution, but corrosion studies concluded that S$_2$O$_3^{2-}$ by itself does not have a corrosive effect on carbon steel beyond the local generation of H$_2$S by a cathodic reaction [3]. A complication related to the use of thiosulfate in acid solutions is that the ion spontaneously disproportionates, yielding elemental sulfur [1, 4], a known corrosive [5]. Finally, an iron sulfide film can form on carbon steel exposed to thiosulfate-containing solutions [1, 6, 7]. The objective of this chapter is to quantify each of those thiosulfate reaction paths as a function of thiosulfate concentration.
Hydrogen sulfide was detected in a bulk thiosulfate solution containing acetic acid and sodium chloride during carbon steel corrosion [1, 8], and is believed to form by the following reactions [1, 4]:

$$S_2O_3^{2-} + 6H^+ + 4e^- = 2S^0 + 3H_2O \quad E_0 = 0.465 \text{ V}_{\text{SHE}} \quad 3.1$$

$$2S^0 + 4H^+ + 4e^- = 2H_2S \quad E_0 = 0.142 \text{ V}_{\text{SHE}} \quad 3.2$$

These reactions are spontaneous at the corrosion potential of carbon steel, which in this solution is near -0.4 V_{SHE}. The bulk concentration of H_2S in the cell, reported by Tsujikawa as a function of the solution chemistry over a period of 24 h [1], is not exclusively dependent on the kinetics of thiosulfate reduction to H_2S, but also on experimental variables like N_2 flow rate and hydrodynamic conditions like stirring. Deareation is a common practice in sour corrosion and stress corrosion cracking testing [9], because it mimics well environments and prevents oxidation of hydrogen sulfide by oxygen. After an initial period of nitrogen deareation, continuous bubbling of hydrogen sulfide or hydrogen sulfide mixtures maintains a small overpressure in the cell that prevents oxygen ingress. A safer alternative to this practice is the use of thiosulfate solutions and nitrogen bubbling. However, in this case part of the hydrogen sulfide generated by thiosulfate reduction will be flushed away with the nitrogen. The amount of sulfide lost as a function of time by this process has not been reported in the literature.

Precipitation of sulfur from acid thiosulfate solutions is a well known process [10, 11]. This reaction is from homogeneous disproportionation of thiosulfate, producing elemental sulfur and bisulfite [1, 4]
\[ S_2O_3^{2-} + H^+ = S^0 + HSO_3^- \]

\[ \Delta G^0 = -3.1 \text{ kJ/mol} \]

3.3

The change in standard Gibbs free energy was calculated based on electrochemical data reported in the literature [4]. Chromatographic studies [11] on products of decomposition of thiosulfate in acid media suggested that polythionates (S\(_x\)O\(_6\)^{2-}\), with \(x\) ranging between 3 and 5) might also be present after short periods of time. Thermodynamics predicts that those species and bisulfite can further reduce to elemental sulfur and hydrogen sulfide at the corrosion potential of carbon steel [4]. Contact of elemental sulfur with steel can lead to catastrophic corrosion with formation of iron sulfides and hydrogen sulfide [12].

It is known that carbon steel in thiosulfate solutions can develop a black tarnish [6, 7], and EDS studies in sodium chloride base solutions have shown that the film contains sulfur [13]. Furthermore, H\(_2\)S and elemental sulfur, S\(^0\), products of carbon steel corrosion in thiosulfate solutions and thiosulfate disproportionation respectively, are known to lead to formation of iron sulfides. Ferrous sulfide film formation in the presence of hydrogen sulfide has been extensively studied [14-16], and the process can proceed by direct film formation involving adsorbed sulfur or by a dissolution-precipitation reaction [14]. Sulfide film growth is strongly dependent on pH. Iron dissolution has a faster kinetics with decreasing pH, but the solubility of iron sulfides decreases with an increase in alkalinity [15]. Shoesmith [15] reported that the amount of precipitated iron sulfides reached a maximum at pH near 4, which is near the pH of saturated H\(_2\)S solutions.
On the other hand, elemental sulfur dramatically increases the corrosion rate of carbon steel, and the reaction proceeds with formation of iron sulfides [5]. Direct contact between the iron electrode and sulfur particles is required for corrosion to proceed [5, 12]. An incubation time is observed during elemental sulfur corrosion [5], which is believed to be related to formation of iron sulfide film by reaction with H₂S, generated by disproportionation of elemental sulfur:

\[
4S^0 + 4H_2O + H^+ = 3H_2S + SO_4^{2-} + 3H^+ \quad \Delta G^0 = 124 \text{ kJ/mol} \quad \text{(3.4)}
\]

where the standard Gibbs free energy change was calculated based on electrochemical data [4]. The reaction is non-spontaneous in the standard state and this reaction has low kinetics at room temperature [5]. The appearance of a black film of iron sulfide in sulfur-water suspensions can be seen only after a period that is environment-dependent and can be on the order of a day [12]. The film is the result of reaction of H₂S produced in equation 3.4 with steel. Iron sulfide is thought to be a catalyst for sulfur reduction [5, 17], and corrosion after formation of such film can proceed at catastrophic rates and with evolution of hydrogen sulfide [12],

\[
(x-1)Fe + S_{y-1}.S^{2-} + 2H^+ \xrightarrow{FeS} (x-1)FeS + H_2S + S_{y-x} \quad \text{(3.5)}
\]

where the species S_{y-1}.S^{2-} is the result of chemisorption between elemental sulfur and sulfide [12], and the subscript on sulfur represents the fact that the element has tendency to form rings and chains [5]. This reaction essentially represents the reduction of elemental sulfur to hydrogen sulfide, equation 3.2, but it is written with the reactive species encountered in solution.
The objective of this study is to quantify the amounts of hydrogen sulfide, iron sulfide and elemental sulfur that are produced during carbon steel corrosion in thiosulfate solutions. Due to continuous deaeration, the system is open and the amount of sulfur species in the cell is not constant with time. The kinetics of H$_2$S generation needs to be studied to ascertain optimal ratios of volume of solution per exposed area of steel or critical times for replenishment of thiosulfate. Moreover, a caustic trap at the exit of the cell is required to minimize any venting of H$_2$S to the environment. A method will be presented here where periodic sulfide measurements in the trap are used to estimate the amount of sulfide lost due to deaeration. It will be shown that the cell, due to its low pH, is a weak trap for H$_2$S. Therefore, the measurements of the amount of sulfide in the trap are expected to be near the total amount of H$_2$S generated. Furthermore, equilibrium and mass conservation will be used to estimate the concentration of H$_2$S at the steel surface. Other advantages of this method are the simpler chemistry of the trap compared to the cell environment. The trap is a mixture of sodium sulfide and sodium hydroxide, whereas the cell contains thiosulfate and its byproducts, among other species. The simple trap chemistry minimizes interferences in the analytical detection of S$^{2-}$. Another advantage of this method is that the sensitivity in sulfide detection can be controlled by altering the trap to cell volume ratio, taking care that the hydrogen sulfide generated does not saturate the trap volume. Finally, the amount of sulfide lost in the film and the amount of sulfur in solution will be estimated by weight difference of corrosion coupons and filter papers. The growth of films in thiosulfate solutions is of interest in sour stress corrosion cracking simulation because they can behave as barriers to hydrogen absorption [7, 18], therefore
affecting embrittlement. Elemental sulfur can lead to catastrophic corrosion and can constitute an extra reactant for hydrogen sulfide generation [12], equations 3.2 and 3.5. However, contact with the steel is required and in situations with a large solution to steel area ratio, transport to the metal surface can be tortuous. The amount of sulfur generated during disproportionation can be considered as lost thiosulfate.

3.2. Experimental

All electrochemical experiments were conducted in a glass cell with ground glass ports for deaeration and insertion of electrodes. The solution adopted for all experiments was a variation of NACE TM0177-96 solution A, which contains 0.5 wt% glacial acetic acid, 5 wt% sodium chloride and is saturated with hydrogen sulfide [9]. This base solution is commonly used in stress corrosion cracking evaluation of materials for sour service. Instead of continuous hydrogen sulfide bubbling, a single addition of sodium thiosulfate at the beginning of the test was adopted. Therefore, it is referred to as substituted NACE TM0177-96 solution A. The target $S_2O_3^{2-}$ concentration was reached by addition of aliquots from a 1 M $Na_2S_2O_3.5H_2O$ solution, except for the $10^{-1}$ M solution, where crystals of $Na_2S_2O_3.5H_2O$ were directly weighed and added to the base solution. For experiments conducted to estimate the amount of sulfur in the bulk solution, the solution was placed in a separate beaker inside the cell, which facilitated handling during subsequent filtration at the end of the corrosion test. Pure nitrogen (99.999%) was used for deaeration, and stainless steel tubes and valves connected the exit of the tank to a Teflon® sparger, in an effort to minimize corrosion of the tubing by the solution. The connection between the sparger and the stainless steel tube was placed inside the cell.
The electrode was pipeline grade X65 carbon steel and was cast in epoxy and polished to
600 grit. A special sample holder was constructed that allowed deaeration of the solution
without contact to the sample. After 1 hour of deaeration, the sample was immersed by
lowering into the solution without opening the cell.

3.2.1. Hydrogen sulfide generation tests

The amount of H$_2$S generated during OCP immersion of a steel specimen in
substituted NACE TM0177-96 solutions with varying thiosulfate concentrations was
estimated by measuring the S$^{2-}$ content in the trap. Aliquots were taken once per day for
three days. To ensure that all the hydrogen sulfide was absorbed by the trap, a second trap
was placed in series with the first one. The sulfide ion concentration in this second trap
was always below the detection limit (<0.5 ppm). The nitrogen flow rate was high during
the first hour, and then decreased to 0.30 ml/s after the sample was immersed. A
magnetic stirrer was utilized to ensure good mixing of the cell solution.

The cell used for the H$_2$S generation experiments had a capacity of 400 ml, and
300 ml of solution were used for all thiosulfate concentrations, except $10^{-4}$ M where it
was increased to 400 ml. The electrode area was also increased, as detailed in Table 3.1,
to generate more H$_2$S and facilitate its detection. The nitrogen gas exited the cell through
a glass tube and then passed through a trap containing 0.01 M NaOH. The volume in the
trap was 100 ml, and 5ml aliquots were extracted once per day. The pH of those aliquots
was controlled to ensure that it was between the limits suggested by the sulfide detector
tube manufacturer and then its sulfide content was measured.
Gastec® 211L (0.5 to 20 ppm) and 211M (2 to 300 ppm) sulfide ion detector tubes were used for sulfide ion measurements. These tubes have a graded scale and are filled with a reactive species containing lead acetate, which turned brown in contact with sulfide due to precipitation of lead sulfide. The manufacturer reports a measurement error of 10%. The value in the graded scale was multiplied by the trap volume and used to estimate the number of moles of $S_{2}^{-}$ lost from the cell due to deareation. The number of moles lost from the 5 ml sampling process was considered in the subsequent calculations of lost $S_{2}^{-}$. Other authors [1, 8] estimated the generation of $H_{2}S$ by taking aliquots from the cell, and then adding sodium hydroxide to convert the $H_{2}S$ to $S_{2}^{-}$. However, thiosulfate and sulfite, which is expected to be present in the cell due to thiosulfate disproportionation, interfere with the response of the detector tubes and with alternative detection methods like ion selective electrodes. By analyzing the sulfide content of the trap, interferences are minimized.

The diffusion layer thickness, $\delta$, is required for the calculation of $[H_{2}S]_{\text{steel surface}}$, the concentration of hydrogen sulfide close to the steel surface corroding in the thiosulfate containing solution. The same cell under the same deareation and stirring conditions was used to measure the limiting oxidation current of $Fe(CN)_{6}^{4-}$ on a platinum electrode that was mounted in the same fashion as the steel samples. A platinum counter electrode was separated from the cell main compartment by a glass frit. The same content of sodium chloride as in the other tests was adopted, 5 wt %, but acetic acid was not added due to potential production of toxic HCN. Since acetic acid is a weak acid, the ionic strength of both solutions should be similar. The limiting current was plotted
against the concentration of Fe(CN)$_6^{4-}$ and $\delta$ can be obtained from the slope of the curve using this form of Fick’s first law:

$$i_{\text{lim}} = -nFD\n C \approx nFD \frac{C_{\text{bulk}} - C_{\text{surface}}}{\delta}$$

where $n$ is the number of electrons transferred, $F$ the Faraday constant, $D$ the diffusion coefficient of the electroactive species, and $C_{\text{bulk}}$ and $C_{\text{surface}}$ are the concentrations of the electroactive species in the bulk and surface, respectively. By using a reversible couple with fast electron transfer kinetics, it is possible to assume that $C_{\text{surface}}$ is zero, which simplifies the calculations. A diffusion coefficient of $6.67 \times 10^{-5}$ cm$^2$/s was assumed for Fe(CN)$_6^{4-}$, which was measured in a 1.00 M KCl solution at 25º [19], which are similar to the ionic strength and temperature of the experiments reported herein.

The surface pH in the corroding steel can be higher than the bulk pH, because cathodic reactions consume protons. The mesh-capped surface pH probe developed by Han et al. [20], was adopted to measure the surface pH of steel corroding in thiosulfate solution, which is expected to affect the speciation of $[\text{H}_2\text{S}]^{\text{steel surface}}$. A flat tip pH electrode is compressed against a carbon steel mesh with a compression fitting. One side of the mesh is exposed to the solution, while the other side is in direct contact with the pH electrode. A Thermo Scientific Orion® 8135BN flat tip pH electrode and woven carbon steel wire cloth were used. The pH electrode had a double junction, which minimized contamination by sulfide. Iron mesh circles were cut from a woven iron wire cloth with a 30% open area and 60 x 60 holes/in$^2$. The mesh circles were degreased with acetone, immersed in 5% HCl solution to remove the air formed oxide, rinsed with DI
water and finally rinsed with methanol prior to being inserted in the surface pH electrode assembly. Two new circles were secured at the tip of the electrode at each test, because it was found that steady state was reached faster with this design [20]. The surface pH electrode assembly was immersed in N₂ deareated NACE TM0177-96 solution A and in the same solution with thiosulfate concentrations ranging from $10^{-4}$ to $10^{-1}$ M. The pH electrode was connected to a Gamry® Ref600 potentiostat used as a data acquisition device and its potential was recorded for a period of 22 h. The potential of the pH electrode in each solution was measured in the bulk at the beginning and end of each experiment for comparison purposes. Also, the potential of the pH electrode in buffers with pH equal to 4.00 and 7.00 was measured at the beginning and end of the test. The potentials measured at the beginning of the test in each buffer were used to linearly convert the potential to pH at each time. The potentials in the buffer at the end of the test were checked to estimate drift in potential. These values were also used to estimate the error in the measurements, which was on the order of 0.2 units of pH.

3.2.2. Quantification of sulfide film

The electrode weight change was used for estimating the amount of sulfide present in the surface film. Because three orders of magnitude of thiosulfate concentration were investigated, it was not possible to use the same exposure time for all conditions. Long exposure times were required to generate enough corrosion products for the most diluted solutions, while for the most concentrated solution there was a threshold time after which the film started to spall off and fall into the solution. Separation of this film from the solution is complicated due to presence of sulfur particles generated by
thiosulfate disproportionation. Therefore, the exposure times were 72 h for all the solutions except for the one with $10^{-1}$ M $\text{S}_2\text{O}_3^{2-}$, which was 20.17 h. Prior to starting the experiments, the samples were thoroughly cleaned in ethanol in an ultrasonic bath and dried for a day in a desiccator. Samples weights, $W_1$, were measured with an analytical balance. The samples were carefully extracted from the cell after exposure in the thiosulfate-containing solution, rinsed with deionized (DI) water and acetone, and inserted in a desiccator that was purged continuously with pure nitrogen in an effort to minimize oxidation of the iron sulfide [21]. Following overnight exposure in the desiccator, the weight of the sample with the corroded film, $W_2$, was measured. Then the film was removed using a procedure that minimized the corrosion of the underlying steel by immersing the sample in a solution containing 250 ml of hydrochloric acid, 5 g of antimony trioxide ($\text{Sb}_2\text{O}_3$) and 14.877 g of stannous chloride dihydrate ($\text{SnCl}_2\cdot2\text{H}_2\text{O}$) [22] prepared from reagent grade chemicals. The difference in color between the black iron sulfide containing film and the metallic grey uncorroded steel was used to assess the time for complete removal of the corrosion products. A blank experiment was conducted to estimate the weight loss due to corrosion of steel by this cleaning solution. A polished steel sample with an exposed area of 7.61 cm$^2$ was cleaned in the same way as the corroded samples with the inhibitor containing HCl solution and a decrease in weight of 0.2 mg was measured, which is negligible compared to the differences in weight reported here. Once the film was removed, the samples were carefully washed with deionized water, rinsed with ethanol and dried in a stream of air prior to being placed back in the N$_2$ purged desiccator for one day. Finally the weight of the uncorroded steel was measured,
W₃, and the weight difference W₃-W₂ was calculated, to yield the weight of the film. The weight difference W₃-W₁ is a measure of corrosion rate and will be reported in next chapter. It will be shown in the next chapter that the main crystalline phases in the film are mackinawite, Feₓ(1+x)S, and cementite, Fe₃C, present as a result of preferential ferrite dissolution. The x in the iron sulfide varies between 0.057 and 0.064 [16] due to the non-stoichiometry of this phase. The amount of sulfide in the film was obtained as a product between the wt% of sulfur in the film, measured with scanning electron microscope (SEM) and energy Dispersive X-ray Spectroscopy (EDS) analyses, and the total weight of the film. Therefore, corrections due to non-stoichiometry of the film are not necessary.

The cell used in the weight loss experiments had a volume capacity of 1800 ml, but was filled with 1500 ml of solution, except for the solution with $10^{-1}$ M of $\text{S}_2\text{O}_3^{2-}$ where it was filled with 500 ml of solution due to the shorter exposure time. The electrode area exposed to the solution was near 7 cm². It was larger than with the hydrogen sulfide generation experiments in order to have greater weight differences. The deaeration nitrogen was also forced through the caustic trap for safety purposes.

3.2.2.1. SEM-EDS analyses of the film and underlying metal

The film morphology was investigated using SEM after 24 h of exposure to the thiosulfate-containing solutions at the corrosion potential, except for the sample exposed to $10^{-4}$ M thiosulfate where the time was increased to 48 h to generate more corrosion products.

The dependence of film thickness on concentration of $\text{S}_2\text{O}_3^{2-}$ at OCP was estimated with electron microscope images of polished cross sections. Such coupons
were mounted in conductive epoxy to minimize the falling out of the film during the grinding and polishing process. Samples exposed to the $10^{-1}$ M and $10^{-2}$ M $S_2O_3^{2-}$ solutions exhibited a cracked film while still in the solution. For the $10^{-1}$ M solution, part of the film spalled off and fell to the bottom of the cell. Due to the various sources of error in this method, rather than attempting the construction of a thickness vs. time curve, images of the cross sections after 72 h of exposure to the corrosion potential for all four thiosulfate concentrations will only be compared. EDS analyses of the cross sections were obtained, and the weight percent of sulfur was multiplied by the weight of the film to obtain the total amount of sulfide in the film. For the $10^{-4}$ M solution, since the film was too thin to be resolved in the SEM, the EDS analysis was performed at the surface of a sample exposed for 143 h at OCP.

3.2.3. Quantification of sulfur in the bulk of the solution

Filtration was used to measure the amount of elemental S in the solution. A carbon steel sample was immersed at OCP for 24 h in 700 ml of $10^{-2}$ M and $10^{-1}$ M thiosulfate solutions. A Whatman® grade 1 filter paper was placed in a desiccator for 48 hours and weighed prior to being placed in the glass funnel. The solution from the OCP experiment was filtered through the paper. This was attempted exclusively for the two most concentrated solutions, since the other solutions remained clear throughout all the experiments. The beaker was washed several times with DI water and, to remove all sulfur adhered to the walls, scraped with a rubber policeman, which was rinsed with water that was also drained through the filter. The filter was rinsed several times with DI water and was finally placed in a desiccator for 48 hours. The weight gained by the filter
is an indication of the amount of sulfur produced by disproportionation of thiosulfate. The technique was validated by obtaining the XRD pattern of the remaining, yellow powder for the $10^{-1}$ M solution. A powder diffractometer, operated with a Cu anode ($\lambda_{\text{Cu K}\alpha 1}=1.54056$ Angstrom) and a Ge solid state detector, was used to collect the diffraction spectrum of the residue, from 5 to 70° at a scanning rate of 0.1°/minute.

3.3. Results

3.3.1. Hydrogen sulfide generation tests

The amount of sulfide detected in the trap as a function of time normalized by the exposed steel area is presented in Figure 3.1. The error bars represent the 10% error in sulfide concentration measurement, as reported by the sulfide detector tubes manufacturer. Results of the blank tests revealed that concentration of sulfide in the trap when steel was not immersed were below the detection limits (0.5 ppm) after 24 h of continuous deareation of thiosulfate-containing solutions. Results for the solution with $10^{-4}$ M [$S_2O_3^{2-}$] were multiplied by 10 so that they could be resolved in the same scale used for the more concentrated solutions. The trap concentration increased linearly with time and the slope increased with thiosulfate concentration up to $10^{-2}$ M, after which point it decreased slightly.

The number of moles of sulfide in the trap ($S^{2\text{trap}}$) at time $t_f$ is related to the molar fraction of hydrogen sulfide in the gas ($\chi_{H_2S^{\text{gas}}}$) by the following equation:

$$S^{-2\text{trap}}(t_f) = \int_{0}^{t_f} \chi_{H_2S^{\text{gas}}(t)} \cdot Q \cdot dt$$

3.7
where \( Q \) is the flow rate in mol/s, \( t_r \) is the elapsed time from the immersion of the steel electrode in the solution and \( t \) is a dummy integration variable representing time. This equation assumes that the sodium hydroxide trap is a perfect sink for \( \text{H}_2\text{S} \) in the gas. This is a reasonable assumption, because the content of \( \text{S}^{2-} \) in the second trap was always below the detection limit. Because the results in Figure 3.1 are well fitted by straight lines and the flow rate was constant, the concentration of \( \text{H}_2\text{S} \) in the gas was constant with time for each thiosulfate concentration. Therefore, the molar fraction of hydrogen sulfide in the gas can be calculated by

\[
\chi_{\text{H}_2\text{S}}\text{gas} = \left( \frac{\Delta S^{\text{S}_2\text{trap}}}{\Delta t \cdot A_{\text{steel}}} \right) \cdot \frac{A_{\text{steel}}}{Q} \tag{3.8}
\]

where the factor in brackets is the slope of the fitted lines in Figure 3.1 and \( A_{\text{steel}} \) is the exposed area of the electrode. All of the values are given in Table 3.1 for each concentration of thiosulfate.

The equilibrium solubility of hydrogen sulfide in the acid solution present in the reaction cell is related to the molar fraction of hydrogen sulfide in the gas by Henry’s law. Therefore, with knowledge of the molar fraction of \( \text{H}_2\text{S} \) in the gas it is possible to estimate the concentration of hydrogen sulfide in the cell under the following assumptions: the gas is in equilibrium with the solution, good mixing of solution and gases, no leaks in the cell and flow lines connecting the cell with the trap, and good efficiency of the trap. Although equation 3.8 is exclusively valid for the case where hydrogen sulfide generation rate is at steady state, it should be possible to use time
derivatives from equation 3.7 to calculate the time evolution of the molar fraction of hydrogen sulfide in the gas.

Calculations using the Stream Analyzer software package from OLI Systems provide an estimation of the H$_2$S content dissolved in solution that is equilibrated with a gas phase, which is useful for understanding the H$_2$S generation experiments in thiosulfate solutions. The equilibrium concentration of H$_2$S in a solution with the same base composition as NACE TM0177-96 was calculated with the software for different molar fractions of H$_2$S in a mixture with N$_2$ gas that would be bubbled through the solution, Figure 3.2. This equilibrium relationship between dissolved concentration and gas partial pressure is described by Henry’s law. A slope of 0.0903 mol/l.atm was obtained, which is near the value reported for the Henry’s law constant for H$_2$S in pure water at 25ºC, 0.0996 mol/l.atm [23]. If one were bubbling a mixture of H$_2$S and nitrogen through the cell, it would be expected that the concentration of hydrogen sulfide in the cell would increase uniformly until the point where it equilibrated with the partial pressure of H$_2$S, controlled by the flow rates of N$_2$ and H$_2$S. During the initial transient time, the H$_2$S flow rate at the entrance of the cell would be greater than the flow rate at the exit of the cell. After equilibration the two flow rates would be equal, because no more H$_2$S could be dissolved in the saturated solution.

In the H$_2$S generation experiments, the steel electrode combined with the thiosulfate in solution to produce H$_2$S. It is expected that, as described above for gas bubbling through the cell, the H$_2$S flow rate would increase until reaching equilibration. After this point, the rate of increase of S$^{2-}$ measured in the trap would be equal to the rate
of H$_2$S production at the steel surface. The saturation concentrations of H$_2$S in the solution in equilibrium with the gas, [H$_2$S]$^{\text{cell}}$, are presented in Table 3.1 for each thiosulfate concentration.

Mass conservation can also be used to estimate the surface concentration of H$_2$S at the surface of the steel electrode. The measured bulk pH at the beginning of each test was near 2.7, independently of the amount of thiosulfate added to the base solution. It rose during the experiment due to corrosion but not more than one pH unit, Figure 3.3. The pK$_a$ of the first dissociation of H$_2$S is 7.02 [24]. It is clear based on these observations that H$_2$S predominates over HS$^-$ and S$^{2-}$ in the bulk solution. On the other hand, the surface pH increased more due to corrosion, but remained below 5 for all solutions except the one with 10$^{-1}$ M S$_2$O$_3^{2-}$, as presented in Figure 3.3. Because the pK$_a$ of H$_2$S/HS$^-$ is 7.02 [24], H$_2$S/HS$^-$ > 100 even at the surface of the corroding electrode for the solutions with 10$^{-2}$ M or less S$_2$O$_3^{2-}$. For the 10$^{-1}$ M S$_2$O$_3^{2-}$ solution, H$_2$S/HS$^-$ > 10 at the surface. H$_2$S generated by the thiosulfate reduction can react with steel to form iron sulfide, or it can be transported to the bulk of the solution by diffusion. It is assumed that the amount of hydrogen sulfide that reacted with steel was a small fraction of the total amount of hydrogen sulfide generated. It will be shown below by comparison of H$_2$S generation tests against weight loss and weight gain experiments that this is a good approximation for this system. Under the assumptions above, the surface concentration of H$_2$S can be estimated by solving the steady state diffusion equation.
\[ J_{\text{H}_2\text{S}}(\text{steel surface}) = -D_{\text{H}_2\text{S}} \nabla C_{\text{H}_2\text{S}}(\text{steel surface}) \]

\[ \approx D_{\text{H}_2\text{S}} \left( \frac{[\text{H}_2\text{S}]_{\text{steel surface}} - [\text{H}_2\text{S}]_{\text{bulk}}}{\delta} \right) \quad (3.9) \]

where \( J_{\text{H}_2\text{S}}(\text{steel surface}) \) is the flux of \( \text{H}_2\text{S} \) at the steel surface, \( D_{\text{H}_2\text{S}} \) its diffusion coefficient, \( C_{\text{H}_2\text{S}} \) its concentration and \( \delta \) the diffusion layer thickness. \( D_{\text{H}_2\text{S}} \) is assumed to be equal to \( 1.89 \times 10^{-5} \text{ cm}^2/\text{s} \), which was measured in pure water at 25°C [23]. At steady state, and neglecting reaction with iron, all of the generated \( \text{H}_2\text{S} \) will end up in the trap, and conservation of mass implies that

\[ \frac{\Delta S_{\text{2-trap}}}{\Delta t} \approx J_{\text{H}_2\text{S}}(\text{steel surface}) A_{\text{steel}} \]

\[ \approx A_{\text{steel}} D_{\text{H}_2\text{S}} \left( \frac{[\text{H}_2\text{S}]_{\text{steel surface}} - [\text{H}_2\text{S}]_{\text{bulk}}}{\delta} \right) \quad (3.10) \]

Finally, solving for the concentration of \( \text{H}_2\text{S} \) at the steel surface,

\[ [\text{H}_2\text{S}]_{\text{steel surface}} \approx \frac{\Delta S_{\text{2-trap}}}{A_{\text{steel}} \Delta t} \frac{\delta}{D_{\text{H}_2\text{S}}} + [\text{H}_2\text{S}]_{\text{bulk}} \quad (3.11) \]

The term in the parentheses is the slope of the fitted lines in Figure 3.1 for each thiosulfate concentration. The remaining unknown in this equation, the diffusion layer thickness, \( \delta \), was estimated from polarization experiments on Pt in \( \text{Fe(CN)}_6^{4-} \) solutions, Figure 3.4a. The diffusion limited current density was plotted against the concentration of the ferrous complex in Figure 3.4b. Using equation 3.6, a value of 55.0 \( \mu \text{m} \) was obtained for the diffusion layer thickness. With this value and equation 3.11, the surface concentrations of \( \text{H}_2\text{S} \) were estimated and are presented in Table 3.1 for each concentration of thiosulfate. The flow rate of nitrogen controls \( [\text{H}_2\text{S}]_{\text{bulk}} \) through Henry’s
law and also affects \([H_2S]_{\text{steel surface}}\) through its influence on \(\delta\). Table 3.1 shows that the surface concentration of \(H_2S\) is always at least one order of magnitude greater than the bulk concentration of \(H_2S\), suggesting a weak dependence of \([H_2S]_{\text{steel surface}}\) on nitrogen flow rate.

Table 3.1 also shows the amount of \(H_2S\) in the cell at steady state, which is seen to be a small fraction of the number of moles of \(H_2S\) in the trap at the end of the test. Therefore, the fraction of thiosulfate originally added to the cell (\(S_2O_3^{2-\text{cell}}\)) that was transformed to hydrogen sulfide, \(f_{\text{trap}}\), can be estimated by:

\[
f_{\text{trap}} = \frac{S_2O_3^{2-\text{trap}}}{2 \cdot S_2O_3^{2-\text{cell}}}
\]

The factor of 2 in the denominator is a result of the stoichiometry of the thiosulfate reduction reaction, equation 3.1 and 3.2. Table 3.1 shows that \(f_{\text{trap}}\) varies from about 0.01 for the 0.1 M \(S_2O_3^{2-}\) solution to about 0.4 for the \(10^{-3}\) and \(10^{-4}\) M \(S_2O_3^{2-}\) solutions. It should be mentioned that there are other thermodynamically possible reaction paths for \(H_2S\) generation that could have a different factor in the denominator, as will be discussed more in depth in the next chapter. The factor \(f_{\text{trap}}\), unlike \([H_2S]_{\text{steel surface}}\), is dependent on the ratio of steel area to solution volume. It is also dependent on time and original thiosulfate concentration. In long term tests, it can determine when replenishment of \(S_2O_3^{2-}\) would be necessary.
3.3.2. Quantification of sulfur content in the film and in the bulk solution

Sulfide content in the film, obtained by weight difference and EDS measurements, is presented in Table 3.2, and was calculated according to the following equation:

\[
\frac{\text{mols } S^{2-} \text{ film}}{A^{\text{steel}}} = \frac{\text{weight film} \cdot \text{wt}\%S^{\text{film}}}{M^S \cdot A^{\text{steel}}}
\]

where \(\text{weight}^{\text{film}}\) is the weight of the sulfur-containing film obtained by weight differences, \(\text{wt}\%S^{\text{film}}\) is the concentration in weight percent in the film obtained by EDS, \(M^S\) is the molar mass of sulfur and \(A^{\text{steel}}\) is the exposed area of the steel electrode. The results are expressed in terms of moles of sulfide per cm\(^2\) of steel, so that they can be compared with results of \(H_2S\) generation rate shown in Figure 3.1. The fraction of the originally added thiosulfate that ends as sulfide in the film, \(f^{\text{film}}\), is also presented in Table 3.2. This fraction increased with decreasing \(S_2O_3^{2-}\) concentration, but is dependent on the area steel/volume of solution ratio and on the exposure time. The sample containing 10\(^{-1}\) M \(S_2O_3^{2-}\) was immersed for 20.17 h in 500 ml solution, in contrast to the rest of the samples which were exposed to the environment for 72 h in 1500 ml of solution. The lower amount of solution was selected so that \(f^{\text{film}}\) could still be comparable with the other solutions despite the lower exposure time, assuming linear film growth.

Initially, concentrated thiosulfate solutions looked cloudy, but with time sulfur adhered to the walls, especially to the bottom of the cell where it settled because of gravity. It was visually observed that sulfur particles increased in size with time, which facilitated the filtration process. The number of moles of sulfur generated due to
homogeneous thiosulfate disproportionation and the fraction of the total, \( f_{\text{bulk}} \), were estimated for the two most concentrated thiosulfate solutions, Table 3.2. The number 2 does not appear in the denominator of the fraction of thiosulfate that was disproportionated due to the stoichiometry of equation 3.3. In Figure 3.5 the diffraction pattern of the residue obtained after filtration of the solution remaining after the 12 h long OCP experiment in \( 10^{-1} \text{ M S}_2\text{O}_3^{2-} \) and the expected peak positions and relative intensities of \( \text{S}_8 \) are presented. The good fit confirms the disproportionation reaction and also validates the filtration and rinsing procedure. A poor rinsing procedure could leave behind NaCl or other crystals mixed with the sulfur powder. However, only \( \text{S}_8 \) is seen in the diffraction pattern, so the weight of S was not overestimated because of contamination with other crystalline phases. On the other hand, \( \text{S}_8 \) is the thermodynamically stable form of sulfur under normal conditions [5]. Its low solubility in water at room temperature [5] indicates that none dissolved during rinsing of the filter.

Secondary electron images of the film formed in the thiosulfate containing solutions after exposure to OCP are presented in Figure 3.6. Energy dispersive spectroscopy (EDS) confirmed that the film was rich in sulfur, Figure 3.7. The film had a mudcrack appearance in all cases, and for the \( 10^{-2} \text{ M S}_2\text{O}_3^{2-} \) solution, it tended to spall, revealing the underlying steel surface. For the \( 10^{-1} \text{ M S}_2\text{O}_3^{2-} \) solution, the film cracked and detached from the surface, and revealed an underlying second layer of iron sulfide film. Spalling and cracking of sulfide containing films was reported previously in \( \text{H}_2\text{S} \) [25] and \( \text{S}^0 \) [12] corrosion studies.
Figure 3.7 shows cross sections of carbon steel coupons exposed to substituted NACE TM0177-96 solution A with different thiosulfate additions. Images were obtained with a solid state backscattered electron detector. Therefore, the brightness is related not only to surface profile but also to Z number of elements present therein. The film, richer in lighter elements like carbon and sulfur than the matrix, appears darker than the uncorroded steel, but brighter than the epoxy. The EDS spectra suggest the presence of sulfur in the films for all concentrations except $10^{-4}$ M $S_2O_3^{2-}$. Sulfur was found in an EDS spectrum of a plane section of a sample exposed to this environment, probably due to the larger sampled volume. The Ni peaks in the EDS spectra most likely originate from the conductive epoxy, which contains nickel and carbon. Oxygen peaks are probably the result of partial oxidation of the iron sulfide film, due to exposure to air before placing the specimens in the SEM chamber.

3.4. Discussion

In blank tests, the concentration of sulfide in the trap was always below the detection limit of 0.5 ppm (less than $1.6 \times 10^{-5}$ M of $S^{2-}$ in the trap). Those results differ from those by Tsujikawa [1], where a concentration of hydrogen sulfide near $2.5 \times 10^{-5}$ M was measured directly in the cell solution containing $10^{-1}$ M $S_2O_3^{2-}$ even before immersion of the steel electrode. Hydrogen sulfide concentration was calculated by Tsujikawa with an ion selective electrode from an aliquot from the cell solution, not the trap solution, after increasing its pH to transform the H$_2$S to S$^{2-}$. Sulfur was present in the $10^{-1}$ M solution due to thiosulfate disproportionation, and can itself disproportionate according to equation 3.4 to yield hydrogen sulfide [5]. However, the kinetics of this
reaction are believed to be low at ambient temperature [5]. Macdonald, studying corrosion of carbon steel in wet elemental sulfur, could not detect hydrogen sulfide in a silver nitrate trap before the induction time [12], despite the fact that an iron electrode was immersed in the cell. During Macdonald’s experiments, hydrogen sulfide was detected in the trap only after iron sulfide was observed on the steel surface, and corrosion of carbon steel proceeded at a catastrophic rate, suggesting that H$_2$S detected in the trap was a byproduct of carbon steel corrosion in sulfur suspensions, equation 3.5, rather than a product of a homogeneous disproportionation reaction. This could be the reason why S$^{2-}$ was not detected in the trap in the present study when the steel electrode was not immersed in the solution, despite the fact that the solution was deaerated in the cell for 24 h and the cell/trap volume ratio would have concentrated the S$^{2-}$ by a factor of 4. Furthermore, current recommendations from the manufacturer of the sulfide ion selective electrode used by Tsujikawa state that thiosulfate ions can interfere with sulfide measurements when [S$_2$O$_3^{2-}$]/[S$^{2-}$] is greater than 10 [26]. Therefore, it could be that the presence of hydrogen sulfide in the cell reported by Tsujikawa in a blank experiment is related to an artifact from the analytical technique used.

For the 10$^{-4}$ M solution, sulfide concentration did not increase in the trap from 48 to 72 h. This could be related to the fact that conversion ratio was above 40% even at 48 h. A large value of electrode area was chosen for this concentration of thiosulfate ad hoc, to have a better sensitivity to sulfide generation rate. This fact might have contributed to the earlier exhaustion of thiosulfate. It is feasible that the use of a larger volume of solution to surface of steel ratio would have resulted in continual increase in trap
concentration. Therefore, the slope reported in Error! Reference source not found. was obtained excluding the point corresponding to 72 h from the linear fitting.

Analysis of Table 3.1 and Figure 3.1 reveals that even after 24 h, the number of moles of $S^{2-}$ in the trap at the end of the experiment was at least 30 times greater than the calculated number of moles of $H_2S$ in the cell. This validates the assumption that the amount of $S^{2-}$ detected in the trap was almost the total amount of $H_2S$ generated in the cell. It should be mentioned that this assumption would not have been valid if a lower ratio of nitrogen flow rate to cell volume were used. Nevertheless, it is likely that there was a transitory state at the start of the exposure during which the concentration of hydrogen sulfide in the cell increased and the amount of $S^{2-}$ in the trap was lower than the amount of $H_2S$ in the cell. During this stage, concentration of $H_2S$ in the cell increased from the initial zero value just before immersion of the electrode to the point where it equilibrated with the molar fraction of $H_2S$ in the gas, which was controlled by the kinetics of $H_2S$ generation and the flow rate. Tsujikawa [1] measured the $H_2S$ concentration evolution in the bulk of the cell during 24 h and found a maximum near 3 h after immersion of the electrode. However, the results cannot be directly compared to those obtained here because the $N_2$ flow rate was not reported. The approximately linear kinetics observed in Figure 3.1 suggests that the $H_2S$ molar fraction in the gas is constant, and that any transitory state should be limited to less than the first 24 h of the experiment, assuming equilibrium between gas and solution.

Reactions 3.1 and 3.2 are expected to occur for all thiosulfate containing solutions exposed to iron, and they consume protons. Moreover, sulfide ions react with iron to
form a film, reducing the amount of metallic ions available for hydrolysis, which could otherwise lead to a pH decrease. Despite these, no significant increase in surface pH was measured for thiosulfate concentration up to $10^{-2}$ M, Figure 3.3. The surface pH for all solutions studied, except the one with $10^{-1}$ M thiosulfate, stabilized near a surface pH of 4.7, which was almost 2 pH units above the bulk value. This could be related to the large content of acetic acid, which acted as buffer. With $10^{-1}$ M thiosulfate, the surface pH stabilized near 6.0. The higher surface pH at this concentration is not what would be predicted from the hydrogen sulfide generation tests. Production of hydrogen sulfide consumes protons, but it was shown in Figure 3.1 that hydrogen sulfide generation for the $10^{-1}$ M $S_2O_3^{2-}$ solution is lower than for the $10^{-2}$ M $S_2O_3^{2-}$ solution. Moreover, the increase in surface pH for this concentration cannot be related to a faster corrosion rate, because as it will be shown in next chapter the corrosion rates of the $10^{-1}$ M $S_2O_3^{2-}$ solution were near those measured in $10^{-2}$ M $S_2O_3^{2-}$ solution. Other possible causes of this increase in surface pH are the larger amount of sulfur generated by reaction 3.3, which consumes protons, or blockage of open spaces in the mesh used for the surface pH measurements by the more voluminous corrosion products formed at this concentration, Figure 3.7d. The bulk pH measured at the end of the test also increased significantly more for the $10^{-1}$ M $S_2O_3^{2-}$ solution, suggesting that the larger extent of thiosulfate disproportionation might be playing an important role. Blockage of open spaces in the mesh by the corrosion products could result in a more tortuous path for acetic acid transport, leading to a greater increase in the surface pH.
In Figure 3.8 the surface concentration of H$_2$S was plotted vs. the bulk concentration of thiosulfate at the beginning of the test. The H$_2$S surface concentration sharply increased as the thiosulfate concentration increased from $10^{-4}$ to $10^{-3}$ M, and then remained at the same order of magnitude with further increases in thiosulfate concentration. For each surface concentration of H$_2$S, there is an H$_2$S+N$_2$ gas mixture that will yield the same concentration of H$_2$S in the bulk of a 0.5 wt% HAc + 5 wt% NaCl solution. Concentrations of H$_2$S for those mixtures were obtained by use of Henry’s law, Figure 3.2, and are given in Table 3.3 for each S$_2$O$_3^{2-}$ concentration.

Figure 3.8 also shows the number of moles of sulfide in the film and in the trap, after 72 h. For proper comparison, the results for the sulfide content in the film after 72 h for the $10^{-1}$ M thiosulfate solution had to be extrapolated because of difficulties previously explained. Film thickness can increase with time according to linear, parabolic or logarithmic laws, depending on whether the kinetics are controlled by an interface reaction, diffusion of ions or by diffusion of electrons through the film, respectively [27]. Linear extrapolation was used to estimate the sulfide content in the film after 72 h for the $10^{-1}$ M S$_2$O$_3^{2-}$, shown as a hollow circle in Figure 3.8. Linear extrapolation of content of sulfide in the film would yield a value that is either close to or larger than the actual amount of film generated. Moreover, the continuous cracking and spalling of the film observed in the tests of the most concentrated thiosulfate solution, Figure 3.7, supports the selection of linear film growth kinetics. Therefore, Figure 3.8 conservatively shows that the amount of sulfide in the trap is at least one order of magnitude higher than the amount of sulfide in the film after 72 h for all concentrations of thiosulfate studied. This
measurement validated the assumption needed to calculate the surface concentration of H$_2$S in each solution. For the two most dilute solutions, the ratio of sulfide in the trap to sulfide in the film was even larger. Therefore, the use of dilute thiosulfate concentrations to simulate hydrogen sulfide solutions is encouraged.

Due to the complex chemistry of acid thiosulfate solutions, the data obtained in this work cannot be used to conclude whether iron sulfide is the product of hydrogen sulfide reaction with iron or by another path involving elemental sulfur. Elemental sulfur might be present on the electrode surface by the reaction shown in equation 3.1, or by bulk thiosulfate disproportionation followed by elemental sulfur adsorption, equation 3.5. Tsai [28] measured a 0.5 μm thick sulfide film on carbon steel immersed for 24 h in an H$_2$S saturated NACE TM0177 solution A. Figure 3.7b shows that the film thickness was as large as 10 μm after 3 days for the 10$^{-3}$ M S$_2$O$_3^{2-}$ solution. Assuming linear growth and dividing this value by 3 will constitute a good approximation or an under estimation of the actual film thickness at 1 day [27]. This would give a film thickness of near 3 μm after 24 h, which is much larger than that measured by Tsai in a hydrogen sulfide saturated solution. Moreover, the surface concentration of H$_2$S in thiosulfate solutions was considerably lower than the value expected for the saturated H$_2$S solution used by Tsai. Therefore, it can be conservatively concluded that H$_2$S surface concentration by itself cannot be used to explain the large values of film thickness and the dependence on bulk thiosulfate concentration. Results presented here are in contrast with conclusions made by Crolet [3], who suggested that the corrosive effect of thiosulfate on carbon steel was caused by the presence of H$_2$S generated by cathodic reduction. Other factors that
might cause faster film growth in thiosulfate solutions are a local increase in pH, the presence of elemental sulfur and higher concentration of Fe\(^{++}\) due to the faster corrosion in thiosulfate vs. hydrogen sulfide solutions, as will be discussed in the next chapter. This higher concentration of Fe\(^{++}\) could increase the driving force for iron sulfide precipitation. There is approximately a tenfold increase in film thickness in going from 10\(^{-3}\) M S\(_2\)O\(_3\)\(^{2-}\) to 10\(^{-2}\) M, Figure 3.7b and c, despite the fact that the calculated surface concentration of H\(_2\)S remained on the same order of magnitude, Figure 3.8. On the other hand, 10\(^{-3}\) M solutions remained clear throughout the test, with no visual evidence of thiosulfate disproportionation. These results suggest that presence of elemental sulfur due to thiosulfate disproportionation might cause the faster growth of film in concentrated thiosulfate solutions.

Because elemental sulfur was directly detected for the two most concentrated solutions and no precautions were taken to isolate the metal from the S particles, corrosion by elemental sulfur has to be considered as a possible mechanism of sulfide film growth in thiosulfate solutions. In contrast to corrosion in sulfur suspensions, where an induction period of tens of hours can be observed [12] before onset of iron corrosion, a black film, probably mackinawite, was observed to develop on the steel electrode just minutes after immersion. The induction period observed in sulfur suspensions is related to the time required to generate H\(_2\)S by disproportionation, which has a slow kinetics, equation 3.4 [5]. The lack of induction period for corrosion, hydrogen sulfide generation and film formation in this work could result from hydrogen sulfide generation on the steel electrode directly by thiosulfate reduction, compared to sulfur suspensions where onset of
corrosion required generation of H$_2$S. Chlorides can also eliminate the induction period [5]. Furthermore, the reaction in equation 3.1 generates sulfur directly at the steel electrode, so contact between sulfur and metal is enhanced. This reaction is possible even for the two most diluted solutions, which remained clear throughout the tests, suggesting no formation of elemental sulfur in the bulk. No quantifications of the rate of film generation were reported in the literature for systems similar to the one under study, but it will be shown in next chapter that corrosion rates in the two most concentrated thiosulfate solutions are well beyond carbon steel corrosion rate reported in H$_2$S saturated NACE TM0177-96 [29], but on the same order of magnitude as in elemental sulfur suspensions in brines [17].

Arzola [25] reported a film thickness of about 70 $\mu$m in an H$_2$S saturated 3 wt% NaCl solution of bulk pH 4 after 24 h, which is much larger than the 0.5 $\mu$m reported by Tsai for the same time period [28] in the H$_2$S saturated NACE TM0177-96 solution A, which has a pH near 2.6 [9] before H$_2$S saturation. This is consistent with the results obtained by Shoesmith [15], who reported that the amount of iron sulfide is maximum near 4. Those literature results suggest that the film growth kinetics can be affected by the pH of the solution. The pH of all the substituted solutions was near 2.7 at the beginning of the test, but a surface increase in pH during mild steel corrosion in the thiosulfate substituted NACE TM0177-96 solution A was found in this work, Figure 3.3, in accord with literature results [20]. It is interesting to note that, except for the $10^{-1}$ M S$_2$O$_3^{2-}$ solution, surface pH stabilized near the value for maximum iron sulfide growth [15]. While a similar effect can be expected for hydrogen sulfide saturated solutions, the
presence of this gas can increase the buffer capacity of the solution. Han et al. [20] showed that carbon dioxide saturated solutions exhibited a lower increase in surface pH if compared against acetic acid solutions of the same bulk pH. Therefore, it could be that the surface increase in pH in hydrogen sulfide saturated solution might be less than in thiosulfate containing solutions. This difference can be another cause for the faster film growth kinetics in thiosulfate compared to hydrogen sulfide solutions.

The fraction of thiosulfate that disproportionated according to equation 3.3 is larger than the fraction that reduced to yield H₂S for the 10⁻¹ M S₂O₃²⁻ solution, as seen by comparison of f_{\text{bulk}} in Table 3.2 with f_{\text{trap}} in Table 3.1. Newman [30] reported that 5 wt% of the total sulfur present as S₂O₃²⁻ precipitated as sulfur in a 0.5 M S₂O₃²⁻ solution acidified to pH 3 with sulfuric acid, in accord with results presented here given the similar experimental conditions. Considering the calculated surface concentration of H₂S, Table 3.1, the use of thiosulfate solutions of concentration greater than 10⁻² M for sour corrosion simulation purposes is not advised. While elemental sulfur was directly detected for the two most concentrated solutions, it should be stated that based on standard Gibbs free energy of disproportionation of thiosulfate, equation 3.3, disproportionation is spontaneous for all four concentrations of S₂O₃²⁻ studied, except for the one with 10⁻⁴ M S₂O₃²⁻. Assuming that bisulfite concentration is 10⁻⁶ M, a common practice in corrosion studies when initial concentrations are not known [31], a pH of 2.7 measured at the beginning of the test and an activity of 1 for sulfur because it is a pure substance, the value of the reaction quotient (Q) for the 10⁻⁴ M solution is 5.51, against an equilibrium constant of 3.48 at 25°C, calculated with the standard Gibbs free energy of
the reaction. The quotient Q decreases a decade with every tenfold increase in S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} concentration, thus increasing the driving force for the reaction. The concentration of bisulfite could be increased to the point where disproportionation reaction is non-spontaneous, which is calculated to be 7x10\textsuperscript{-4} M for the 10\textsuperscript{-1} M S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} solution and decreases one decade per tenfold decrease in S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} concentration. However, it should be noted that sulfite is a common oxygen scavenger, because it reacts with oxygen yielding sulfate [4]. Therefore, addition would have to proceed after deareation of the base solution and prior to addition of thiosulfate, since the disproportionation reaction was fast enough to make sulfur visible during the initial deareation for the two most concentrated solutions. A complication associated with the use of sulfite is that the ion is not stable in the pH and electrode potential window of interest. Therefore, it can undergo several reactions [4] and even reduce to H\textsubscript{2}S [3], the stable species in such window. If kinetics of sulfite reactions is faster than thiosulfate reaction, the driving force for thiosulfate disproportionation could be reestablished.

3.5. Conclusions

The reaction pathway of sulfur in acid thiosulfate solutions exposed to steel was studied for a range of thiosulfate concentrations. The chemistry is complex and various byproducts can be generated during carbon steel corrosion so an exact relationship between products and reactants could not be established. Three of those byproducts, namely, hydrogen sulfide, iron sulfide and elemental sulfur were quantified with ex-situ techniques. The following conclusions can be made:
• The rate of H₂S generation increases with thiosulfate concentration up to 10⁻² M, after which point it slightly decreases.

• A method for estimating the surface concentration of H₂S during carbon steel corrosion in S₂O₃²⁻ solutions was presented, which assumes equilibrium and mass conservation. This is of interest in environmental cracking processes since H₂S increases hydrogen embrittlement. For the system studied, it was determined that surface concentration of H₂S has a sharp increase when concentration of thiosulfate increases from 10⁻⁴ M to 10⁻³ M. The rate of H₂S generation was constant, which facilitated the calculations.

• Calculations revealed that the amount of hydrogen sulfide generated for all thiosulfate concentrations were well above content of sulfide in the film, suggesting that there should be a high amount of H₂S available to poison the hydrogen recombination reaction.

• Thickness of film obtained in the various thiosulfate containing solutions and comparison with literature values for H₂S solutions of similar conditions suggested that the film grows faster in acid thiosulfate solutions than in H₂S saturated solutions, when [S₂O₃²⁻] >10⁻³ M. The extent of growth cannot be explained based on surface concentration of H₂S, but other contributions could arise from a local increase in pH, a local increase in Fe³⁺ due to the faster corrosion rate or presence of elemental sulfur, an intermediate product in the thiosulfate reduction to H₂S and a product of thiosulfate disproportionation.
• Elemental sulfur, present due to a disproportionation reaction, constitutes a small fraction of the total sulfur added as thiosulfate and was only detected in the two most concentrated solutions. It can contribute to the corrosion, film growth and H₂S generation process, especially when the electrode area to solution volume ratio is high.

• The evidence presented here suggest that 10⁻⁴ M and 10⁻³ M S₂O₅²⁻ additions to acid brines could be used for replacing continuous bubbling of dilute H₂S/N₂ mixtures in tests of degradation of carbon steels, with H₂S partial pressures ranging between 0.03 and 0.56 kPa.

• The concentration of hydrogen sulfide in thiosulfate solutions is expected to be maximum at the surface of carbon steel. With knowledge of the kinetics of S₂O₅²⁻ to H₂S reaction presented here, the exposed area of carbon steel and time extension of the experiment, it is possible to calculate the required size of a solution reservoir, so that the concentration of H₂S on the surface of carbon steel remains at steady state.
Table 3.1. Results of the H$_2$S generation test experiments. *Slope* is the slope of the fitting line in Figure 3.1, $\chi H_2S^{\text{gas}}$ is the molar fraction of H$_2$S in the gas, $S^{2-}$-*trap* (end of test) is the number of mols in the trap at the end of the test, $\chi H_2S^{\text{solution}}$ is the molar fraction of H$_2$S in the solution at steady state, $H_2S^{\text{cell}}$ is the number of mols in the cell at steady state, $[H_2S]^{\text{cell}}$ is the concentration of H$_2$S in the cell at steady state, $[H_2S]^{\text{steel surface}}$ is the concentration of H$_2$S close to the steel surface and $f^{\text{trap}}$ is the fraction of thiosulfate that ended up as sulfide in the trap.

<table>
<thead>
<tr>
<th></th>
<th>$[S_2O_3^{2-}]$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0001</td>
</tr>
<tr>
<td>steel area cm$^2$</td>
<td></td>
</tr>
<tr>
<td>$\text{slope} = \frac{\Delta S^{2-}<em>{\text{trap}}}{\Delta t \cdot A</em>{\text{steel}}}$</td>
<td></td>
</tr>
<tr>
<td>$\chi H_2S^{\text{gas}}$</td>
<td>-</td>
</tr>
<tr>
<td>$S^{2-}_{\text{trap}}$ (end of test) mol</td>
<td>3.31x10$^{-5}$</td>
</tr>
<tr>
<td>$\chi H_2S^{\text{solution}}$</td>
<td>-</td>
</tr>
<tr>
<td>$H_2S^{\text{cell}}$ mol</td>
<td></td>
</tr>
<tr>
<td>$[H_2S]^{\text{cell}}$ M</td>
<td>1.28x10$^{-6}$</td>
</tr>
<tr>
<td>$[H_2S]^{\text{steel surface}}$ M</td>
<td>2.62x10$^{-5}$</td>
</tr>
<tr>
<td>$f^{\text{trap}} = \frac{S^{2-}_{\text{trap}}}{2 \cdot S_2O_3^{2-}\text{cell}}$ -</td>
<td>0.414</td>
</tr>
</tbody>
</table>
Table 3.2. Estimations of amount of sulfide in the film and $S^0$ in the bulk of the solution

<table>
<thead>
<tr>
<th></th>
<th>$[S_2O_3^{2-}]$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0001</td>
</tr>
<tr>
<td>steel area</td>
<td>cm$^2$</td>
</tr>
<tr>
<td>exposure time</td>
<td>h</td>
</tr>
<tr>
<td>wt% S in film</td>
<td>%</td>
</tr>
<tr>
<td>film weight</td>
<td>g</td>
</tr>
<tr>
<td>mols $S^{2-}$/Area</td>
<td>mol/cm$^2$</td>
</tr>
<tr>
<td>$f_{film}^* = \frac{S_{2-}^{film}}{2 \cdot S_{2}O_{3}^{2-\text{cell}}}$</td>
<td>-</td>
</tr>
<tr>
<td>$S^0$ bulk solution</td>
<td>g</td>
</tr>
<tr>
<td>$S^0$ bulk solution</td>
<td>mol</td>
</tr>
<tr>
<td>$f_{bulk}^* = \frac{S_{0}^{\text{bulk solution}}}{S_{2}O_{3}^{2-\text{cell}}}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3.3. Molar fraction ($\chi_{H_2S}^{gas}$), weight percentages, and partial pressure of $H_2S$ ($pH_2S$) in an $H_2S + N_2$ gas mixture at 101.3 kPa (1 atm) that will yield a bulk $H_2S$ concentration in a 5wt% NaCl + 0.5 wt% HAc solution equivalent to the concentration obtained at the surface of a steel electrode immersed in each thiosulfate solution

<table>
<thead>
<tr>
<th>$[S_2O_3^{2-}]$ (M)</th>
<th>$\chi_{H_2S}^{gas}$</th>
<th>wt% H$_2$S</th>
<th>pH$_2$S (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>2.91x10$^{-4}$</td>
<td>0.035</td>
<td>2.9x10$^{-2}$</td>
</tr>
<tr>
<td>0.001</td>
<td>5.49x10$^{-3}$</td>
<td>0.667</td>
<td>5.6x10$^{-1}$</td>
</tr>
<tr>
<td>0.01</td>
<td>1.46x10$^{-2}$</td>
<td>1.77</td>
<td>1.5</td>
</tr>
<tr>
<td>0.1</td>
<td>1.17x10$^{-2}$</td>
<td>1.42</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Figure 3.1. Time evolution of the content of sulfide in the trap as a function of thiosulfate concentration, as indicated in the graph. Results for the $10^{-4}$ M $S_2O_3^{2-}$ solution were multiplied by 10 so that they could be resolved in the same scale. Slopes of the lines are given in Table 3.1.
Figure 3.2. Dependence of equilibrium concentration of hydrogen sulfide in an aqueous 0.5wt% HAc + 5wt% NaCl solution vs. partial pressure of hydrogen sulfide.
Figure 3.3. Evolution of the surface pH of a corroding steel electrode in deaerated 5 wt% NaCl acidified with 0.5 wt % acetic acid and with additions of thiosulfate as indicated in the legend.
Figure 3.4. Current density vs. platinum potential, a), and limiting current density vs. concentration of Fe(CN)$_6^{4-}$, b).
Figure 3.5. XRD spectrum of the filtrand of the solution originally containing $10^{-1} \text{M} \text{S}_2\text{O}_3^{2-}$ at the end of a 12 h exposure of pipeline steel at OCP, suggesting bulk disproportionation of thiosulfate with generation of elemental sulfur. Red peaks indicate theoretical diffraction maximums of S$_8$ phase.
Figure 3.6. Secondary electron images of the surface of a carbon steel specimen immersed at OCP to NACE substituted solution containing a) $10^{-4}$, b) $10^{-3}$, c) $10^{-2}$ and d) $10^{-1}$ M $S_2O_3^{2-}$. 

continued
Figure 3.6 continued

c)

d)
Figure 3.7. Back scattered electron images of cross sections of pipeline steel coupons exposed to NACE substituted solutions for 72 h at OCP, containing a) $10^{-4}$, b) $10^{-3}$, c) $10^{-2}$ and d) $10^{-1}$ M $\text{S}_2\text{O}_3^{2-}$. An energy dispersive spectroscopy (EDS) spectrum obtained at the film is presented at the right of each picture.
Figure 3.7 continued

c)

d)
Figure 3.8. Surface concentration of hydrogen sulfide, obtained by mass conservation analysis at steady state and comparison of moles of sulfide per unit area in film and in trap vs. thiosulfate concentration. Content of sulfur in the film for the sample tested in $10^{-1}$ M $S_2O_3^{2-}$ was linearly extrapolated to 72h, so that it could be compared in the same graph.
3.8. References


CHAPTER 4. CORROSION BEHAVIOR OF CARBON STEEL IN ACIDIFIED THIOSULFATE-CONTAINING BRINES

4.1. Introduction

Corrosion testing in solutions containing hydrogen sulfide, $\text{H}_2\text{S}$, is challenging due to the toxicity, flammability and corrosive character of this gas, which require the use of special installations to ensure safety. An interesting alternative is the use of substances that can decompose to produce $\text{H}_2\text{S}$ in the testing environment. Tsujikawa et al. [1, 2] proposed the possibility of replacing $\text{H}_2\text{S}$ with thiosulfate ($\text{S}_2\text{O}_3^{2-}$) for studying pitting and stress corrosion cracking susceptibility of stainless steels and carbon steels in sour environments. The Tsujikawa approach is consistent thermodynamically, because the open circuit potential of carbon steel in a solution of 5 wt% NaCl + 0.5 wt% acetic acid solution (NACE TM0177-90 base solution A [3]) with $10^{-3}$ M $\text{S}_2\text{O}_3^{2-}$ is in the region in a Pourbaix diagram where $\text{H}_2\text{S}$ is stable [2]. The kinetics of $\text{H}_2\text{S}$ generation from thiosulfate solutions as well as reactions yielding iron sulfide and elemental sulfur were presented in the last chapter.

One of the main dangers associated with $\text{H}_2\text{S}$ environments from a corrosion perspective is that it increases the rate of hydrogen absorption, which enhances embrittlement [4, 5]. Therefore, the ability of thiosulfate solution to mimic the behavior of hydrogen sulfide might depend on the amount of hydrogen absorbed in thiosulfate
solutions. The permeation of hydrogen through carbon steel exposed to thiosulfate solutions was found to be dependent on the thiosulfate concentration with a maximum rate at $10^{-3}$ M $S_2O_3^{2-}$ [2, 6]. The loss in elongation in slow strain rate tests, SSRT, was also maximum at this concentration [2], but the embrittlement did not reach that measured in $H_2S$-saturated solutions. No mechanistic explanations were provided in the literature for the maximum in hydrogen permeation vs. thiosulfate concentration. It is not clear whether it results from blocking of hydrogen ingress as reported in $H_2S$ environments [7, 8] or a decrease in corrosion rate with thiosulfate concentration. Such a decrease could be associated with the formation of corrosion protecting films.

Studies of the effect of thiosulfate on hydrogen absorption in NACE TM0177-90 base solution A at room temperature [2, 6, 9] have shown that thiosulfate does not lead to the sharp increase in hydrogen permeation observed when pure hydrogen sulfide is added to the same base solution [5, 9]. Hydrogen permeation currents through a steel membrane with a thickness of 0.22 mm in NACE TM0177-90 solution A saturated with $H_2S$ were 100 - 200 $\mu$A/cm$^2$, which represents about 70% of the free corrosion rate [5, 9]. In contrast, the permeation through steel of the same thickness exposed to a $10^{-1}$ M thiosulfate solution were only 2 - 10 $\mu$A/cm$^2$, representing less than 3% of the corrosion rate [9]. In other studies, the permeation current through a 2 mm thick steel sample in NACE TM0177-90 solution A saturated with $H_2S$ was near 60 $\mu$A/cm$^2$ [10], whereas a 1.5 mm steel sample in the same solution but with $H_2S$ substituted by $10^{-5}$ to $10^{-2}$ M $S_2O_3^{2-}$ had permeation currents below 3 $\mu$A/cm$^2$ [6]. Tsujikawa [2] proposed lowering the solution pH to enhance embrittlement, but the results for a solution of pH 1.5 were near
those values reported for the original solution of pH 2.7 [6]. In last chapter, it was shown that the growth of surface films in 10^{-3} M thiosulfate solutions is faster than in H_2S saturated solutions of the same pH and chloride content. The concentration of H_2S at the steel surface, as discussed in last chapter, might be well below that in saturated H_2S solutions. Therefore, blockage by films and the lower surface concentration of H_2S in thiosulfate solutions compared to H_2S saturated solutions, as discussed in last chapter, could be the cause behind the lower hydrogen permeation rates. Moreover, acidic thiosulfate solutions contain more sulfur species than H_2S solutions [2, 11]. The cathodic current is not limited to the hydrogen evolution reaction because contributions from the reduction of thiosulfate, elemental sulfur or sulfite, present due to thiosulfate disproportionation, are possible [2]. Those species might compete with protons for electrons, thereby decreasing the proton discharge rate.

Despite several papers where thiosulfate has been studied as a substitute for H_2S [12-16], little is known about the time evolution of corrosion rate, crystal structure of the films formed at the open circuit potential and their influence on polarization curves. Literature results on hydrogen sulfide solutions showed that protective and non-protective films can form depending on solution conditions and immersion time [5, 17, 18], but this was not studied for acidic thiosulfate solutions. It is critical to know the time evolution of corrosion rate because environmental assisted cracking tests can last from several hours to days. The objective of this paper is to investigate these issues and to relate them to results of hydrogen absorption published in the literature [2, 6, 9].
4.2. Experimental

4.2.1. Electrochemical tests

A three electrode cell with deaeration capabilities was constructed for the corrosion behavior studies of pipeline steel in thiosulfate solutions. All solutions were deaerated with high purity (99.999%) N$_2$ during 1 hour prior to insertion of the steel sample, in accord with recommendations for hydrogen sulfide testing [3]. During this time, the steel sample remained in the cell but in the vapor space above the solution level without contacting it, which was accomplished by the construction of a special sample holder. After the initial deaeration period, the sample could be lowered to the fully immersed position without opening any port, which minimized oxygen contamination. N$_2$ deaeration continued until completion of the electrochemical tests. The N$_2$ exiting the cell was forced through a NaOH scrubber to capture any H$_2$S generated during the tests for safety reasons. Potential was measured with a saturated calomel electrode through a Luggin capillary. A platinum wire was used as a counter electrode, which was placed in a bridge tube with a glass frit tip, thus providing isolation from the cell main compartment, while maintaining ionic conductivity. Such practice minimizes contamination by products from reactions occurring at the counter electrode. A Gamry® Ref 600 potentiostat was used for the electrochemical tests.

Samples were extracted from a piece of reeled X65 pipeline steel, far from welds or any other macroscopic discontinuities, and abraded to 1200 grit with emery papers. NACE TM0177-90 solution A [3] substituted with thiosulfate instead of H$_2$S was prepared from reagent grade chemicals. The base solution was prepared by mixing 50 g
of NaCl with 5 g of glacial acetic acid in 945 g of water [3]. Thiosulfate was added right before starting the test to minimize losses due to disproportionation in acidic solutions, as studied in the previous chapter. Due to this spontaneous reaction, the actual concentration of thiosulfate in the prepared solutions is unknown and the values reported correspond to the amount originally added to the solution. Experiments were conducted in the base solution, i.e. NACE TM0177-90 solution A with no sulfur containing species added, as well as in solutions with $10^{-4}$, $10^{-3}$, $10^{-2}$ or $10^{-1}$ M $\text{S}_2\text{O}_3^{2-}$. The target $\text{S}_2\text{O}_3^{2-}$ concentration was reached by addition of aliquots of a 1 M $\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ solution, except for the $10^{-1}$ M solution, where crystals of $\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$ were directly weighed and added to the base solution. The initial pH of the solution was near 2.7 in all cases. The pH did not change appreciably after exposure for 1 h at the open circuit potential, OCP, followed by a polarization experiment. However, the pH increased by about 1 unit for experiments lasting a day or more.

Potentiodynamic polarization experiments were performed at 0.2 mV.s$^{-1}$ in each of the solutions. Anodic and cathodic potentiodynamic polarization curves were obtained after 1 h at OCP, and after 24 h at OCP, to evaluate whether films have any corrosion inhibiting or enhancing effect. At the end of each test, an electrochemical impedance spectrum (EIS) was measured from 10 kHz to 1 Hz. The solution resistance, $R_s$, evaluated as the high frequency limit of the impedance, was used to correct the potential for ohmic drop, $I\cdot R_s$, where $I$ is the current measured at each potential. The potential drop was calculated at each potential and subtracted from the applied potential. Potential
excursions during all polarization experiments were within the H$_2$S stable window of a S$_2$O$_3^{2-}$-water Pourbaix diagram [2].

Rotating disk electrode experiments were conducted to identify the reactant of the reduction reaction in deaerated base NACE TM0177-96 solution A. The pH of this solution was 2.59 at 25°C. An epoxy disk holder was constructed and cathodic polarization curves were obtained at 1000, 1500, 2000 and 2500 rpm at a scan rate of 0.2 mV/s. Those curves were also corrected for ohmic drop by the same method adopted for the static polarization experiments. The limiting current density ($i_L$) was plotted vs. the square root of the rotation speed ($\omega$) and linearly fitted. The slope of the line is related to the diffusion coefficient and concentration of the reduction species by the Levich equation [19]:

$$i_L = 0.620nFD^{2/3}r^{-1/6}\omega^{1/2}c_\infty$$

where $n$ is the number of electrons transferred during the rate determining step, $F$ is the Faraday constant, $r$ the radius of the electrode, $D$ and $c_\infty$ the diffusion coefficient and concentration of electroactive species and $\nu$ the kinematic viscosity of the solution. The kinematic viscosity of the base NACE TM0177-96 solution was approximated by 9.31x10$^{-3}$ cm$^2$/s, the viscosity of a 5 wt% NaCl solution. This value was determined by interpolation from kinematic viscosity values published for 0.5 mol/kg (2.9 wt%) and 1.0 mol/kg (5.8 wt%) NaCl solutions [20].

Time evolution of the corrosion potential was measured in each of the solutions for a 72 hour period. During this time, several EIS measurements were conducted to obtain the corrosion rate evolution with time. The exposed area of the electrode was near
1 cm\(^2\) and the solution volume was 300 cm\(^3\). The results presented in the last chapter were used to select these values, with the objective that the total amount of S\(_2\)O\(_3\)^{2-}\) transformed to H\(_2\)S was below 40% at the end of the test. Polarization resistance, R\(_p\), which is inversely related to corrosion rate by the Stern-Geary equation [21], was obtained after fitting the impedance spectra to the simple equivalent circuit presented in Figure 4.1. Constant phase elements were used instead of capacitors for modeling the double layer capacitance, Figure 4.1, because they provide a better fit to depressed semicircles [22]. The impedance of a constant phase element is mathematically given by [22]

\[
Z = \frac{1}{Y_0(j\omega)^\alpha}
\]

where \(j\) is the square root of -1, \(Y_0\) is a real, positive number and \(\alpha\) is between 1 and 0. The circuit provided 4 independent variables to fit the impedance data, R\(_p\), Y\(_0\), \(\alpha\), and R\(_s\), the electrolyte resistance. The known frequency dependence of the impedance of the equivalent circuit presented in Figure 4.1 was fitted to the measured spectra with Gamry Echem Analyst software, and the time evolution of the parameters was obtained for each solution.

The hydrogen sulfide gas generated during OCP monitoring and EIS experiments was collected in a 100 ml 0.01 M NaOH trap, and at the end of the test the sulfide content in the trap was analyzed with Gastec\textsuperscript{®} 211L (0.5 to 20 ppm) and 211M (2 to 300 ppm) sulfide ion detector tubes. The measurement error is reported to be 10% by the manufacturer. It was shown in last chapter that the number of moles of S\(^2-\) collected in
the trap is near the number of moles of \( \text{H}_2\text{S} \) generated by the electrochemical reaction, because the cell with its acidic pH is a weak trap for \( \text{H}_2\text{S} \). The concentration of sulfide in the trap was multiplied by the volume of the trap to obtain the total amount of sulfide present, and those values were then converted to units of mA/cm\(^2\) by use of Faraday’s law, assuming the following mechanism for \( \text{H}_2\text{S} \) generation \[2, 23\]:

\[
S_2\text{O}_3^{2-} + 6\text{H}^+ + 4e^- = 2S^0 + 3\text{H}_2\text{O} \hspace{2cm} E_0=0.465 \text{ V}_{\text{SHE}}
\]

\[
2S^0 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{S} \hspace{2cm} E_0=0.142 \text{ V}_{\text{SHE}}
\]

which gives a value of 4 equivalents/mole \( \text{H}_2\text{S} \). However, if the reaction proceeds from elemental sulfur that formed by thiosulfate disproportionation, the \( n \) value is 2 equivalents/mole \( \text{H}_2\text{S} \).

Corrosion rates were also obtained by weight loss for comparison against results obtained with EIS. Coupons were kept in a dessicator for 24 h, weighed with an analytical balance and exposed to NACE TM0177-96 solution substituted with \( 10^{-1}, 10^{-2}, 10^{-3} \) or \( 10^{-4} \) M thiosulfate for 72 h. The exposed area was about 7.3 cm\(^2\) for the solutions with \( 10^{-3} \) and \( 10^{-4} \) M \( \text{S}_2\text{O}_3^{2-} \) and about 2.5 cm\(^2\) for the solutions with \( 10^{-2} \) and \( 10^{-1} \) M \( \text{S}_2\text{O}_3^{2-} \). The exposed area was larger for the two solutions with the lowest concentration of thiosulfate in an effort to increase the weight loss and decrease the relative error in this measurement. Samples exposed to the thiosulfate containing environments were covered by a film, which was removed by dipping in a solution of 5 g \( \text{Sb}_2\text{O}_3 \) + 14.877 g \( \text{SnCl}_2\cdot2\text{H}_2\text{O} \) dissolved in 250 ml of HCl until the black film was completely removed, revealing the underlying carbon steel surface \[24\]. It was shown in last chapter that the mass loss associated with cleaning by the HCl concentrated solution is 0.0002 g for a
sample with an exposed area of 7.61 cm². This mass lost due to the cleaning procedure is negligible compared to the minimum mass lost in the thiosulfate containing environments due to corrosion, 0.056 g for the most dilute thiosulfate concentration. After the cleaning step with the inhibited HCl solution, samples were rinsed with water and methanol, dried in a stream of cold air and kept in a desiccator for another 24 h to eliminate any solvent residue. The weight loss was converted to corrosion rate in mils/year and mA/cm² assuming complete Faradaic dissolution of iron. Micrographs of the film-free steel surface were obtained in a scanning electron microscope (SEM) equipped with a secondary electron detector, in an effort to determine whether corrosion occurred in a general or localized fashion.

4.2.2. Characterization of film structure

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to characterize the film formed in thiosulfate-containing solutions. Samples were exposed in NACE TM0177 substituted solutions with 10⁻¹, 10⁻², 10⁻³ and 10⁻⁴ M S₂O₃²⁻ at OCP for 24, 72, 96 and 143 h, respectively. The exposure times were increased as S₂O₃²⁻ concentration decreased in an effort to produce enough corrosion products for XRD detection. An XRD spectrum of a polished steel specimen was also collected for reference. X-ray diffraction spectra were obtained in a powder diffractometer, equipped with a Cu anode (λ_{Cu Kα1}=1.54056 Angstrom) and a germanium solid state detector. Samples were rinsed with DI water and dried in a stream of nitrogen prior to being inserted in the diffractometer. For the sample exposed to the environment containing 10⁻¹ M of S₂O₃²⁻, the corrosion products were cracked and lifted up, so they were scraped off.
of the sample and placed on a zero-background quartz plate. The angle was scanned between 14° and 70°, at a rate of 0.1°/minute. EVA software was used to determine the phases present in the film.

The XRD diffraction pattern of a carbon steel specimen immersed in the two most diluted thiosulfate solutions at the OCP potential could not resolve the presence of sulfide films, in contrast with the solutions richer in thiosulfate. On the other hand, there is evidence in the literature that formation of this phase could occur in environments with low H₂S concentration [25], where its presence can only be resolved with XPS due to the thin nature of the film. To determine whether this is the case for the current study, XPS analysis was performed using a monochromatic Al Kα source (1486.6 eV). Due to the higher surface sensitivity of XPS, samples were exposed at OCP to a NACE solution substituted with 10⁻³ M S₂O₃²⁻ for only 24 hours and for the one with 10⁻⁴ M S₂O₃²⁻ for only 48 hours. They were then rinsed with DI water, followed by acetone, dried in a stream of N₂, immediately placed in the XPS chamber, and stored in a 10⁻⁹ torr vacuum overnight before data collection. A single scan survey spectrum was collected with 80 eV pass energy, a step size of 1 eV and a dwell time of 100 ms. Narrow XPS spectra, collected with 20 eV pass energy were obtained for sulfur and iron. Iron sulfides are unstable in air and are expected to react with air yielding iron oxides [26] during the transfer of the sample from the aqueous environment to the XPS chamber. This situation makes the iron peak fitting process very complex. Therefore, the sulfur spectrum was analyzed and used to determine presence or absence of iron sulfide. The high resolution spectra correspond to the combination of 16 sweeps obtained with a 0.1 eV step size and
a dwell time of 500 ms. A Shirley background was subtracted from the raw spectra and Gaussian-Lorentzian (GL) shaped peaks were used to fit the data.

4.3. Results

4.3.1. Electrochemical tests

Cathodic polarization curves in NACE TM-0177-90 solutions with and without thiosulfate additions are presented in Figure 4.2, obtained after 1 h exposure at OCP. The curves were the most representative of three independent tests for each solution concentration. It is seen that the most prominent effect of thiosulfate additions was an increase in the cathodic current at low overpotentials. At potentials more negative than -1.0 V\text{SCE}, all curves seem to converge to the same limiting current. Bubbles were seen at this stage for all solutions studied. At more positive overpotentials, another electrochemical reaction seems to take over, and vigorous bubble evolution was seen at this stage. Anodic polarization curves, obtained after 1 h exposure at OCP, are presented in Figure 4.3, and it is readily seen that there was a strong dependence of anodic current on thiosulfate content. The curves exhibit some noise near the open circuit potential. This could be due to the low scanning rate (0.2 mV/s) and high sampling rate (1 data point/second) adopted, combined with the corrections by ohmic drop performed at the end of the test. The figure suggests that thiosulfate enhanced anodic dissolution of carbon steel. Figure 4.2 and Figure 4.3 also show cathodic and anodic polarization curves obtained after 24 h in thiosulfate containing solutions. Only one concentration of thiosulfate is shown in each graph, for clarity in the presentation, but the effect of time
was similar for the rest of the concentrations of thiosulfate. At this time, the film was well developed on the surface of the steel electrode. The film was as good catalyst for cathodic reactions, Figure 4.2, but slightly inhibited the anodic reaction, Figure 4.3.

Cathodic polarization curves measured using a rotating disk electrode at various angular speeds in deaerated NACE TM0177-96 solution with no thiosulfate addition are presented in Figure 4.4a, along with a graph of the limiting current vs. square root of the angular speed, $\omega$, Figure 4.4b. The bending of the curves and the dependence of current on rotation speed suggest transport limited behavior. The limiting current density was considered to be the value at $-1.36 \text{ V}_{\text{SCE}}$ as indicated in the figure. Transport of protons to the surface could occur by diffusion of $\text{H}^+$ or HAc [27]. Since the bulk pH for this solution was 2.59, and assuming a pKa of 4.757 for acetic acid [28], the bulk concentrations of both species can be calculated, yielding 0.0821 M for HAc and 0.00257 M for $\text{H}^+$. With the slope of the graph in Figure 4.4b and equation 4.1, each concentration value can be inserted to estimate the diffusion coefficient of the given species, which can be checked against values reported in literature. Assuming HAc is the dominating reducing species, a value of $D^{\text{HAc}} = 8.46 \cdot 10^{-6}$ cm$^2$/s is obtained, whereas if $\text{H}^+$ is the dominating species a value of $D^{\text{H}^+} = 1.53 \cdot 10^{-3}$ cm$^2$/s would be obtained. Reported values at 25°C are $1.200 \cdot 10^{-5}$ cm$^2$/s for HAc [29] and $7.9 \cdot 10^{-5}$ cm$^2$/s for $\text{H}^+$ [30]. Therefore, the error in $D$ is 30% assuming HAc is the reducing species, whereas it is a factor of about 20 assuming protons are the reducing species. This suggests that reduction of acetic acid dominated in the diffusion controlled region, in accord with results presented by Garsany [31].
The evolution of corrosion potential with time, recorded between EIS measurements for a total experiment period of 72 h, is presented in Figure 4.5. It is seen that in the solutions containing thiosulfate, the potential increased from an initial value lower than that measured in the base solution, and remained at a higher value after ca. 4 hours. The potential of carbon steel in the base solution decreased and reached a steady state value after 15 h. The highest potential was measured for the 10^{-1} M S_{2}O_{3}^{2-} containing solution. The increase in potential is expected considering inhibition of the anodic reaction by the film, Figure 4.3, and the deposition of a noble film on top of the steel surface, Figure 4.2, which was a good catalyst for cathodic reactions.

Nyquist plots for the EIS data obtained after 24 h are presented in Figure 4.6. Depressed semicircles were obtained for all solutions at all testing times. The shapes of the spectra were similar at the other times for each respective solution. Low frequency noise is observed when the sulfur containing anion is present, and can be indicative of fluctuations in the surface condition [22]. The low frequency loop observed in the environment with no thiosulfate was ignored during the fitting process because the focus was an estimation of the corrosion rate, but it can be indicative of adsorption processes [32].

The time evolution of the fitting parameters is presented in Figure 4.7, for each solution. In general, polarization resistance values decreased with an increase in thiosulfate concentration and did not exhibit a strong dependence on time, except for the solution containing 10^{-1} M S_{2}O_{3}^{2-}, where Rp increased slightly with time. The base solution also showed an increase in polarization resistance with time. For solutions
containing $10^{-4}$ M and $10^{-3}$ M S$_2$O$_3^{2-}$, the largest increase in polarization resistance occurred between the first and second measurements, suggesting some protection provided by the film. Comparison with anodic polarization behavior after 24 h, Figure 4.3, suggests that the mechanism of protection provided by the film could be anodic inhibition, since the film was a good catalyst for cathodic reactions, Figure 4.2. $Y_0$ is related but is not equal to the capacitance of the corroding system [33]. The equivalent capacity, $C_{eq}$, was calculated from the parameters describing the constant phase element, $Y_0$ and $\alpha$, with the following equation presented by Hsu and Mansfeld [33]

$$C_{eq} = Y_0 (\omega''_m)^{\alpha-1}$$  

where $\omega''_m$ is the frequency at which the imaginary part of the impedance has a maximum. The evolution of $C_{eq}$, $Y_0$ and $\alpha$ are shown in Figure 4.7. For the base solution, $C_{eq}$, $Y_0$ and $\alpha$ remained at a nearly constant value during the time of the experiment. $C_{eq}$ and $Y_0$ increased with time and with the amount of thiosulfate in solution. On the other hand, $\alpha$ was the lowest for the 3 solutions with the greatest concentration of thiosulfate.

Results of weight loss (WL) experiments are presented in Table 4.1. Time averages of polarization resistance were calculated for each thiosulfate concentration and converted to corrosion rates with use of Stern-Geary equation [21]:

$$i_{corr} = \frac{b_a \cdot b_c}{2.3 \cdot (b_a + b_c)}$$  

where $b_a$ and $b_c$ are the anodic and cathodic Tafel Slopes. The time evolution of Tafel slopes was not studied, but the slopes were assumed to be equal to the ones measured
from polarization curves obtained after 24h. The maximum error associated with changes in Tafel slope with time is expected to be a factor of 5 [21]. Table 4.1 shows that there is a fair correlation between measurements of corrosion rate by both techniques. The highest divergence is observed for the $10^{-4} \text{M S}_2\text{O}_3^{2-}$ solution, but is still within a factor of 2.

The results from sulfide ion measurements in the trap were converted to current values assuming a 4 electron Faradaic process, equations 4.3 and 4.4, and are presented in Table 4.1. The current associated with reduction of thiosulfate to hydrogen sulfide was an appreciable fraction of the corrosion current, assuming the Tsujikawa [2] mechanism was valid. SEM images of the surface of the carbon steel after stripping the film with the inhibited HCl solution show that corrosion proceeded in a uniform fashion, Figure 4.8.

4.3.2. Characterization of film structure

X-ray diffraction spectra are presented in Figure 4.9. All samples exposed to the substitute NACE TM0177 solutions exhibited an appreciable amount of iron carbide, which was not detected for the polished sample. This is likely due to the typically low concentration of carbon (<0.10%) in X65 pipeline steel [34, 35]. The presence of cementite in the exposed samples suggests that ferrite was preferentially dissolved in this environment, leaving behind a layer of undissolved cementite on the surface and making it detectable by XRD. Mackinawite was detected in the film formed in the two most concentrated solutions of $\text{S}_2\text{O}_3^{2-}$. Mackinawite is an iron sulfide commonly observed in environments containing hydrogen sulfide [26, 36, 37] or elemental sulfur [38]. Mackinawite is non-stoichiometric and has a rich defect structure, with a formula given
by Fe_{(1+x)}S, with x ranging between 0.057 and 0.064 [39]. The cementite peaks in the sample exposed to 10^{-2} M S_2O_3^{2-} solution are the weakest of all solution exposed samples, Figure 4.9. This suggests that Fe_{(1+x)}S was enriched on the surface, probably due to iron ions diffusing through the film and reacting with sulfur containing species in solution. The scan for 10^{-1} M S_2O_3^{2-} corresponds to the film scraped off of the steel surface. Cementite peaks are stronger in this case, probably due to mixing of the superficial and sub-superficial layers of the film.

The XPS survey spectra and of the S 2p region are presented in Figure 4.10 and Figure 4.11, for the samples exposed for 48 h to 10^{-4} M S_2O_3^{2-} and 24 h to 10^{-3} M S_2O_3^{2-} substitute solutions. In both cases, iron, manganese, oxygen, carbon and sulfur were observed. Manganese is a common element added in steel manufacture to control shape of inclusions, while the oxygen peak is probably related to surface oxidation that might have occurred during air exposure between extraction of the sample from the deaerated environment and placement in the vacuum chamber of the XPS instrument. The carbon peak can be present due to aliphatic contaminants or present in steel as carbides, Figure 4.9, or solid solution. To determine whether iron sulfide forms in the deaerated substituted NACE TM0177 solution with a concentration of 10^{-3} M and 10^{-4} M S_2O_3^{2-}, which could not be concluded from XRD measurements, the S 2p region was fitted with GL peaks. Both S 2p spectra contain peak doublets, consisting of individual peaks centered 1.18 eV apart and with an area relation of 1:2, taking into consideration spin orbit splitting of 2p electrons [40]. Under such constraints, GL fitting of the results for the 10^{-4} M S_2O_3^{2-} solution yielded 2p 3/2 peaks centered at 161.6 eV and 167.1 eV. For
the $10^{-3}$ M $\text{S}_2\text{O}_3^{2-}$ solution, 2p 3/2 peaks were centered at 161.8 eV and 168.0 eV. As mentioned before, the 2p ½ peaks were centered at +1.18 eV and with half the area. The position of the first pair of doublet peaks was in close accord with mackinawite shifts reported in literature [26, 41], suggesting that mackinawite was also the predominant sulfur containing species at those low thiosulfate concentration. The second doublet peak was near the expected shift for iron sulfate [40, 41]. However, it cannot be concluded at this point whether sulfate was formed during exposure to the environment of interest or is a result of *a posteriori* oxidation of iron sulfide.

### 4.4. Discussion

In last chapter it was determined that the amount of H$_2$S generated per unit area during carbon steel corrosion in $\text{S}_2\text{O}_3^{2-}$ solutions is at least one order of magnitude larger than the amount of iron sulfide produced in the film per unit area. XRD and XPS results presented here confirmed the oxidation number of sulfur in the film, and identified the structure with mackinawite, an iron sulfide. Due to the predominance of H$_2$S as reduction product, Faraday’s law was used to calculate the average currents associated with reduction of $\text{S}_2\text{O}_3^{2-}$ to H$_2$S. Figure 4.12, constructed from values reported in Table 4.1, suggest that the corrosion rate scales with the H$_2$S generation rate. If thiosulfate generation is in fact described by equation 4.3 and equation 4.4, those reactions account for a large fraction of cathodic current for all thiosulfate concentrations. This would leave little current for hydrogen generation, and could explain the low hydrogen absorption reported in literature for thiosulfate solutions at OCP [9, 42]. However, other reactions could include reduction of elemental sulfur or sulfite, which are present due to thiosulfate
disproportionation. If elemental sulfur was the active species, the actual current of H₂S generation would be half the value reported in Table 4.1 for thiosulfate, while if sulfite was the active species, current would be double the one obtained for thiosulfate. Current could be between those boundaries if there were multiple reactants that yielded hydrogen sulfide. Irrespective of the actual nature of the reactant, it seems that thiosulfate reduction constituted an important fraction of the total cathodic current at OCP. This contrasts with the situation in H₂S environments, where cathodic current is exclusively associated with hydrogen evolution reaction [5]. However, the hydrogen permeation currents on the order of μA/cm² [6, 9, 43] in the exact same solution studied here and with a similar steel composition suggest that hydrogen evolution is a non-zero fraction of the total cathodic current at OCP.

Tsujikawa reported that the electrode potential of a platinum electrode immersed in 10⁻³ and 10⁻² M S₂O₃²⁻ solutions was the value expected for the redox equilibrium expressed in equation 4.3 [2]. However, despite the mechanism proposed by Tsujikawa [2] for thiosulfate reduction to H₂S, equation 4.3 and 4.4, no elemental sulfur was detected on the surface of carbon steel electrodes exposed to 10⁻⁴ M and 10⁻³ M S₂O₃²⁻ solutions, Figure 4.10 and Figure 4.11, in accord with the finding of Horowitz [44]. A peak near 164 eV [26] should have been present if elemental S was present on the steel surface. On the other hand, cyclic voltammetry studies of gold in a thiosulfate solution combined with Auger electron spectroscopy confirmed the presence of such layer [45]. It is possible that elemental S was not observed in this work because of oxidation during transfer from the cell to XPS chamber. Conversion ratios of thiosulfate to H₂S, the
dominant cathodic reaction, never reached values beyond 45%, as presented in the last chapter. The stoichiometry of the mechanism predicted by Tsujikawa predicts a limit of 100%, if disproportionation and film formation reactions are neglected. Hemmingsen [46] mentioned another mechanism of H$_2$S formation that would explain the limiting value presented here and the absence of elemental sulfur in XPS scans,

$$S_2O_3^{2-} + 3H^+ + 2e^- = H_2S + HSO_3^- \quad E_0=-0.146 \text{ V}_{\text{SHE}}$$

However, the author [46] did not detect any reduction wave in a voltammogram obtained in sodium chloride solution with a platinum electrode beyond that corresponding to reduction of hydrogen. The solution was not acidified, but no secondary analytical techniques were applied to prove that the wave observed corresponds in fact to hydrogen evolution. Despite the complexity of the chemistry, it can be concluded that at least one electrochemical reaction contributing to cathodic current at OCP involves the generation of H$_2$S from thiosulfate. Hydrogen sulfide generation with no electrode immersed in the solution was not detected, as reported in last chapter. This suggests that hydrogen sulfide generation by a sequential disproportionation of thiosulfate to sulfur and sulfite and of sulfur to hydrogen sulfide and sulfate did not occur. Moreover, it was mentioned in last chapter that disproportionation of sulfur to hydrogen sulfide and sulfate has slow kinetics. While those reactions could be catalyzed by the steel surface, this possibility can be ruled out based on the fact that it could not yield an amount of H$_2$S greater than 37.5 % of the originally added thiosulfate, vs. 41.4% and 44.3% reported for the $10^{-4}$ and $10^{-3}$ M $S_2O_3^{2-}$ solutions in the last chapter.
Fractions of hydrogen permeation current vs. total cathodic current at OCP presented by Horowitz [9] for a base solution identical to the one studied here with $10^{-1}$ M $S_2O_3^{2-}$ were on the order of 2%, for a 0.22 mm thick membrane. This is extremely low compared to the situation described in the same work when $H_2S$ was added as poison, where permeation was near 70% for the same thickness, in accord with results by Berkowitz [5]. Hörlund [42], working in a similar environment but with no acetic acid present, also found low hydrogen permeation exhibited by steel in thiosulfate solutions when compared with sulfide, dithionite ($S_2O_4^{2-}$) or sulfite solutions. The author speculated that this could be related to the formation of films that block hydrogen ingress. Results obtained in this and last chapter suggest that this mechanism could be controlling hydrogen ingress in the thiosulfate solutions. Due to the good electron conductivity of iron sulfide and $Fe_3C$ [39, 47] films, acetic acid can be reduced on the external side of the film in contact with the solution. Therefore, hydrogen atoms would need to diffuse across the film, which increases in thickness with time and with thiosulfate concentration, leading to blockage of the H flux. It was stated in the last chapter that growth of films in thiosulfate solutions is faster than in $H_2S$ solutions of the same pH, suggesting that the film blockage mechanism could be more important in thiosulfate solutions. Since corrosion rate increases with thiosulfate concentration but film thickness also increases with the amount of the sulfur-containing anion, a maximum in hydrogen permeation is expected. Another possibility is that the low fraction of hydrogen permeation vs. corrosion current reported by Horowitz [9] could be related to a small fraction of hydrogen evolution reaction vs. the total cathodic current, especially if the Tsujikawa
mechanism [2] for H₂S generation is valid, Table 4.1. It is interesting to note that the degree of embrittlement in thiosulfate solutions was not near that obtained in saturated hydrogen sulfide solutions in a slow strain rate tensile test [2], where the surface film is continuously disrupted. However, this could also be related to the lower concentration of hydrogen sulfide at the steel surface in thiosulfate solutions. Lastly, after units conversions from Table 4.1 it can be shown that the rate of corrosion in thiosulfate solutions ranges from 2 to 30 μm/day. Membranes for hydrogen permeation studies with the Devanathan and Stachursky [48] method need to be much thicker than this so that steady state equations using initial thickness can still be used.

The reduction of thiosulfate to hydrogen sulfide might explain the dependence of cathodic current on thiosulfate content observed at low cathodic overpotentials during potentiodynamic tests, Figure 4.2. Similar results were reported by Zucchi [6], but the author did not provide any mechanistic reason for the increase in current with thiosulfate content. Furthermore, the overpotential applied by the author was too low to reach the diffusion controlled region, observed in the cathodic potentiodynamic curves presented in this work. Because all curves converge to the same limiting current at high overpotentials, independently of the concentration of thiosulfate, it is likely that the reducing species in this region is a component in the base solution rather than thiosulfate. This could be related to a potential dependence of sulfur adsorbance on iron and iron sulfide. Sulfur adsorption diagrams presented by Marcus [49] for a thiosulfate solution with a concentration equal to 0.5·10⁻⁴ M have shown that adsorbed sulfur predominates over adsorbed water and oxygen at potentials corresponding to the range of corrosion
potentials of carbon steel measured in the solutions studied herein. Sulfur in this monolayer can further reduce giving H₂S [49], as suggested by experiments reported here and in the previous chapter. Based on thermodynamic calculations by Marcus, at potential lower than -1 V SCE, concentration of adsorbed water is 100 times greater than adsorbed sulfur [49], as shown in Figure 2.3 in the literature review section. At lower potentials, differences in current between polarization curves obtained in solutions with and without thiosulfate reported in this work are minimal. However, the thermodynamic calculations for iron obtained by Marcus cannot be directly extrapolated to this system due to differences in solution chemistry, including thiosulfate content, and electrode surface structure. Thermodynamic calculations of predominance of surface species were dependent on whether the electrode was iron, nickel or chromium [49]. Therefore, it is reasonable to expect differences in the diagram presented by Marcus for iron with a diagram considering a carbon steel electrode covered by iron sulfide and Fe₃C.

After the transport limited current region, the polarization curves exhibited a rapid increase in current at a potential that is more noble with higher thiosulfate content, Figure 4.2. Such increase was also observed in the curves obtained after 24 h. Vigorous bubbling was observed at this point. It is likely that reduction of water to hydrogen occurs in this region [27, 28],

\[
\text{H}_2\text{O} + e^- = \frac{1}{2}\text{H}_2 + \text{OH}^- \quad \text{E}^0 = -0.828 \text{ V}_{\text{SHE}}
\]

The reversible potential at the pH of the base solution, 2.7, is -0.402 V SCE. The extensive formation of films after 24 h resulted in a decrease in the potential at which the current
from this reaction starts to increase. This is consistent with the observation that sulfide films exhibit low overvoltage for hydrogen evolution [39].

Anodic dissolution of carbon steel is greatly enhanced by the presence of thiosulfate anions, Figure 4.3, which is in accord with work by Zucchi [6] and Horowitz [9, 44]. Since the potential at any point still corresponded to the H$_2$S stable window [2], it is unlikely that the increase of current is related to oxidation of thiosulfate. On the other hand, another manifestation of the catalytic effect of thiosulfate on iron dissolution was studied by Newman [50] on stainless steel pitting. For artificial pits made with steel containing 19 wt% Cr and 10 wt% Ni, the anodic current increased more than an order of magnitude with addition of 6.5 mM of S$_2$O$_3^{2-}$ to a 1 M KCl solution [51]. It was postulated that sulfur adsorption on the metal surface enhanced anodic dissolution and prevented passivation, based on the observation that pits repassivated at potentials above that corresponding to sulfur-thiosulfate metastable equilibrium [50]. The mechanism proposed by Newman is thermodynamically possible in the entire range of potentials applied during the anodic polarization experiments. Horowitz [44], studying carbon steel passivation peaks in anodic voltammograms, also concluded on the catalytic effect of thiosulfate in iron dissolution based on the increasing peak currents with S$_2$O$_3^{2-}$ content. Chemical analysis of the solution showed that very little thiosulfate was consumed during the experiments done by Horowitz. This suggests that currents measured in polarization curves presented in this work, Figure 4.3, correspond in fact to iron dissolution, which seems to be greatly enhanced by thiosulfate additions. Figure 4.3 shows that as a result of
film formation after 24 h, the rate of anodic current decreased with respect to that measured 1h after immersion of the sample.

Corrosion rates presented in Table 4.1 are well above those reported by Ezuber [52] for solutions containing $10^{-3}$, $10^{-2}$ and $10^{-1}$ M $S_2O_3^{2-}$ in a 1M NaCl solution. While the sodium chloride concentration is near the one used here, Ezuber [52] did not add any acetic acid, resulting in a pH between 6.5 and 7. This resulted in corrosion currents on the order of 6 mpy at 22°C, which are well below values obtained here for the same thiosulfate concentrations, Table 4.1. It seems that corrosion rate in thiosulfate solutions is strongly dependent on solution pH and, because it was shown before that reduction of thiosulfate to $H_2S$ is a large fraction of corrosion rate, it can be speculated that kinetics of $H_2S$ generation have a strong dependence on pH. Moreover, thiosulfate disproportionates spontaneously in acid solutions like the one used in this work, giving $S^0$, a known corrosive [38] that can be a reactant in cathodic reactions, therefore increasing corrosion currents. The potential evolution in $10^{-1}$ M $S_2O_3^{2-}$ solution is similar to results reported for sulfur suspensions [53] and corrosion rates in the two most concentrated solutions are well beyond values reported in $H_2S$ literature in the same base solution [5, 18], but similar to results presented in elemental sulfur suspensions [54]. Sulfur, thiosulfate and other species present in acid thiosulfate brines can react at the corrosion potential providing sources of cathodic current beyond protons, the exclusive reactant in acid $H_2S$ solutions. This also can explain the high corrosion rates obtained.

The capacitance of the system stays on the order of $1x10^{-4}$ F/cm² only for the base solution, which is a reasonable order of magnitude of double layer capacitance for iron in
acid solutions [32]. Therefore, it is probable that the electrochemical process in the $S_2O_3^{2-}$ containing solutions is more complicated than simple Faradaic dissolution. It is known from the last and the present chapter that extensive film formation occurs in such solutions. However, the EIS spectra presented in Figure 4.6 exhibit a single time constant. High values of $C_{eq}$ were reported by Bonnel (~1000-2000 μF/cm$^2$) [55] and by Mansfeld (~1000-11000 μF/cm$^2$) [56] during formation of porous and conductive corrosion products on the surface. Capacitance is related to film thickness, $d$, and area, $A$, by the following equation [21]:

$$C = \frac{\varepsilon \varepsilon_0 A}{d}$$  \hspace{1cm} 4.9$$

where $\varepsilon$ is the relative permittivity of the film and $\varepsilon_0$ is the permittivity of vacuum. It is suggested [55] that the increase in the effective area of the layer might lead to an increase in the capacitance seen by the electric field, despite the increase in thickness of the film. The increase in $C_{eq}$ with time reported by Bonnel and Mansfeld is in accord with results presented here, where a thick layer was also formed on the electrode surface. Those high values of $C_{eq}$ might explain why, even though EIS measurements were made down to 1 mHz, the real axis was not crossed in Nyquist plots for the two most concentrated solutions, Figure 4.6b.

Literature results [57] for $\alpha$ for an electrode/solution interface usually range between 1 and 0.8, but it is seen that for the 3 most concentrated solutions the value of $\alpha$ is much smaller. Departures of this parameter from 1 are related to roughness in the electrode surface, heterogeneities, non-uniform current distribution and generation of
porous corrosion products [58]. Porous electrodes can present $\alpha$ values near 0.5 [59]. Lastly, it should be mentioned that if the system contains in fact two time constants, the attempt to fit the results with a single time constant would contribute to the extraordinary low value of $\alpha$ obtained. Therefore, the equivalent capacitance values presented might be in error for those concentrations. On the other hand, polarization resistance values, if taken as the low frequency limit of the real impedance, should be less sensitive on the actual model chosen for fitting the data. Moreover, it is seen that corrosion rates calculated with $R_p$ values are consistent with values obtained by weight loss technique, Table 4.1.

Comparison of anodic polarization curves obtained after 1 h and after 24 h of OCP exposure in the solution containing $10^{-3}$ M S$_2$O$_3^{2-}$, Figure 4.3, and the evolution of $R_p$ with time for all thiosulfate containing solutions, Figure 4.7a, suggest that some degree of inhibition is provided by the film. The effect is minimal, since $R_p$ stays at the same order of magnitude for each solution during the course of the experiment, Figure 4.7a. This is consistent with the constant hydrogen sulfide generation rate law found in the previous chapter. The order of magnitude of polarization resistance for the two most concentrated thiosulfate solutions is near 30 $\Omega$.cm$^2$, which gives a corrosion current near 1 mA/cm$^2$, Table 4.1, suggesting that the film is non-passivating. Non passivating films are common in H$_2$S solutions [60]. It could be that the defect structure and tendency to crack reported elsewhere for mackinawite films [36, 39] and in previous chapter make the film a bad barrier for iron cation diffusion, which is required for iron dissolution during
anodic polarization experiments. The SEM micrographs presented in Figure 4.8 suggest that corrosion was uniform underneath the film.

Results obtained about the structure of films formed in thiosulfate solutions can be used to understand polarization curves after 24 h and evolution of OCP. Properties of iron sulfides were reviewed by Smith [39]. Iron sulfides are good electronic conductors and have a noble potential with respect to carbon steel. Mackinawite has a chemical formula given by Fe$_{1-x}$S, with x between 0.057 and 0.064 [39], giving it a structure rich in defects. Its tendency to crack, observed in the two most concentrated thiosulfate solutions, was also reported by other authors [36]. On the other hand, cementite, present in the film due to preferential ferrite dissolution, is also a good electron conductor and can lead to galvanic coupling with the underlying steel [47]. The shift in potential from an initial low value to higher values, Figure 4.5, observed for all thiosulfate containing solutions, can be understood in terms of the creation of a noble film of iron sulfide and Fe$_3$C contacting the solution and galvanically coupled to the underlying steel. The kinetics of anodic reactions had a stronger dependence on thiosulfate content than the cathodic reactions, Figure 4.3 and Figure 4.2. This resulted in the initial shift to negative values of the corrosion potential just after immersing the electrode in thiosulfate solutions, Figure 4.5, but as the noble film forms on the surface, potential is driven to more positive values. The fact that the steel covered with the film formed after 24 h exhibited good kinetics for cathodic reactions, Figure 4.2, constitutes a further proof of the conductivity of those phases. It was visually corroborated that bubbles nucleated on
this film during cathodic polarization experiments. Inhibition of anodic reaction can also lead to a shift in the open circuit potential to noble values, Figure 4.3.

Rotating disk electrode experiments showed that the hydrogen evolution reaction in the base solution is controlled by diffusion at high potentials and, based on the value of diffusion coefficient found, it is expected that transport was controlled by diffusion of acetic acid. Due to the predominance of HAc vs H$^+$ in the solution studied, it is reasonable that transport of protons to the electrode was dominated by diffusion of undissociated acid. Other authors have also speculated about acetic acid being actively involved in the hydrogen evolution reaction, and the following steps were proposed [31, 61-63]:

$$\text{Fe} + \text{HAc} + e^- = \text{FeH}_{ads} + \text{Ac}^- \quad \text{(4.10)}$$

$$\text{FeH}_{ads} + \text{FeH}_{ads} = \text{Fe} + \text{H}_2 \quad \text{(4.11)}$$

Garsany [31] proposed that, due to the fast dissociation of HAc, the electrode cannot distinguish between a free proton and a proton donor. The author discussed that the reduction potential for platinum in a voltammogram was near the reversible potential of the H$^+/\text{H}_2$ couple at the corresponding solution pH, but transport was controlled by diffusion of acetic acid. George and Nesic [63] also concluded that undissociated HAc acted as a proton carrier in transport, after analyzing the dependence of the limiting current with acetic acid content in acetic acid and sodium acetate solutions of pH 4. In accord with the work of George and Nesic, the results obtained here show that OCP reaction seem to be charge transfer controlled, because the corrosion current is more than an order of magnitude lower that the limiting current [63] and because the corrosion
potential does not change with angular speed. Reported values for the Tafel slope of acetic acid reduction range from 120 mV/decade [62], for a 5wt% HAc solution without supporting electrolyte to 262 mV/decade [61] for a 0.04 M HAc/Ac at a pH of 3.5 with 0.52 M (3 wt%) of NaCl. Tafel slopes cannot be larger than 118 mV/decade if describing a charge transfer controlled process. However, in the cathodic polarization curves obtained in this work, the cathodic linear region is small, Figure 4.2, probably related to the fact that transport limits current about 500 mV below the corrosion potential. Berkowitz [5] found a larger linear region in the exact base solution as the one studied here, and it was well fitted by a slope of 118 mV/decade. However, unlike the results presented here, the applied cathodic potentials were not low enough to determine if a transport limited region was also present. The curve obtained in this work after 24 h for a stationary electrode was corrected by the Koutecky-Levich equation [64],

$$\frac{1}{i_k} = \frac{1}{i} - \frac{1}{i_l},$$

where $i$ is the current density measured potentiodynamically, $i_l$ is the limiting current and $i_k$ is the current density that would have been obtained in the absence of any mass-transfer limitations [64]. Figure 4.13 shows that, even after this correction, the Tafel slope obtained, 133 mV/decade, is slightly greater that the expected value, 118 mV/decade. Another effect that could explain discrepancies could be related to the surface condition of the sample. Previous work on carbon steels polarized in similar solutions suggested that the rate of cathodic reactions in this environment depends strongly on the surface condition of the sample [5], because the original surface oxide layer can be retained in the steel until removed by anodic polarization or other
corrodents, according to Horowitz [9]. On the other hand, for the thiosulfate containing solutions, not only hydrogen evolution reaction but hydrogen sulfide evolution reactions might be occurring simultaneously at the open circuit potential. Therefore, correction with the Koutecky-Levich equation was not attempted.

4.5. Conclusions

- Thiosulfate increases the rate of anodic and cathodic reactions in carbon steel, and corrosion proceeds with extensive film formation.
- Films formed in thiosulfate solution consist of mackinawite, a non-passivating iron sulfide commonly encountered in hydrogen sulfide solutions, and cementite, which is left behind after preferential ferrite dissolution. Such layer offers minor anodic protection, probably by hindering iron ion transport. Due to the good electron conducting characteristics of those phases, the film cannot inhibit the occurrence of cathodic reactions.
- Films might block hydrogen absorption, because proton reduction reactions can occur on their surface due to their good electron conductivity.
- Corrosion rate increases with thiosulfate concentration from $10^{-4}$ M to $10^{-2}$ M, but stays nearly constant beyond that. Cathodic current at OCP in acid thiosulfate solutions arises from hydrogen sulfide generation and hydrogen evolution reactions.
- Corrosion rates in thiosulfate solutions are higher than in hydrogen sulfide saturated solutions, despite the lower $H_2S$ surface concentration. This could
correspond to the presence of elemental sulfur and extra sources of cathodic currents beyond proton reduction, the dominant reaction in H$_2$S solutions.

- Results presented in this work were limited by the fact that various species can react to yield H$_2$S, which prevented determination of the exact percentage of current at open circuit corresponding to hydrogen sulfide generation vs. hydrogen evolution reactions. If H$_2$S generation proceeds by sequential reduction of S$_2$O$_3^{2-}$ to S and then to H$_2$S, those reactions would consume the largest fraction of electrons available from open circuit corrosion.
4.6. Tables

Table 4.1. Corrosion rates measured with weight loss technique and average of polarization resistance measurements, for a total exposure time of 72h.

<table>
<thead>
<tr>
<th></th>
<th>[S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}]</th>
<th>0.0001</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>corrosion rate</td>
<td>mA/cm\textsuperscript{2}</td>
<td>0.104</td>
<td>0.481</td>
<td>0.937</td>
<td>1.146</td>
</tr>
<tr>
<td>mpy</td>
<td></td>
<td>47.4</td>
<td>219</td>
<td>428</td>
<td>523</td>
</tr>
<tr>
<td>Rp measurement</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>corrosion rate</td>
<td>mA/cm\textsuperscript{2}</td>
<td>0.050</td>
<td>0.407</td>
<td>0.794</td>
<td>0.977</td>
</tr>
<tr>
<td>mpy</td>
<td></td>
<td>22.8</td>
<td>186</td>
<td>362</td>
<td>446</td>
</tr>
<tr>
<td>i S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-} → H\textsubscript{2}S</td>
<td>mA/cm\textsuperscript{2}</td>
<td>0.043</td>
<td>0.29</td>
<td>0.75</td>
<td>0.50</td>
</tr>
</tbody>
</table>
4.7. Figures

Figure 4.1. Equivalent circuit used to fit the impedance spectra obtained for pipeline steel freely corroding in a deaerated solution containing 5wt% NaCl and 0.5 wt% HAc with and without thiosulfate additions.
Figure 4.2. Potentiodynamic cathodic polarization curves of pipeline steel in base N₂ deaerated NACE TM0177-90 solution A and with varying additions of thiosulfate after 1 h (black lines) and after 24 h (light grey line) of OCP exposure. The effect of time on the cathodic polarization curves measured in the rest of the thiosulfate containing solutions was similar to the one presented in the graph for $[S_2O_3^{2-}]=10^{-2}$ M, but were excluded for clarity in the presentation.
Figure 4.3. Potentiodynamic anodic polarization curves of pipeline steel in N₂ deaerated base NACE TM0177-90 solution, with and without additions of thiosulfate after 1 h (black lines) and after 24 h (light grey line) of OCP exposure. The effect of time on the anodic polarization curves measured in the rest of the thiosulfate containing solutions was similar to the one presented in the graph for \([S₂O₃²⁻]=10^{-3}\) M, but were excluded for clarity in the presentation.
Figure 4.4. Polarization curves, a), obtained in N$_2$ deaerated base NACE TM0177-96 solution A with a rotating disc electrode, operated at the angular speeds indicated in the graph. Dependence of the limiting current with angular speed, b). The limiting current was measured from the polarization curves at the potential indicated by the dashed line.
Figure 4.5. Evolution of OCP with time for various thiosulfate additions to a N$_2$ deaerated solution containing 0.5 wt% HAc and 5 wt% NaCl.
Figure 4.6. Nyquist plots for impedance data obtained after ca. 24 h of immersion in base NACE TM0177-90 solution A, a), and with different additions of thiosulfate shown by the legends, a) and b). Scatter corresponds to measurements and lines to fitted impedance of the equivalent circuit. Notice the different scales for the two plots.
Figure 4.7. Time evolution of parameters obtained after fitting EIS results for each solution, a) $R_p$, b) $C_{eq}$, c) $V_0$, d) $\alpha$. 

continued
Figure 4.7 continued

c) $Y_0$ (s$^{-1}$/Ω·cm$^2$) vs. time (h)

- No $S_2O_3^{2-}$
- $[S_2O_3^{2-}]=10^{-4}$ M
- $[S_2O_3^{2-}]=10^{-3}$ M
- $[S_2O_3^{2-}]=10^{-2}$ M
- $[S_2O_3^{2-}]=10^{-1}$ M


d) $\alpha$ vs. time (h)

- No $S_2O_3^{2-}$
- $[S_2O_3^{2-}]=10^{-4}$ M
- $[S_2O_3^{2-}]=10^{-3}$ M
- $[S_2O_3^{2-}]=10^{-2}$ M
- $[S_2O_3^{2-}]=10^{-1}$ M
Figure 4.8. Secondary electron images of the corroded steel, after chemically stripping the film formed after 72 h OCP immersion in substituted NACE TM0177 solution A substituted with a) $10^{-4}$ M S$_2$O$_3^{2-}$, b) $10^{-3}$ M S$_2$O$_3^{2-}$, c) $10^{-2}$ M S$_2$O$_3^{2-}$ and d) $10^{-1}$ M S$_2$O$_3^{2-}$. 
Figure 4.8 continued

c)  


d)
Figure 4.9. XRD diffraction scans of (from top to bottom) a polished iron steel sample, and the same steel specimen after OCP immersion for 143 h in $10^{-4}$ M $\text{S}_2\text{O}_3^{2-}$, 96 h in $10^{-3}$ M $\text{S}_2\text{O}_3^{2-}$, 72 h in $10^{-2}$ M $\text{S}_2\text{O}_3^{2-}$ and 24 h in $10^{-1}$ M $\text{S}_2\text{O}_3^{2-}$ substituted NACE TM0177 solutions. Peak labels are F: Ferrite ($\alpha$ Fe), C: Cementite ($\text{Fe}_3\text{C}$), M: Mackinawite ($\text{Fe}_{(1-x)}\text{S}$).
Figure 4.10. XPS survey spectra, a), and XPS spectra of the S 2p region, b), for the sample exposed to $10^{-4}$ M $S_2O_3^{2-}$ substituted NACE TM0177 solution at OCP for 48 h.
Figure 4.11. XPS survey spectra, a), and XPS spectra of the S 2p region, b), for the sample exposed to $10^{-3}$ M $S_2O_3^{2-}$ substituted NACE TM0177 solution at OCP for 24h.
Figure 4.12. Comparison of average corrosion current and H$_2$S evolution current vs. thiosulfate concentration. H$_2$S evolution current was calculated assuming a 4 e$^-$ reduction path.
Figure 4.13. Current density, corrected by the Koutecky-Levich equation, vs. potential, for a carbon steel sample in NACE TM0177-96 base solution A after 24h of OCP immersion. The cathodic Tafel slope was $b_c = 133 \text{ mV/decade}$. 

\[ b_c = 133 \text{ mV/decade} \]
4.8. References


CHAPTER 5. COMPARISON OF HYDROGEN PERMEATION AND CORROSION FATIGUE CRACK GROWTH RATES IN THIOSULFATE VS. HYDROGEN SULFIDE ACID BRINES

5.1. Introduction

Thiosulfate solutions have been studied [1-8] as substitutes for hydrogen sulfide solutions in sour corrosion and sulfide stress cracking studies due to safety concerns. Thiosulfate is an innocuous substance, in contrast to hydrogen sulfide, a flammable and lethal gas. However, in situ generation of hydrogen sulfide during steel corrosion in thiosulfate solutions was reported in the literature [1, 4] and previous chapters. Therefore, caustic traps and hydrogen sulfide detectors are required for thiosulfate testing, but the main advantage is related to the fact that high pressure hydrogen sulfide cylinders are not required. Despite the in-situ generation of H₂S, the degree of embrittlement in a slow strain tensile test reached with thiosulfate solutions is well below [4] that obtained with NACE TM0177-90 solution A, which contains 0.5 wt% HAc, 5 wt% NaCl and is saturated with H₂S [10]. This lesser embrittlement was correlated with the lower amount of hydrogen permeation in thiosulfate vs. hydrogen sulfide solutions [4, 11]. It was discussed in the last chapter that there could be several reasons behind the lower hydrogen permeation, i.e. the lower concentration of hydrogen sulfide reached at the
surface of carbon steel corroding in thiosulfate solutions, the formation of thicker films in thiosulfate vs. hydrogen sulfide solutions and the balance of anodic current by the electrochemical reduction reactions involved in hydrogen sulfide generation. One of the objectives of this chapter is to compare hydrogen permeation in thiosulfate solutions to solutions bubbled with mixtures of hydrogen sulfide and nitrogen. Three concentrations of hydrogen sulfide in nitrogen were selected so that they would lead to a concentration of hydrogen sulfide in the bulk of the NACE TM0177-90 solution A that is the same as at the surface of carbon steel corroding in each of the thiosulfate solutions. On the other hand, the rate of hydrogen absorption increases with hydrogen sulfide partial pressure \[12, 13\]. Therefore, those three different concentrations of hydrogen sulfide in nitrogen are expected to yield three well defined amounts of hydrogen absorption.

The second main objective of this chapter is to compare corrosion fatigue crack growth rates in hydrogen sulfide and thiosulfate solutions. To date, no attempts of simulating hydrogen sulfide with thiosulfate solutions in sour corrosion fatigue have been reported in the literature. However, experiments performed by Tsujikawa [4] in carbon steels shown that the maximum loss of ductility during slow strain rate tests in thiosulfate solutions occurred at a concentration of thiosulfate that yielded the maximum amount of hydrogen absorption, suggesting a hydrogen embrittlement mechanism for stress corrosion cracking. The ability of thiosulfate solutions to mimic hydrogen sulfide in corrosion fatigue tests might be dependent on the rate of permeation of hydrogen that they cause. Hydrogen embrittlement is often cited as the mechanism controlling crack growth rates during sour corrosion fatigue [14-18]. Fatigue crack growth rates will be
measured in thiosulfate containing solutions and solutions bubbled with mixtures of hydrogen sulfide and compared to hydrogen permeation measurements.

Crack growth rate during corrosion fatigue is frequency dependent, in contrast to fatigue in inert environments. An increase in crack growth rate with a decrease in frequency is often observed for corrosion fatigue [14, 16, 19]. This is related to increased time at lower frequency for electrochemical reactions at the crack tip, hydrogen charging, hydrogen diffusion and hydrogen metal interactions [20, 21]. The rate of crack growth, da/dN, can be considered to be the sum of three components, applying the superposition principle proposed by Wei et al. [20, 22],

\[
\frac{da}{dN} = \left(\frac{da}{dN}\right)_{\text{ref}} + \left(\frac{da}{dN}\right)_{\text{cf}} + \left(\frac{da}{dN}\right)_{\text{SCC}}
\]

where \(\left(\frac{da}{dN}\right)_{\text{ref}}\) is the rate of crack growth in an inert environment and therefore exclusively related to mechanical forces, \(\left(\frac{da}{dN}\right)_{\text{cf}}\) is the contribution from the interaction between fatigue and the environment and is frequency dependent, and \(\left(\frac{da}{dN}\right)_{\text{SCC}}\) is the contribution from stress corrosion cracking (SCC), which should be considered only when the maximum stress intensity factor is above \(K_{\text{ISC}}\), the threshold \(K_1\) for SCC in the particular environment. It can be shown [16, 21, 22] that if reaction at the crack tip is the rate limiting step, the frequency dependent component of corrosion fatigue crack growth rate, \(\frac{da}{dN}_{\text{cf}}\), can be expressed by the following equation

\[
\left(\frac{da}{dN}\right)_{\text{cf}} = \left(\frac{da}{dN}\right)_{\text{sat}} \left(1 - \exp\left(-\frac{f_0}{f}\right)\right)
\]

where \(\left(\frac{da}{dN}\right)_{\text{sat}}\) is the value of frequency dependent crack growth rate obtained when surface coverage of the fresh metal at the crack tip is complete, \(f\) is the frequency and
$f_0$ is a characteristic frequency, related to the rate constant of the reaction at the crack tip. On the other hand, $(da/dN)_{cf}$ could be controlled by diffusion of hydrogen through the fracture zone, in which case the following equation would hold [20, 23]:

$$
\left( \frac{da}{dN} \right)_{cf} = A_0 \exp \left( -\frac{H_b}{RT} \right) \sqrt{\frac{D}{f}} \Delta K^2
$$

where $A_0$ is a constant, $H_b$ is the binding enthalpy of hydrogen to dislocations, $R$ is the universal gas constant, $T$ is the absolute temperature, $D$ is the hydrogen diffusion coefficient, $f$ is the frequency and $\Delta K$ is the stress intensity factor range. Both equations for the frequency dependent component of the corrosion fatigue crack growth rate predict a plateau at a sufficiently low frequency. For reaction at the crack tip control, this frequency is related to the time required for complete surface coverage of the metal at the crack tip. On the other hand, for hydrogen diffusion control, a plateau would be observed at the frequency when hydrogen can diffuse through the length of the plastic zone in a cycle [16]. The low frequency plateau has been experimentally observed for carbon steels in sour environments [16, 19]. Another contribution to the frequency dependency of crack growth rates could be related to crack closure effects [24] and crack tip blunting, which would lead to a $\Delta K$ at the crack tip lower than the applied value. Both effects are expected to be more important at lower frequencies, due to the longer times for film formation and metal dissolution. The $da/dN$ dependence on $\Delta K$ during corrosion fatigue is characterized by a threshold, below which crack growth rate is not observed, followed by a region of increasing $da/dN$ with $\Delta K$, and then a plateau, where crack growth rate is independent of $\Delta K$ [24]. Therefore, crack closure and crack tip blunting could decrease
the crack growth rate measured at low frequency in the \( \frac{da}{dN} \) – f curve, if the change in \( \Delta K \) is sufficiently large. Comparison of crack growth rate vs. frequency for thiosulfate and hydrogen sulfide solutions can indicate whether the mechanism of crack growth is the same in both environments.

Hydrogen absorption during corrosion fatigue can proceed by one or both of the following paths: crack tip charging by reaction of the metal with the particular solution created in the occluded environment, or bulk charging of hydrogen at the entire exposed surface followed by diffusion to the crack tip region. For carbon steels in sea water, Turnbull [25] showed that the pH in the crack region during corrosion fatigue is near the bulk pH or slightly more alkaline. The increase in pH is expected to be even higher in sour environments, because the presence of sulfide decreases the amount of metal ions, which can otherwise hydrolyze to produce protons. This higher pH would suggest a lower rate of hydrogen absorption with respect to the bulk, because it has been shown that hydrogen absorption decreases with an increase in pH [12, 13, 26]. However, the rupture of film due to the load cycling process exposes bare metal at the crack tip, which could lead to increasing rates of hydrogen production because of the enhanced reactivity of the bare metal. Bulk charging is expected to dominate in aggressive solutions, like NACE TM0177-96 solution A [15, 27], which is saturated with \( \text{H}_2\text{S} \) (0.1 MPa) and has a pH near 2.7. Holtam [15] performed sour corrosion fatigue in a solution saturated with 7% \( \text{H}_2\text{S} \) and showed that shallow cracks grew faster than deep cracks. Results were rationalized based on a bulk hydrogen charging mechanism [15]. Shallow cracks had their tip closer to the exposed surface, therefore they grew faster due to the shorter path
for hydrogen diffusion. A crack closure effect was discarded, given the high ratio of $K_{\text{min}}/K_{\text{max}}$. Post-mortem analysis of un-coated bend specimens showed that crack fronts were also deeper at the lateral surfaces of the specimen, despite the fact that triaxiality of stresses is not observed in free surfaces. The effect was also related to a higher concentration of hydrogen due to bulk charging. On the other hand, Eadie [14] performed corrosion fatigue tests at different partial pressures of hydrogen sulfide, and showed a small increase in crack growth rate (4 X) despite a large increase in hydrogen sulfide partial pressure (80 X). Those results were rationalized based on hydrogen ingress controlled by crack tip charging. Those experiments were performed in different conditions than those chosen by Holtam, namely, pH near 6.5 and partial pressure of H$_2$S between 0.02 and 1.65 MPa. A final objective of this chapter is to compare crack growth rates in NACE TM0177-96 solution A to those measured during air fatigue of a hydrogen charged specimen, where crack tip charging is not possible. This will help to clarify the relative importance of crack tip vs. bulk hydrogen charging, and give estimates about the relative importance of secondary effects during sour corrosion fatigue, like crack tip blunting and crack closure.

5.2. Experimental

Samples for all experiments were extracted from a piece of X65 seamless carbon steel pipeline, of 25.4 mm thickness. The yield strength of this steel is 448 MPa (65 ksi). Solutions used were based on the NACE TM0177-96 solution A [10]. However, instead of H$_2$S saturation, thiosulfate was added to different target concentrations. Thiosulfate was added right before starting the experiment to minimize thiosulfate
disproportionation. In chapter 3, the surface concentration of hydrogen sulfide during open circuit corrosion of steel in thiosulfate solutions was estimated. It was shown that, for each concentration of thiosulfate, the same concentration of hydrogen sulfide could be reached in the bulk of a NACE TM0177-96 solution A if bubbling the correct mixture of H$_2$S and N$_2$. The partial pressures of H$_2$S in those gas mixtures for 10$^{-4}$, 10$^{-3}$ and 10$^{-2}$ M thiosulfate solutions are 0.029 kPa (0.0043 psi), 0.56 kPa (0.081 psi) and 1.5 kPa (0.21 psi). Those partial pressures were obtained assuming ideal behavior of gases and a total absolute pressure of 101.3 kPa. The concentrations in units of weight percent are 0.035 wt%, 0.667 wt% and 1.77 wt% of H$_2$S in N$_2$, respectively. In other words, the concentration of hydrogen sulfide in a bulk solution saturated with those gas mixtures will be near that obtained at the surface of a corroding steel in NACE TM0177-96 solution A substituted with 10$^{-4}$, 10$^{-3}$ and 10$^{-2}$ M S$_2$O$_3^{2-}$, respectively. It was discussed in preceding chapters that 0.1 M thiosulfate resulted in high corrosion rate, extensive film formation and flaking, and higher amount of elemental sulfur in the bulk. However, the 10$^{-1}$ M S$_2$O$_3^{2-}$ solution is expected to have an H$_2$S concentration slightly lower than the 10$^{-2}$ M S$_2$O$_3^{2-}$ solution, as discussed in chapter 3. Therefore, permeation and corrosion fatigue tests were not performed at this level of thiosulfate content. Hydrogen permeation experiments were performed in 6 solutions: 3 obtained with each gas mixture and 3 obtained with the different additions of thiosulfate, namely 10$^{-4}$, 10$^{-3}$ and 10$^{-2}$ M. The target S$_2$O$_3^{2-}$ concentration was reached by addition of aliquots from a 1 M Na$_2$S$_2$O$_3$.5H$_2$O solution. Additionally, a permeation experiment was performed in NACE TM0177-96 solution A deaerated with N$_2$. The permeation experiment in 10$^{-2}$ M S$_2$O$_3^{2-}$
revealed a low absorption of hydrogen in this environment. Therefore, fatigue crack growth rate (FCGR) measurements were performed in the hydrogen sulfide solutions and in the solutions with $10^{-4}$ and $10^{-3}$ M $S_2O_3^{2-}$. In addition, FCGR was measured in standard NACE TM0177-96 solution A (saturated with $H_2S$) and with the same solution deaerated with $N_2$ with no addition of sulfur species to obtain an upper boundary and a baseline, respectively.

5.2.1. Hydrogen permeation

Hydrogen permeation experiments used a modified version of the Devanathan and Stachurski [28] cell. A hydrogen gas detector was used at the exit side of the sheet instead of the anodic cell described in [28]. The main advantages of this were that palladium coating of the exit side of the sheet and a potentiostat were not required. A 3 mm thick steel sheet was used for those experiments, exposing an area of 28.5 cm$^2$ to the solution. The surface exposed to the solution was normal to the radial direction of the parent pipe. The solution was deaerated in a separate container with nitrogen, saturated with the $H_2S/N_2$ gas mixture if required and then transferred to the cell, where it was allowed to contact the steel specimen. For the solution without thiosulfate additions, 800 ml of solution was transferred to the cell, and the $H_2S/N_2$ gas mixture was bubbled during the test. For the solutions containing thiosulfate, the large exposed area of the steel specimen required the use of a 12 L reservoir of solution. Otherwise, there was risk that the concentration of thiosulfate could fall to a very low value before completion of the test, due to reaction with steel to give hydrogen sulfide and subsequent removal of this gas by the continuous nitrogen bubbling. A pump provided continuous recirculation of
the solution from the cell to the 12 L reservoir. For both cases, one side of the steel sheet was exposed to the solution of interest at the open circuit potential. An Ion Science Hydrosteel 6000 hydrogen detector was placed on the other side of the sample to detect diffusible hydrogen [29]. The detector consisted of a collector plate, which was attached to the sample by magnets. The collector had a spiral trench, with a hole at the center of the spiral, which was connected to a pneumatic pump that transported ambient air across the steel surface confined by the collector, and to an amperometric detector. The device recorded the flux of hydrogen as a function of time. The detection technique relies on hydrogen recombination at the exiting surface. For fluxes between 0.4 to 240 \( \mu \text{A/cm}^2 \), the close correlation between theory and experiments reported in literature suggests that hydrogen transport is controlled by diffusion through the sample [29], so the use of this detector is valid.

Hydrogen permeation transients were obtained with the irreversible traps saturated. Irreversible traps are those with high binding energy of hydrogen and thus low probability of releasing hydrogen or very long residence time [30]. The saturation of the irreversible traps was accomplished by an initial test with the solution bubbled with the \( \text{H}_2\text{S}/\text{N}_2 \) mixture with an \( \text{H}_2\text{S} \) partial pressure of 0.56 kPa, for 20 h to allow saturation of irreversible traps [31]. The sample was then annealed at 50 °C overnight to allow diffusible hydrogen to exit the sample. Then the same sample was used for obtaining fluxes of hydrogen for the different solutions. The same annealing treatment was performed between tests, and samples were repolished to 600 grit before starting each experiment. Due to the combination of temperature and low partial pressure of hydrogen
in air (0.05 Pa) during the annealing heat treatment, hydrogen is expected to be fully removed from perfect lattice sites and weak traps such as expanded regions near edge dislocations and partially removed from reversible traps like dislocations cores, grain boundaries and AlN interfaces [30, 32]. Hydrogen population in irreversible traps like matrix-\(\text{Fe}_3\text{C}\) and -\(\text{TiC}\) interfaces is expected to be unaltered as a consequence of the annealing heat treatment [30, 32]. Therefore, the permeation curves correspond to a specimen with only reversible traps like grain boundaries and dislocations active [31], since irreversible traps like matrix-\(\text{Fe}_3\text{C}\) and -\(\text{TiC}\) interfaces are expected to remain saturated even after the annealing heat treatment. There is a slight difference in thickness between each test due to the polishing steps between each hydrogen permeation experiment. Therefore, results are reported normalized by thickness, but the maximum difference in thickness, measured between the first and last experiment, was below 10%.

5.2.2. Corrosion Fatigue

Compact tensile specimens were machined from the pipe, to the dimensions shown in Figure 5.1. The crack was machined in the L-C direction [33], i.e., the crack plane was normal to the axis of the tube, and the direction of increasing crack length was parallel to the circumferential direction. The initial notch had a size near 6.9 mm (0.27 in), and a crack was grown by air fatigue to a target \(a\) size of 8.89 mm (0.35 in). Machining and precracking were performed at Westmoreland Mechanical Testing and Research, Inc. The final pre-crack length was measured microscopically and by the compliance method. Final \(K_{\text{max}}\) and \(\Delta K_{\text{max}}\) values during precracking were near 13
MPa·m$^{1/2}$ (12 ksi·in$^{1/2}$) and 11 MPa·m$^{1/2}$ (10 ksi·in$^{1/2}$) respectively, which are well below $K_{\text{max}}$ and $\Delta K_{\text{max}}$ values used for subsequent corrosion fatigue studies.

Corrosion fatigue experiments were performed in a servoelectric tensile frame of 5000 lb capacity (Interactive Instruments). The cell, clevises, pins and pulling rods were made of Hastelloy C276 to minimize corrosion in the sulfide containing environments. Solution was deaerated in a separate glass container and then transferred to the cell, which was also deaerated with high purity nitrogen. For the solutions without thiosulfate additions, 3.5 L of solution were transferred to the cell after deaeration and saturated with the corresponding H$_2$S/N$_2$ gas mixture. For the thiosulfate containing solutions, there was risk of depletion of thiosulfate due to reactions that yield hydrogen sulfide combined with the nitrogen purging. Therefore, the solution was recirculated during the test from a deaerated 13.5 L reservoir. For all experiments, the specimens were soaked in the respective solution for 72 h prior to cycling the load. It is expected that during this time hydrogen would have saturated the region where the crack would later propagate.

Crack growth rate tests were performed at $\Delta K$ of 19.1 MPa·m$^{1/2}$ (17.4 ksi·in$^{1/2}$) and R of 0.13. $K_{\text{max}}$ and $K_{\text{min}}$ values corresponding to these conditions are 22.0 MPa·m$^{1/2}$ (20.0 ksi·in$^{1/2}$) and 2.86 MPa·m$^{1/2}$ (2.60 ksi·in$^{1/2}$), respectively. Holtam [34] recently reported that, for X65 pipeline steel in NACE TM0177-96 solution A, $K_{\text{ISC}}$ was between 800 to 850 N·mm$^{-3/2}$ (25.3 to 26.9 MPa·m$^{1/2}$ or 23.0 to 24.5 ksi·in$^{1/2}$). NACE TM0177-96 solution A is the most aggressive solution studied in this work and it is expected that $K_{\text{ISC}}$ values for the remaining solutions are higher than in this H$_2$S saturated solution. Because the $K_{\text{max}}$ values used for the FCGR experiments are below those values required
for static load crack propagation, it can be considered that the term \((da/dN)_{SCC}\) from equation 5.1 is zero. Frequency was scanned in FCGR experiments in the decreasing direction, from 3 Hz to 3 mHz or 1 mHz. Cracks were allowed to grow about 0.5 mm (0.020 in) before each change in frequency to obtain sufficient data for evaluation of crack growth rate. Corrosion fatigue crack growth rates for each solution were obtained from a single specimen. Crack growth rates measured from specimens extracted from the same pipeline tested in identical conditions were reported to be reproducible within a 20% error [35].

Crack length was monitored with the direct current potential drop (DCPD) technique. In this technique a constant direct current is passed through the specimen and the potential drop across the crack plane is measured [36]. The clevises were electrically isolated from the cell and rest of the load train by use of plastic washers. Load was applied with ceramic coated Hastelloy C276 pins for the same reason. Two pieces of silver wire were spot welded at the top and bottom of the compact tensile specimen, so that current flow for DCPD measurements would be normal to the crack plane. An Agilent 6611C was used to apply a current of 4 A. The potential drop was measured using two pieces of platinum wire spot welded to the specimen at either sides of the crack plane and a NI-PXI1033 chassis equipped with a NI-PXI4071 digital multimeter and a NI-PXI2527 switch (National instruments Corporation). All wires were coated with heat-shrink PTFE to avoid galvanic coupling with the sample. All faces of the sample, except the crack and notch faces but including the spot welds, were coated with epoxy paint.
(Epoxy Systems™ Product 641, Carboline Company). Increments in potential difference due to crack growth were monitored through the tests to estimate crack length.

Crack length measurements were used to calculate the load required to keep $\Delta K$ constant during frequency scans. A LabView program used the values of potential drop across the crack, $V$, to calculate the value of crack size, $a$. Additional inputs required were the initial crack size, $a_0$, the voltage drop at this reference value, $V_0$, the half-distance between voltage leads, $Y_0$, and the sample width, $W$ [37]:

$$a/W = \frac{2}{\pi} \cos^{-1} \left[ \frac{\cosh(\pi Y_0/2W)}{\cosh \left( \frac{V}{V_0} \cosh^{-1} \left( \frac{\cosh(\pi Y_0/2W)}{\cosh(\pi a_0/2W)} \right) \right)} \right]$$

Potential measurements to determine crack length were lower during unloading cycles, due to contact of crack faces which provided decreased resistance. To minimize this artifact, crack length was only updated by the LabView program when crack length increased, which corresponded to an increase in resistance. The Labview program used the instant crack length value to estimate the required load range ($\Delta P$) with the following equation, valid for a compact specimen [38] with $a/W \geq 0.2$,

$$\Delta K = \frac{\Delta P}{B \sqrt{W}} \frac{(2 + \alpha)}{(1 - \alpha)^{\frac{3}{2}}} \left(0.886 + 4.64\alpha - 13.32\alpha^2 + 14.72\alpha^3 - 5.6\alpha^4\right)$$

where $\alpha = a/W$. Once all frequencies were scanned, the sample was quenched in liquid nitrogen and the remaining ligament was broken. The crack surfaces were observed with a stereoscope and final crack length during fatigue was measured and compared to final in-situ measurements with the DCPD method. Differences between the final value given
by the DCPD method and the final crack length, measured according to ASTM E399 [33], was below 10 % for all tests.

Crack growth rates were divided by air values, to obtain knock-down factors. Air fatigue values were calculated from published guidelines [39]. For ferritic steels with yield strength lower than 700 MPa (110 ksi), R<0.5 and ∆K higher than 363 N/mm$^{3/2}$ (11.5 MPa·m$^{1/2}$, 10.5 ksi·in$^{1/2}$), air fatigue follows the Paris law, with the following coefficients [39]:

$$\frac{da}{dN}_{air} = 3.98 \times 10^{-13}(\Delta K)^{2.88}$$

where ∆K is in N/mm$^{3/2}$ and da/dN is in mm/cycle. The ∆K value used throughout this work is 604.6 N/mm$^{3/2}$, yielding a value of 4.08 x 10$^{-5}$ mm/cycle for air fatigue crack propagation rate.

A test was also performed in the H$_2$S saturated solution on a compact specimen that was completely uncoated except for the points were it was spot welded to the silver and platinum wires necessary for crack growth measurements. Before starting the FCGR frequency scan, the sample was left at OCP for 72 h. This test was performed with the objective of assessing the effect of prior bulk hydrogen charging on corrosion fatigue.

5.3. Results

5.3.1. Hydrogen permeation

Figure 5.2 shows the first and second hydrogen permeation transients across the 3 mm sheet of pipeline steel, exposed to NACE TM 0177-96 solution A saturated with the
H$_2$S/N$_2$ mixture with an H$_2$S partial pressure of 0.56 kPa. The second transient was obtained after annealing the sample at 50 °C after the first transient and repolishing to 600 grit. Therefore, the difference between transients shown in Figure 5.2 is related to irreversible trapping [30, 31]. The two curves converge at longer times once traps are saturated, showing a good reproducibility of the measurement technique. The rest of the experiments were performed on samples with the same preparation as that for the second transient in the figure, and therefore depict the transport of hydrogen through a lattice with only reversible traps active [30]. To compensate for the small decrease in thickness (<10%) as a consequence of the successive OCP exposure and polishing steps, results of all hydrogen permeation experiments are presented normalized by thickness (L). The product of current and thickness, i·L (left axis), was plotted vs. time normalized by the square of thickness, $t/L^2$. The right axis shows the product of flux with thickness, with the flux in units of mols of hydrogen permeating through the specimen per unit time and area.

The amount of hydrogen permeating through a 3 mm sample in 5 wt% NaCl + 0.5 wt% HAc deaerated with nitrogen could not be resolved with the sensing technique used in this study, which had a detection limit of 0.16 μA/cm$^2$. For the exact same solution, Berkowitz et al. [40, 41] reported a value on the order of 3 μA/cm$^2$ for a 0.2 mm thick AISI 4130 steel sheet. Assuming Fick’s first law, and the same value of hydrogen diffusion coefficient, the predicted current for the 3 mm thick sheet used in this work would be 0.2 μA/cm$^2$, which is near the detection limit of the instrument. Figure 5.3 shows hydrogen permeation transients for solutions bubbled with H$_2$S/N$_2$ mixtures, and
Figure 5.4 shows hydrogen permeation transients for thiosulfate containing solutions. The transient for 100 % H$_2$S was obtained by Mueller et al. for a 9.6 mm thick steel sheet from the same pipeline [9] and was re-plotted in Figure 5.3 for comparison. Both figures are for samples with active reversible traps and saturated irreversible traps [30]. All solutions containing thiosulfate or hydrogen sulfide exhibited a hydrogen permeation transient with several common features: the measured hydrogen flux exhibited an initial value of zero followed by a sharp increase, a maximum, and then a decrease. The initial time transient is related to the time required for hydrogen to diffuse through the sample and saturate the reversible traps (the irreversible traps were prefilled). The decrease in flux is common in environments containing sulfide ions [12, 42, 43] and is related to the formation of iron sulfide on the exposed surface, which blocks hydrogen entry into the steel.

The time lag method [28] was used for calculation of the hydrogen diffusion coefficient, $D_{\text{lag}}$. The time lag, $t_{\text{lag}}$, was determined from the intersection of the extrapolated integrated flux (equal to the amount of permeated hydrogen) with the time axis. $D_{\text{lag}}$ is related to $t_{\text{lag}}$ and the sample thickness, L, by [28]:

$$D = \frac{L^2}{6t_{\text{lag}}} \quad (5.7)$$

$D_{\text{lag}}$ is the actual value of the diffusion coefficient when transport is controlled by Fick’s law [28]. Traps were present and active during the rising transient of the flux of hydrogen. Therefore, the diffusion coefficient determined by this method is an apparent
or phenomenological diffusion coefficient that is dependent on the concentration of diffusible and trapped hydrogen.

Table 5.1 shows values for the $D_{\text{tlag}}$ of hydrogen in X65 pipeline steel immersed in each of the solutions studied. All values were on the order of $10^{-6}$ cm$^2$/s, but it is seen that the biggest divergences were measured for the solution saturated with the H$_2$S/N$_2$ mixture with an H$_2$S partial pressure of 0.029 kPa, 100% H$_2$S environment [9] and $10^{-2}$ M S$_2$O$_3^{2-}$ solution. The environment with $10^{-2}$ M S$_2$O$_3^{2-}$ yielded a permeation curve which was only slightly above the detection limit of the instrument, and therefore has the highest error. On the other hand, the environments saturated with 100% H$_2$S and with an H$_2$S partial pressure of 0.029 kPa exhibited the highest and lowest values of permeation current of Figure 5.3, respectively. Therefore, such divergences could be explained in terms of the differences in time required to fill reversible traps, which affects $t_{\text{tlag}}$ and therefore $D_{\text{tlag}}$. A higher concentration of hydrogen at the charging surface could lead to a faster saturation of reversible traps, leading to the higher $D_{\text{tlag}}$ measured for the solution saturated in H$_2$S [9]. The reverse effect could be the reason behind the lower $D_{\text{tlag}}$ measured in the solution saturated with an H$_2$S partial pressure of 0.029 kPa.

5.3.2. Corrosion Fatigue

Figure 5.5 shows a typical crack length vs. time curve, obtained during corrosion fatigue in the solution saturated with an H$_2$S partial pressure of 0.56 kPa. Each change in slope in this curve corresponds to a change in frequency, and was linearly fitted to obtain the rate of crack growth. Curves for the rest of the solutions studied were similar, with changes in the slope at each frequency. The slope was later divided by the frequency to
obtain the corresponding value of crack growth per cycle, \( \frac{da}{dN} \). Finally, \( \frac{da}{dN} \) was divided by air values calculated with equation 5.6 [39] to obtain the normalized fatigue crack growth rate (FCGR), \( \frac{(da/dN)}{(da/dN)_{air}} \).

A plot of normalized FCGR vs. frequency is presented in Figure 5.6 for the NACE TM0177-96 solution A saturated with different \( \text{H}_2\text{S}/\text{N}_2 \) mixtures and in Figure 5.7 for the thiosulfate containing solutions. Normalized FCGR increased with decreasing frequency, until a plateau was reached at a certain frequency. The normalized FCGR in the two studied thiosulfate containing solutions was close to that measured in the solution saturated with an \( \text{H}_2\text{S} \) partial pressure of 0.56 kPa, which was added to Figure 5.7 for comparison. The regions of increasing crack growth rate, Figure 5.6 and Figure 5.7, were linearly fitted, and the slopes are presented in Table 5.2 for all solutions studied. The normalized FCGR values at the low frequency plateau are also shown in Table 5.2. A plateau value was not evident in the FCGR vs. frequency curve obtained in 100% \( \text{H}_2\text{S} \) with the coated specimen, therefore, the maximum value is reported in the table.

Figure 5.8 shows FCGR obtained for the uncoated specimen immersed in NACE TM0177-96 solution A saturated with 100% \( \text{H}_2\text{S} \), for a specimen from the same pipeline tested in air after a 72 h immersion in this solution [9], and for the same specimen after annealing at 60°C for 4 days [9]. The slopes and plateau values are given in Table 5.2. Even though the sample tested in air had the crack tip region coated with epoxy [9], thereby inhibiting crack tip charging of hydrogen, FCGR values are the highest of this set. This shows that charging of hydrogen from the bulk is sufficient to explain the high crack growth rates measured in sour environments. Unlike the test performed in solution,
neither test in air exhibited a plateau for the range of frequencies studied. Therefore, this shows that the effect of the environment in sour corrosion fatigue is not limited to charging of hydrogen into the steel, but it is more complex, including inhibiting processes such as crack tip blunting or crack closure. The sample containing only trapped hydrogen exhibited the lowest FCGR of this set, but the values are still about an order of magnitude higher than air values [39]. This suggests that trapped hydrogen has an important role in corrosion fatigue.

5.4. Discussion

5.4.1. Hydrogen permeation in thiosulfate solutions

The maximum hydrogen permeation current in thiosulfate containing solutions was measured for the environment containing $10^{-3}$ M of this anion, Figure 5.4. Tsujikawa [4] and Zucchi [6] independently reached the same conclusions. It was shown in chapter 3 that the concentration of $\text{H}_2\text{S}$ at the surface of carbon steel freely corroding in thiosulfate solutions is expected to increase continuously from $10^{-4}$ M $\text{S}_2\text{O}_3^{2-}$ to $10^{-2}$ M $\text{S}_2\text{O}_3^{2-}$. Literature results [12, 13] and Figure 5.3 show that the permeation current increases with the concentration of $\text{H}_2\text{S}$ in the gas, which controls the concentration of $\text{H}_2\text{S}$ in the solution. On the other hand, it was also shown in chapter 3 that the film thickness increases uniformly with the concentration of $\text{S}_2\text{O}_3^{2-}$. Therefore, the maximum in permeation current reported in this work and in the literature is likely due to a competition between $\text{H}_2\text{S}$ concentration and formation of thicker films, which block hydrogen entry. It is interesting that the decay that follows the maximum in permeation
current is faster for the solution containing $10^{-3}$ M $S_2O_3^{2-}$ than for the one containing $10^{-4}$ M $S_2O_3^{2-}$, Figure 5.4. Therefore, after about 4 h the permeation current measured in $10^{-4}$ M $S_2O_3^{2-}$ was higher than in $10^{-3}$ M $S_2O_3^{2-}$. This effect is also expected to be related to the formation of thicker films with increasing thiosulfate concentration.

The permeation current measured in $10^{-3}$ M $S_2O_3^{2-}$ at long exposure times is similar to that measured in the solution saturated with an H$_2$S partial pressure of 0.56 kPa, Figure 5.4. This suggests that the surface concentration of H$_2$S in steel freely corroding in $10^{-3}$ M $S_2O_3^{2-}$ is about equal to the one obtained by bubbling an H$_2$S partial pressure of 0.56 kPa, which was found by the approach discussed in chapter 3. However, the decay in current is faster in the thiosulfate than in the corresponding H$_2$S solution. It was discussed in chapter 3 that films formed faster in thiosulfate than in concentrated hydrogen sulfide solutions. On the other hand, the solution with $10^{-4}$ M $S_2O_3^{2-}$ exhibited a hydrogen permeation transient that was well above that measured in the solution saturated with an H$_2$S partial pressure of 0.029 kPa, which was found previously to have the same H$_2$S concentration, Figure 5.4 and Figure 5.3. In Chapter 3 it was shown that the thickness of film formed at this concentration of thiosulfate could not be resolved with a SEM, suggesting it could be in the sub-micron range. This thin film could be less effective in blocking hydrogen entry than the one formed in the solution saturated with an H$_2$S partial pressure of 0.56 kPa.

5.4.2. Hydrogen diffusion model

Comparison of Figure 5.6, Figure 5.8 and Table 5.2 shows that the FCGR normalized by air increases from 36.9 to 55.0 for a coated vs. a non coated specimen.
exposed to NACE TM0177-96 solution A saturated in H₂S. The amount of hydrogen at
the crack tip region at the end of the 72 h OCP exposure, prior to the beginning of the
corrosion fatigue experiment, was estimated from permeation data using a hydrogen
diffusion model. A computer program based on finite differences was coded in MS Excel
and Mathcad and had two stages. The objective of these programs was to assess the effect
of coating the corrosion fatigue samples on the amount of hydrogen at the crack tip in
100% H₂S solution. The first stage of the program used flux of hydrogen measured for
the solution saturated in H₂S to estimate the concentration of diffusible hydrogen on the
surface of steel. The second stage used the concentration of hydrogen on the surface as
the boundary condition to estimate the concentration profile of hydrogen at the crack tip
region in coated and uncoated specimens.

5.4.2.1. First stage

In the first stage, permeation data [9] for NACE TM0177-96 solution A saturated
in H₂S was used to estimate the evolution of the surface hydrogen concentration on the
charging side of the sample. Hydrogen diffusion was assumed to be uni-dimensional in
the thickness direction of the sample. A similar approach was taken previously [44].
Assuming the diffusion coefficient, D, is independent of concentration, the one-
dimensional Fick’s 2nd law,

\[
\frac{\partial C_H(x, t)}{\partial t} = D \frac{\partial^2 C_H(x, t)}{\partial x^2}
\]

5.8
can be approximated by a finite differences scheme based on the explicit Euler method
[45], after discretization of time and space in intervals of length Δt and Δx, respectively:
where \( t^i = i\Delta t \) and \( x^i = i\Delta x \). Given the concentration profile of hydrogen at time \( t^i \), the concentration at time \( t^{i+1} \) can be calculated by

\[
\frac{C_H(x^i, t^{i+1}) - C_H(x^i, t^i)}{\Delta t} = D \frac{C_H(x^{i+1}, t^i) - 2C_H(x^i, t^i) + C_H(x^{i-1}, t^i)}{(\Delta x)^2}
\]

The right hand side of the equation only has concentrations at time \( t^i \). Since the concentration everywhere at time equal zero is known, the concentration profile at any time and any point can be calculated by stepping forward in time. The stability condition requires that

\[
\frac{D\Delta t}{(\Delta x)^2} < \frac{1}{2}
\]

The surface concentration of hydrogen at the entry side, \( C_H(0, t) \), was assumed to follow [44, 47]

\[
C_H(0, t) = C_1 \exp(-t/\tau) + C_2
\]

where \( \tau \) is a parameter that describes the decay in flux associated with sulfide film growth at the entry surface, and \( C_1 \) and \( C_2 \) are constants. The constant \( C_2 \) was not used by others [44, 47] but a non-zero value was required here to describe the permeation of hydrogen at long times observed experimentally, Figure 5.3. The concentration of hydrogen at the exit side, where the detector was placed, was assumed to be zero for all times and the initial concentration of diffusible hydrogen at time zero everywhere in the sample was also set to zero. With those boundary and initial conditions, a finite difference program was coded in MS Excel. \( D \) was considered to be equal to \( D_{\text{lag}} \), the
apparent diffusion coefficient measured for the solution saturated with 100% H₂S, Table 5.1. The thickness of the sample was discretized in 5 segments. Each segment had a length of about 0.19 mm. Time was discretized in intervals of 5 seconds for t<10 min, 60 seconds for 10 min<t<120 min and 600 seconds for t>120 min. The hydrogen detector measured hydrogen flux at the same time dependent sampling rate. These discretizations in space and time satisfied the stability condition for the value of \( D \) reported in Table 5.1. The flux of hydrogen at the exit side of the sample, \( J_H(x^L,t) \), was calculated by application of Fick’s 1st law and the assumed boundary condition, \( C_H(x^L,t)=0 \):}

\[
J_H(x^L,t) = -D \frac{C_H(x^L,t) - C_H(x^{L-1},t)}{\Delta x} = D \frac{C_H(x^{L-1},t)}{\Delta x}
\tag{5.13}
\]

The calculated flux at the exit surface, \( J_H(x^L,t) \), was compared with the measured flux and the fitting parameters \( C_1, C_2 \) and \( \tau \) of equation 5.12 were manually changed to minimize the error between the measured transient and the calculated transient. This procedure yielded a set of fitting parameters that approximated the time evolution in surface concentration of hydrogen for this particular environment. Figure 5.9, shows the experimental data and the fitted data. The concentration of hydrogen at the entry side was given by equation 5.12 with coefficients as shown in Table 5.3. The error between the fitting line and the experimental data points is highest in the initial transient where the flux increases. This is associated with concentration dependency of the hydrogen diffusion coefficient. Initially, reversible traps are not completely filled, so the diffusion coefficient is the lowest. This low diffusion coefficient results in a larger time lapse between the beginning of the experiment and the time at which hydrogen is detected at the exit of the sample than predicted from the \( D_{\text{lag}} \) used, Figure 5.9. As the traps get
saturated with hydrogen, the diffusion coefficient increases, giving an increasing transient that is steeper than predicted from the model with a single value of $D_{\text{lag}}$, Figure 5.9. Finally, it is expected that at steady state, where all traps are saturated and in equilibrium with the concentration of diffusible hydrogen, permeation of hydrogen is controlled by the lattice diffusion coefficient, $D_{\text{lat}}$ [48]. $D_{\text{lat}}$ was not measured in this work, but can be determined [49] from the initial decay in steady state flux after decreasing the cathodic charging current on the input side of the Devanathan and Stachurski cell [28]. For a sample of X52 pipeline steel oriented in the same direction as in this work, which has a similar metallurgy to the X65 steel used in this work [50], the lattice diffusion coefficient value for hydrogen, $D_{\text{lat}}$, was $7.75 \times 10^{-6}$ cm$^2$/s [51]. Therefore, the value of $D_{\text{lag}}$ used, Table 5.1 is close to the expected value of $D_{\text{lat}}$.

The program was changed to allow a time-dependent diffusion coefficient. For short times, the diffusion coefficient was calculated from the breakthrough time, $t_b$, obtained from the intersection of the extrapolated linear region of the increasing flux with the time axis [52],

$$D_{tb} = \frac{L^2}{2\pi^2 t_b} \tag{5.14}$$

where $L$ is the specimen thickness. For the transient obtained with the solution saturated with H$_2$S, $D_{tb} = 8.23 \times 10^{-8}$ cm$^2$/s. $D_{tb}$ is about two orders of magnitude lower than $D_{\text{lag}}$, therefore, it provides a better fit to the region where traps are being saturated and hydrogen is not detected at the exit surface. For longer times, the diffusion coefficient was considered to be equal to $D_{\text{lat}}$, to provide a better fit to the sharp transient observed once traps are saturated. In other words, the diffusion coefficient was a step function that
changed from $D_{tb}$ to the value of $D_{lat}$ at 4.3 h. Figure 5.9 shows that the calculated curve with time-dependent diffusion coefficient matches the data much better at short times than the curve calculated with a single diffusion coefficient. Fitting parameters for this model with dual diffusion coefficient are given in Table 5.3.

5.4.2.2. Second stage

The second stage of the program requires solving the three dimensional Fick’s law:

$$\frac{\partial C_H(\vec{x},t)}{\partial t} = D \nabla^2 C_H(\vec{x},t) \tag{5.15}$$

where $\vec{x}$ is the position in space, $(x,y,z)$. Application of the explicit Euler Method to equation 5.15 yields [53]:

$$C_H(x^{i},t^{i+1}) = \frac{D \Delta t}{(\Delta x)^2} \left[ C_H(x^{i+1},y^{i},z^{i},t^{i}) + C_H(x^{i-1},y^{i},z^{i},t^{i}) \right. \left. + C_H(x^{i},y^{i+1},z^{i},t^{i}) + C_H(x^{i},y^{i-1},z^{i},t^{i}) + C_H(x^{i},y^{i},z^{i+1},t^{i}) \right. \left. + C_H(x^{i},y^{i},z^{i-1},t^{i}) \right] + \left\{ 1 - 6 \left[ \frac{D \Delta t}{(\Delta x)^2} \right] \right\} C_H(x^{i},y^{i},z^{i},t^{i}) \tag{5.16}$$

Similar to equation 5.10, the right hand side of this equation only has concentrations at time $t^i$, therefore, it can be solved by stepping forward in time. The stability condition [46] in this case requires that

$$\frac{D \Delta t}{(\Delta x)^2} < \frac{1}{6} \tag{5.17}$$

The geometry of the corrosion fatigue compact specimen was approximated by a cuboid, as shown in Figure 5.10. There are two symmetry planes. One is normal to the
notch and is positioned at the mid thickness of the specimen, containing the points with coordinates \( z = B/2 \), and the other one contains the crack plane, Figure 5.10. The flux of hydrogen is zero at those points by symmetry in the concentration profile, which reduces the size of the mesh where equation 5.16 has to be solved. For the coated sample, hydrogen could exclusively be absorbed by notch surfaces. The concentration of hydrogen as a function of time at points in the notch surface is given by equation 5.12, with coefficients as indicated in Table 5.3 for the model with a single diffusion coefficient. The model with dual diffusion coefficient, which provided a better fit to the flux of hydrogen, Figure 5.9, could not be applied here because the time for transition of \( D_{bs} \) to \( D_{lat} \) is expected to be different than the unidimensional case, given the differences in thickness and the fact that transport is not unidimensional. Therefore, the diffusion coefficient used in this part of the model was \( D_{lag} \), which is close to \( D_{lat} \). For the coated sample, hydrogen flux was assumed to be zero at all points in the remaining external surfaces. For the un-coated sample, the concentration of hydrogen at the remaining external surfaces and at the notch was also given by equation 5.12, with the respective coefficients. The initial concentration of hydrogen was assumed to be zero everywhere. A Mathcad program was coded to solve the diffusion equation with these boundary and initial conditions. The output of the program was the concentration of hydrogen as a function of time and position. Figure 5.11 shows the concentration of hydrogen in the crack plane for the un-coated specimens, for two exposure times at OCP in NACE TM0177-96 solution A saturated with 100% H₂S. Figure 5.12 shows the concentration profile at the line contained in the crack plane at mid-thickness for the un-coated (a) and
coated (b) specimens, for several exposure times. The coated specimen exhibited a concentration profile that had a zero derivative in the thickness direction, because the flux of hydrogen along this direction was zero. The concentration of hydrogen at any uncoated surface including the notch is uniform and decreases with time according to equation 5.12. This suggests that there might be a time at which the concentration of hydrogen inside the specimen will be higher than at the surface of the specimen. This was predicted for the uncoated specimen, Figure 5.12a after 14.4 h. Because of the slope of the concentration gradient at this point, application of Fick’s laws predict that hydrogen leaves the specimen. Eventually, hydrogen reaches a nearly constant profile, Figure 5.12a at 72 h and Figure 5.11b, which is near the value of the constant C2 in 5.12, 6.27 x10^-6 mol H/cm^3. The concentration of H inside the specimen for the coated sample increases at a much slower rate, therefore, for those conditions it is predicted that hydrogen will not diffuse out of the specimen.

The main sources of error in this stage of the program are related to the fact that a single value of D independent of concentration was assumed to control the transport of hydrogen at all times. To minimize errors, D was assumed to be equal to Dlag, which lies between Dtb and Dlat.

The boundary condition used at the coated surfaces was zero flux of hydrogen. Holtam [15] measured the concentration profile vs. thickness using gas chromatography in a 15 mm thick plate coated on one side with epoxy and exposed to the solution in the other side. Holtam found that even after 260 h of exposure to a solution of pH 3.5 saturated with 7% H2S in nitrogen, the concentration of hydrogen at the exposed surface
was twice the concentration at the uncoated surface. The reason for the low concentration of hydrogen at the painted surface in [15] could be that hydrogen might have escaped from the painted surface. Considering that the same situation was possible for the coating used in this work, it can be stated that the graph shown in Figure 5.12b constitutes an upper boundary for the concentration of hydrogen. Therefore, it can be conservatively affirmed that the amount of hydrogen at the crack tip is larger for the un-coated than for the coated specimen, even after 72 h of OCP immersion.

5.4.3. Corrosion fatigue

It is difficult to compare FCGRs measured in this work to those reported in literature due to the different experimental parameters such as $\Delta K$, $R$, frequency and environment. However, the crack growth rates measured here are on the same order of magnitude as results obtained in similar conditions. Eadie et al. [14] reported a FCGR of about $1.5 \times 10^{-3}$ mm/cycle at 1 Hz for a carbon steel in NACE TM0177-96 solution A saturated with $H_2S$ at a $\Delta K$ of 19 MPa m$^{1/2}$ and $R=0.3$, which are close to the conditions used here. The value measured in saturated $H_2S$ solutions in this work at 1 Hz was about $1 \times 10^{-3}$ mm/cycle for both the coated and uncoated specimens, in close agreement to the results presented by Eadie. On the other hand, for a dilute brine saturated in 10% CO$_2$ and 1% H$_2$S (1.0 kPa H$_2$S partial pressure), a knockdown factor of 19.7 was measured by Eadie [54] at a frequency of 0.4 Hz, $\Delta K=17.5$ MPa m$^{1/2}$ and $R=0.65$. For a frequency of 0.3 Hz, and in the NACE TM0177-96 solution A saturated with 1.77wt% of H$_2$S (1.5 kPa H$_2$S partial pressure), a knockdown factor of 17.0 was measured in this work, Figure 5.6.
Tests obtained in solutions with H$_2$S/N$_2$ mixtures showed that FCGR increased with the amount of hydrogen sulfide in equilibrium with the solution, Figure 5.6. The decrease in FCGR at low frequency observed for the coated specimen exposed to the solution saturated with 100% H$_2$S could be related to crack closure or crack tip blunting effects, which are expected to be more important at low frequencies [24] and in more aggressive environments.

The FCGR vs. frequency curves obtained in thiosulfate containing solutions were similar to those measured in the solution saturated with an H$_2$S partial pressure of 0.56 kPa, Figure 5.7. Hydrogen permeation results showed that those solutions exhibited a similar flux of hydrogen at steady state, Figure 5.4. This suggests that the mechanism of fatigue crack growth rate in thiosulfate solutions involves hydrogen embrittlement. In chapter 4 it was shown that the corrosion rate in the 10$^{-3}$ M S$_2$O$_3^{2-}$ solution is about 5 times larger than in the 10$^{-4}$ M S$_2$O$_3^{2-}$ solution. The corrosion rate in the solution saturated with an H$_2$S partial pressure of 0.56 kPa was not measured, but it is expected to be even lower than in the 10$^{-4}$ M S$_2$O$_3^{2-}$ solution. This last solution should have a hydrogen evolution rate similar to the one obtained by bubbling the H$_2$S/N$_2$ mixture, otherwise the hydrogen permeation transients would not have been similar. However, in contrast to the solution saturated with an H$_2$S partial pressure of 0.56 kPa, where the only cathodic reaction present at OCP is the hydrogen evolution reaction, in the 10$^{-4}$ M S$_2$O$_3^{2-}$ solution there is also a cathodic reaction that generated H$_2$S, as discussed in previous chapters. It is interesting that, despite the expected differences in corrosion rate between
those 3 solutions, all FCGR were similar. This suggests that the mechanism of FCGR is controlled by hydrogen embrittlement, rather than by crack tip dissolution rate.

Comparison of Table 5.2 and Figure 5.3 reveals a trend of increasing normalized FCGR with increasing hydrogen permeation for all samples obtained in solutions saturated with H₂S or H₂S mixtures. D_{lat} is expected to control transport of hydrogen in the steady state region of the hydrogen permeation transients. The input concentration of hydrogen at steady state, C^{SS}_{H}, can be obtained from Fick’s first law:

\[ C^{SS}_{H} = \frac{J^{SS} L}{D_{lat}} \]  

where L is the thickness of the sample and J^{SS} is the steady state flux, Figure 5.3 and Figure 5.4, and D_{lat} was obtained from [51]. Values of C^{SS}_{H} for all solutions studied are presented in Table 5.4. The C^{SS}_{H} value for the NACE TM0177-96 solution A saturated with N₂ was calculated from data reported by Berkowitz [40] for an AISI 4130 steel, and from [9] for the 100% H₂S solution. C^{SS}_{H} is an environment dependent quantity that controls the amount of hydrogen present in the compact specimen at the end of the 72 h exposure period. Figure 5.13 shows that there is a clear correlation between the low frequency plateau values of the normalized FCGR and the C^{SS}_{H} values. The 10^{-3} M S₂O₃²⁻ solution exhibited a FCGR which was slightly larger than the one measured in 10^{-4} M S₂O₃²⁻ solution, even though the C^{SS}_{H} value was larger for the less concentrated solution, Figure 5.13 and Table 5.4. The maximum in hydrogen permeation was larger for the 10^{-3} M S₂O₃²⁻ solution than for the 10^{-4} M S₂O₃²⁻ solution, Figure 5.4. Therefore, the higher FCGR in the 10^{-3} M S₂O₃²⁻ could correspond to contributions from crack tip hydrogen
charging, enhanced by the film rupture process at the crack tip, or by contributions from anodic dissolution at the crack tip. Anyway, the differences in FCGR between those two thiosulfate solutions and the solution saturated with an H₂S partial pressure of 0.56 kPa are not very large compared to the typical reproducibility of those experiments, [35], and Figure 5.7 shows that there is some overlapping of the curves.

The larger amount of hydrogen at the crack tip in the un-coated vs. coated specimens, Figure 5.12, could be the reason for the differences in FCGR seen for those specimens, Figure 5.6 and Figure 5.8. Results of the hydrogen diffusion model for the un-coated specimen suggest that hydrogen concentration in the center of the specimen reaches a maximum after a few hours and then decreases, Figure 5.12a. A similar time and space evolution of hydrogen concentration was proposed by Tsai et al. [42], Figure 2.4 in Chapter 2, who studied sulfide stress cracking of steel in NACE TM0177-96 solution A saturated with H₂S, the same solution used here. The authors [42] showed that the reduction in area and elongation reached a minimum after 8 h of exposure to OCP in the H₂S saturated solution. After such time, an increase in exposure time resulted in a decrease in the degree of embrittlement. The minimum in ductility was rationalized with the expected decrease in hydrogen content in the specimen after 8 hours. The results of Tsai show that part of the hydrogen absorbed during the initial exposure time left the specimen due to the decrease in the surface concentration of hydrogen by the formation of sulfide films. Brickell et al. [55] also showed that hydrogen can diffuse out of a sample covered by iron sulfides, but at a slower rate than through a bare surface. The hydrogen permeation flux curve shown by Tsai is similar to the one presented here [9]. Kobayashi
[27] and Mishael [44] also presented a hydrogen diffusion model based on finite differences to estimate the maximum concentration of hydrogen reached inside plates of different thickness. Both authors showed that the surface concentration of hydrogen decreased with time due to formation of protective films, leading to a decrease in the concentration of hydrogen at the center of the specimen after certain time. The maximum concentration at the center of the specimens also started to decrease after a certain time in the results obtained here, Figure 5.11 and Figure 5.12a, in accord with results presented for plates in [44] and [27]. Kobayashi used those results [27] to explain a $K_{\text{issc}}$ dependence on thickness of carbon steel exposed to NACE TM0177-96 solution A saturated with $H_2S$. Even though all samples were in the plane strain condition, $K_{\text{issc}}$ increased when the thickness increased. This was related to a decrease in the maximum spatial average concentration of hydrogen as thickness increased. It would be interesting to check whether FCGR shows a higher plateau at lower exposure times, as predicted by Figure 5.11 and Figure 5.12a if a hydrogen embrittlement mechanism is assumed. One complication related to this is that corrosion fatigue tests presented here last usually more than 24 h. The pre-exposure time before cycling loads was selected in this work so that the surface concentration of hydrogen was near steady state during the time required for completion of the experiment.

After finishing the tests, observation of crack fronts revealed that the crack length at the surface was shorter than at the center of the specimens in all cases. The difference between surface and center crack length was always less than 10 %. This situation is common in fracture mechanics tests, because the stress intensity factor is not tri-axial at a
free surface. Another reason behind the curvature in crack length could be related to a lower concentration of hydrogen at the surface, because those surfaces were coated. Assuming a zero flux of hydrogen at the coated surface, the model presented here predicted that the concentration of hydrogen for the coated specimens was not a function of the thickness direction, but if hydrogen could escape through the coating the concentration at the surface would be lower than at the center. An indication that this could be true is that the differences between crack length at the surface and at the center were minimum for the un-coated sample exposed to the 100% H₂S solution. For this solution, such difference was 3% for the un-coated specimen vs. 6% for the coated specimen. In contrast Holtam [15], studying FCGR in a similar environment, reported longer cracks at the surface than at the center of uncoated specimens, but this was not observed for any of the samples tested in this work.

Figure 5.8 shows that the role of hydrogen sulfide in corrosion fatigue is not limited to increased hydrogen embrittlement. If that would be the case, the curve obtained in air after exposure at OCP should have been closer to the one obtained in-situ, or even slightly below it, due to the fact that hydrogen could also be absorbed through the crack tip in the curve collected in-situ and some hydrogen could have been lost in the time elapsed from the instant the sample was removed from the solution and when the experiment was performed. On the other hand, literature results [40] on sulfide stress cracking reported that the same amount of embrittlement as that measured in carbon steel in NACE TM0177-96 solution A saturated with H₂S was obtained in the same solution but deaerated with N₂ and polarized to a cathodic potential. The cathodic potential was
selected so that the N\textsubscript{2} deaerated solution would exhibit the same amount of permeation as the H\textsubscript{2}S solution at OCP \cite{40}. Crack closure is not an issue in tests with monotonic loads, but the fact that the same amount of embrittlement can be obtained with a cathodic potential in sulfide stress cracking suggests that crack tip blunting or anodic contributions to crack growth are minimal in those tests. In contrast, in corrosion fatigue the interaction of the sour environment with the carbon steel must include retarding effects like crack tip blunting or crack closure, for the results in Figure 5.8 to be rationalized.

From Figure 5.8 it can also be deduced that the irreversibly trapped hydrogen and part of the reversibly trapped hydrogen remaining in traps after the annealing heat treatment have a considerable effect on the air-normalized FCGR, about 10X at low frequency. Nakatani et al. \cite{56} also reported a decrease in the endurance curve of a high strength steel after H charging and annealing, where only irreversibly trapped H remained in the sample. The authors \cite{56, 57} proposed that cyclic loading during fatigue can cause release of hydrogen from irreversible traps and subsequent diffusion to the crack tip or high stress region, where it can enhance fracture processes. Enrichment of hydrogen in the crack tip region was proved by the H microprint technique \cite{57}. The FCGR also increased with decreasing frequency, but the effect was more pronounced at values of $\Delta K$ lower than the one used in this work \cite{57}. However, during the annealing heat treatment in this work it is expected that part of the H in reversible traps stayed in those defects \cite{32}, in contrast to the approach adopted by Nakatani where thermal desorption analysis was used to verify that H remained exclusively in irreversible traps. This H in reversible traps could result in the higher influence of trapped H observed in this work. In contrast,
Takai and Watanuki showed that the presence of hydrogen in irreversible traps does not cause embrittlement for monotonic loads [58]. Ductility, yield stress and maximum stress were found to be similar in a sample with irreversibly trapped H and in a sample that was not charged with H at all [58]. It was proposed that cyclic deformation and loads promote the desorption of H from traps [57]. The fundamental mechanism and the driving force for this process is still not clear, considering the high binding energy of H to irreversible trapping sites (about 60 kJ/mol or 0.62 eV) [56]. What is even more intriguing is why it occurs during cyclic loading and not during monotonic loading. Nevertheless, the desorption of H at the crack tip region of a cyclic loaded sample with H in irreversible traps, measured with the H microprint technique [57], and the increase in FCGR of a H charged and annealed specimen shown by Nakatami [57] and here, suggests that the process could be happening fast enough to affect the mechanical properties during cycling loading.

Equation 5.3 predicts a slope of -0.5 for a log-log plot of da/dN vs frequency if corrosion fatigue was controlled by diffusion of hydrogen through the fracture zone. Table 5.2 shows that for solutions containing thiosulfate and saturated with H$_2$S/ N$_2$ mixtures, the high frequency slope is near -0.5. Using the approach detailed by Thodla et al. [16], the frequency at the linear to plateau transition region can be estimated by the frequency for hydrogen to diffuse the length of the plastic zone at the crack tip. The radius of the size of the plastic zone ahead of the crack tip in plane strain, $r_p$, is a function of stress intensity factor and yield strength and can be approximated by [59]
\[ r_p = \frac{1}{6\pi} \left( \frac{K}{\sigma_y} \right)^2 \]  \hspace{1cm} 5.19

For the $K_{\text{max}}$ used here and the minimum yield strength of X65 alloy (65 ksi), $r_p = 0.13$ mm. Using $D_{\text{lat}}$ [51] for the hydrogen diffusion coefficient of hydrogen, the frequency at which hydrogen would diffuse this length in half a cycle is about 0.02 Hz. It is seen in Figure 5.6 and Figure 5.7 that there is a transition from the linear increase region to the plateau region near this frequency. However, Figure 5.8 shows that there is no plateau region for samples tested in air, i.e. the FCGR continues to increase even at lower frequencies. This cannot be explained if diffusion of hydrogen was the controlling mechanism in the entire frequency range. It was discussed in the previous paragraph that crack closure and crack tip blunting are important in causing the plateau in exposed samples, but the reason for the absence of a plateau in the samples tested in air is less obvious. Besides hydrogen diffusion control, fracture in the specimen tested in air could be controlled by partitioning of hydrogen at sites in the microstructure or hydrogen-metal interactions leading to embrittlement at those sites [20]. The reason why the slope departs from -0.5 for the tests performed at 100 % H$_2$S is also not clear.

5.5. Conclusions

- The permeation of hydrogen in $10^{-3}$ M S$_2$O$_3^{2-}$ and $10^{-4}$ M S$_2$O$_3^{2-}$ solutions reached a maximum and then decreased towards steady state. This steady state value was near that measured in the same base solution saturated with an H$_2$S partial pressure of 0.56 kPa.
• Permeation of hydrogen in thiosulfate solutions seems to be controlled by the surface concentration of H\(_2\)S and by the rate of formation of sulfide film.

• Use of concentrations of thiosulfate greater than 10\(^{-3}\) M for simulating H\(_2\)S solutions is not advised for corrosion studies, because the faster rate of film formation results in low hydrogen permeation levels.

• FCGR vs. frequency curves exhibited a linear region at high frequency and a plateau at lower frequencies. FCGR increased as the amount of steady state hydrogen flux measured in hydrogen permeation experiments increased, suggesting a hydrogen embrittlement assisted mechanism.

• FCGR measured in 10\(^{-3}\) M S\(_2\)O\(_3\)^2\(-\) and 10\(^{-4}\) M S\(_2\)O\(_3\)^2\(-\) were similar to the values measured in the same base solution saturated with an H\(_2\)S partial pressure of 0.56 kPa. A coated specimen tested in 100% H\(_2\)S solution exhibited a lower corrosion fatigue crack growth rate than an un-coated specimen. Those results suggest that concentration of hydrogen at the crack tip controls the FCGR.

• The FCGR plateau value seems to be controlled not only by the concentration of hydrogen at the crack tip, but also by other inhibiting effects like crack tip blunting and crack closure, which are expected to be more important at low frequencies and as the aggressiveness of the environment increases.

• Diffusible H and trapped H present in the sample contribute to different extents to the increase in FCGR with decreasing frequency.
5.6. Tables

Table 5.1. Apparent diffusion coefficients calculated with the time lag method, from hydrogen permeation experiments measured in X65 pipeline steel immersed in 0.5 wt% HAc + 5wt% NaCl containing sulfide species as indicated in the table. Data for 100% H$_2$S solution was measured from [9], for a 9.6 mm X65 pipeline steel sample.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$D_{\text{tlag}}$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.029 kPa H$_2$S partial pressure</td>
<td>1.07 x10$^{-6}$</td>
</tr>
<tr>
<td>0.56 kPa H$_2$S partial pressure</td>
<td>2.84 x10$^{-6}$</td>
</tr>
<tr>
<td>1.5 kPa H$_2$S partial pressure</td>
<td>2.61 x10$^{-6}$</td>
</tr>
<tr>
<td>100% H$_2$S [9]</td>
<td>5.56 x10$^{-6}$</td>
</tr>
<tr>
<td>$10^{-4}$ M S$_2$O$_3^{2-}$</td>
<td>2.11 x10$^{-6}$</td>
</tr>
<tr>
<td>$10^{-3}$ M S$_2$O$_3^{2-}$</td>
<td>2.45 x10$^{-6}$</td>
</tr>
<tr>
<td>$10^{-2}$ M S$_2$O$_3^{2-}$</td>
<td>1.49 x10$^{-6}$</td>
</tr>
</tbody>
</table>
Table 5.2. High frequency slope and plateau values, obtained from the graphs of corrosion fatigue knock down factors vs. frequency for each solution, Figure 5.6, Figure 5.7 and Figure 5.8. Coated specimens were painted with epoxy in all faces except the crack and notch faces.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Coated</th>
<th>slope (1/Hz)</th>
<th>(da/dN)/(da/dN)_{air}^{plateau}</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ deaerated</td>
<td>Yes</td>
<td>-0.457</td>
<td>11.3</td>
</tr>
<tr>
<td>0.029 kPa H$_2$S partial pressure</td>
<td>Yes</td>
<td>-0.493</td>
<td>15.2</td>
</tr>
<tr>
<td>0.56 kPa H$_2$S partial pressure</td>
<td>Yes</td>
<td>-0.489</td>
<td>20.0</td>
</tr>
<tr>
<td>1.5 kPa H$_2$S partial pressure</td>
<td>Yes</td>
<td>-0.569</td>
<td>26.6</td>
</tr>
<tr>
<td>100 % H$_2$S</td>
<td>Yes</td>
<td>-0.156</td>
<td>36.9*</td>
</tr>
<tr>
<td>100 % H$_2$S</td>
<td>No</td>
<td>-0.296</td>
<td>55.0</td>
</tr>
<tr>
<td>100 % H$_2$S, in air</td>
<td>No</td>
<td>-0.395</td>
<td>-</td>
</tr>
<tr>
<td>100 % H$_2$S, in air, annealed</td>
<td>No</td>
<td>-0.346</td>
<td>-</td>
</tr>
<tr>
<td>$10^{-4}$ M S$_2$O$_3$ ²⁻</td>
<td>Yes</td>
<td>-0.410</td>
<td>17.6</td>
</tr>
<tr>
<td>$10^{-3}$ M S$_2$O$_3$ ²⁻</td>
<td>Yes</td>
<td>-0.527</td>
<td>22.3</td>
</tr>
</tbody>
</table>

*This curve did not exhibit a plateau FCGR in the low frequency regime, therefore, maximum measured value of the knockdown factor is reported.
Table 5.3. Fitting parameters of the hydrogen flux measured in 100% H$_2$S solution [9], considering a time independent and a time dependent diffusion coefficient, and a concentration of hydrogen given by equation 5.12.

<table>
<thead>
<tr>
<th></th>
<th>D (cm$^2$/s)</th>
<th>$C_1$ (mol H/cm$^3$)</th>
<th>$C_2$ (mol H/cm$^3$)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D≠f(t)</td>
<td>5.56 x 10$^{-6}$</td>
<td>9.34 x 10$^{-6}$</td>
<td>6.27 x 10$^{-6}$</td>
<td>7.7 x 10$^4$</td>
</tr>
<tr>
<td>D(t)</td>
<td>8.23 x 10$^{-8}$, for t&lt;4.3h</td>
<td>7.30 x 10$^{-6}$</td>
<td>4.49 x 10$^{-6}$</td>
<td>7.7 x 10$^4$</td>
</tr>
<tr>
<td></td>
<td>7.75 x 10$^{-6}$, for t&gt;4.3h</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.4. Concentration of hydrogen at steady state at the input side of the sample, $C_H^{SS}$.

<table>
<thead>
<tr>
<th>Solution</th>
<th>$C_H^{SS}$ (mol H/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ [40]</td>
<td>8.02 x 10^{-8}</td>
</tr>
<tr>
<td>0.029 kPa H$_2$S partial pressure</td>
<td>4.00 x 10^{-7}</td>
</tr>
<tr>
<td>0.56 kPa H$_2$S partial pressure</td>
<td>7.40 x 10^{-7}</td>
</tr>
<tr>
<td>1.5 kPa H$_2$S partial pressure</td>
<td>2.00 x 10^{-6}</td>
</tr>
<tr>
<td>100% H$_2$S [9]</td>
<td>4.50 x 10^{-6}</td>
</tr>
<tr>
<td>$10^{-4}$ M S$_2$O$_3^{2-}$</td>
<td>1.03 x 10^{-6}</td>
</tr>
<tr>
<td>$10^{-3}$ M S$_2$O$_3^{2-}$</td>
<td>7.90 x 10^{-7}</td>
</tr>
</tbody>
</table>
Figure 5.1. Dimensions of the compact tension specimen, adapted from [36].

Dimensions are in mm, and numbers in brackets are the dimensions in inches.

Crack length is measured from plane X-X, shown in picture.
Figure 5.2. Transients of the hydrogen flux vs. time obtained in NACE TM0177-96 solution A saturated with an H$_2$S partial pressure of 0.56 kPa in nitrogen. The 1$^{st}$ transient was obtained with a non-charged 3mm thick X65 carbon steel sample, and the second was obtained after polishing to 600 grit and annealing at 50 °C the hydrogen charged sample, in order to remove the diffusible hydrogen. Data shown for the first 20 h.
Figure 5.3. Transients of hydrogen permeation obtained for the X65 pipeline steel sample in NACE TM0177-96 solution A saturated with pure H$_2$S and H$_2$S containing mixtures with partial pressures as indicated in the figure. The sample had a thickness near 3 mm and had irreversible traps saturated with hydrogen in all cases. Data shown for the first 42 h, for all solutions except the one saturated with H$_2$S. Data for the pure H$_2$S solution was adapted from [9], and was obtained with a 9.6 mm thick sample, for about 107 h of OCP exposure.
Figure 5.4. Transients of hydrogen permeation obtained for the X65 pipeline steel sample in NACE TM0177-96 solution A substituted with amounts of thiosulfate as indicated in the figure. The sample had irreversible traps saturated with hydrogen in all cases. The transient obtained in NACE TM0177-96 solution A saturated with an H₂S partial pressure of 0.56 kPa is drawn for comparison. Data shown for the first 72 h, except for the transient obtained in the solution containing 10⁻² M S₂O₃²⁻, where it is 20 h. Sample thickness was near 3 mm in all cases.
Figure 5.5. Corrosion fatigue crack length vs. time during a frequency scan experiment, performed in coated X65 pipeline steel exposed to NACE TM0177-96 solution A saturated with an $\text{H}_2\text{S}$ partial pressure of 0.56 kPa, at a $\Delta K$ of 19.1 MPa-m$^{1/2}$ (17.4 ksi-in$^{1/2}$) and $R$ of 0.13. Each segment was fitted with a straight line to obtain crack length increase vs. time, and the slope was divided by frequency to obtain crack length increase vs. number of cycles.
Figure 5.6. Corrosion fatigue crack growth rates of coated X65 pipeline steel measured in NACE TM0177-96 solution A saturated with \( \text{N}_2 \), \( \text{H}_2\text{S} \) and \( \text{N}_2 + \text{H}_2\text{S} \) mixtures with partial pressure of \( \text{H}_2\text{S} \) as indicated in the legend, at a \( \Delta K \) of 19.1 MPa\( \cdot \text{m}^{1/2} \) (17.4 ksi\( \cdot \text{in}^{1/2} \)) and \( R \) of 0.13. Left scale shows FCGR normalized by values measured in air [39].
Figure 5.7. Corrosion fatigue crack growth rates of coated X65 pipeline steel measured in NACE TM0177-96 solution A with additions of thiosulfate as indicated in the legend, at a $\Delta K$ of 19.1 MPa-m$^{1/2}$ (17.4 ksi-in$^{1/2}$) and $R$ of 0.13. The curve measured in the solution saturated with an H$_2$S partial pressure of 0.56 kPa is shown for comparison purposes. Left scale shows FCGR normalized by values measured in air [39].
Figure 5.8. Corrosion fatigue crack growth rates vs. frequency, at a $\Delta K$ of 19.1 MPa·m$^{1/2}$ (17.4 ksi·in$^{1/2}$) and $R$ of 0.13. Left scale show FCGR normalized by air measured FCGR [39]. Filled squares correspond to FCGR obtained for a X65 pipeline steel immersed in 100 % H$_2$S saturated NACE TM0177-96 solution A. Sample was uncoated, except for the points where it was spot welded. Hollow circles correspond to an air fatigue test, re-drawn from [9], performed after 3 days exposure to the same solution at OCP of an X65 compact tensile specimen extracted from the same pipe, with the crack tip region coated with epoxy. At the end of this fatigue experiment, sample was placed in an oven at 60°C for 4 days and then FCGR vs. frequency were measured, hollow triangles [9].
Figure 5.9. Flux of hydrogen measured at the exit side of a 9.6 mm X65 pipeline steel sample exposed to NACE TM0177-96 solution A saturated H₂S [9]. One of every 5 experimental data points is shown for clarity in the presentation. The black fitting line was obtained considering a single diffusion coefficient, $D_{\text{tag}}$. The grey fitting line was obtained considering a diffusion coefficient given by $D_{\text{bt}}$ for $t<4.3$ h and by $D_{\text{lat}}$ for longer times. Fitting parameters are given in Table 5.3.
Figure 5.10. Geometry used in modeling. a) Schematic of the compact tension specimen, indicating presence of symmetry planes in bold dash and dotted lines. Cuboid used to approximate this geometry for b) coated and c) uncoated specimens. At each symmetry plane the boundary condition was zero flux of hydrogen. The boundary conditions in the rest of the surfaces are indicated.
Figure 5.11. Concentration profiles of hydrogen in the plane containing the crack, obtained with the finite difference program after a) 3.6 h, b) 72 h of OCP exposure in NACE TM0177-96 solution A saturated with H₂S, for the un-coated specimen. Notice the difference in the C_H scale in the two graphs. The concentration profile is shown in half the plane, and it has a symmetry plane that contains the points situated at half thickness, Figure 5.10c. The region of constant concentration of hydrogen in each picture corresponds to the notch.
Figure 5.12. Concentration profile of hydrogen vs. distance, at the line that is contained in the crack plane at the mid-section, obtained with finite difference program, for a) the un-coated and b) coated specimen. Exposure time at OCP in NACE TM0177-96 solution A saturated with H₂S is shown in the figure.
Figure 5.13. Normalized FCGR at the low frequency plateau measured for coated specimens, vs. the surface concentration of hydrogen at steady state for all solutions studied, $C_H^{\text{SS}}$. Pressures are the partial pressures of $\text{H}_2\text{S}$ in the different $\text{H}_2\text{S}/\text{N}_2$ mixtures. The point for the solution saturated in $\text{H}_2\text{S}$ corresponds to the maximum value of the FCGR vs. frequency curve.
5.8. References


56. Nakatani, M. and K. Minoshima, *Influence of activation energy and sensitivity to hydrogen embrittlement on fatigue strength degradation by irreversible hydrogen*


CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1. Conclusions

Previous to this work, the fundamental rationale for the use of thiosulfate solutions to simulate hydrogen sulfide solutions in corrosion studies was limited to thermodynamics prediction and detection of hydrogen sulfide in solution. The key findings of this work that are useful for simulation of hydrogen sulfide with thiosulfate in corrosion studies are:

- $\text{H}_2\text{S}$ is the result of an electrochemical reaction occurring on the corroding carbon steel surface. The reaction requires current from metal corrosion, and represents a big fraction of the corrosion current of carbon steel. The occurrence of this reaction explained the increase in cathodic current with thiosulfate content observed in potentiodynamic polarization curves.

- The kinetics of $\text{H}_2\text{S}$ generation were calculated as a function of thiosulfate content and used to estimate the surface concentration of $\text{H}_2\text{S}$ in the electrode.

- Films formed in carbon steel corroding in acid thiosulfate solutions have the same structure as in hydrogen sulfide solutions. The films are conductive, non-protective and have the ability to block hydrogen absorption.
The studies of kinetics of H$_2$S generation described in chapter 3 predicted the range of partial pressure of H$_2$S in acid solutions that could be simulated with thiosulfate in corrosion of carbon steel studies. The major role of hydrogen sulfide in carbon steel corrosion is to increase hydrogen embrittlement. The maximum in hydrogen permeation reported in the literature and in this work for 10$^{-3}$ M thiosulfate solution was the result of the competition between:

- The rate of film formation, which inhibits hydrogen absorption, that increases with S$_2$O$_3^{2-}$ content.
- The surface concentration of H$_2$S, which is a catalyst for hydrogen absorption, that increases with S$_2$O$_3^{2-}$ content.

Combination of studies on the kinetics of hydrogen sulfide generation and permeation of hydrogen predicted that 10$^{-3}$ M and 10$^{-4}$ M S$_2$O$_3^{2-}$ additions are equivalent to continuous bubbling of an H$_2$S/N$_2$ mixture with an H$_2$S partial pressure of 0.56 kPa, for corrosion fatigue tests. Studies of corrosion fatigue crack growth rate (FCGR) in thiosulfate containing acid brines and in the same solution saturated with an H$_2$S partial pressure of 0.56 kPa in nitrogen confirmed those predictions. On the other hand, the degree of embrittlement in sulfide stress cracking (SSC) of carbon steels in hydrogen sulfide solutions was controlled by the rate of hydrogen permeation [1]. Therefore, results presented in this work predict that NACE TM0177-96 solution A substituted with 10$^{-3}$ M S$_2$O$_3^{2-}$ could simulate NACE TM0177-96 solution A saturated with an H$_2$S partial pressure of 0.56 kPa in SSC studies of carbon steels. The main advantage of this is that handling of H$_2$S cylinders would not be required. The use of caustic traps and H$_2$S
detectors would still be advised, but the vapor over the solution would have a partial pressure of H$_2$S that is much lower than 0.56 kPa. This is related to the fact that H$_2$S is produced at the steel surface, therefore its concentration is maximum exactly where it is needed.

FCGR is controlled by a hydrogen embrittlement mechanism, but the influence of inhibiting effects like crack tip closure and crack tip blunting was important at low frequencies and in aggressive solutions. Comparison of tests in solution vs. tests in air after solution exposure showed that bulk hydrogen charging by itself could explain the high rates of crack propagation observed in saturated H$_2$S solutions.

6.2. Recommendations for future work

This work increased the knowledge on electrochemistry of steel in acid, thiosulfate containing brines and it was shown that thiosulfate solutions have the ability to simulate diluted H$_2$S/N$_2$ mixtures during corrosion fatigue. Nevertheless, several questions remained unsolved during the course of this investigation, and could be topics for future work.

In-situ surface and solution analyses (Raman for example) could yield valuable information. Ex-situ analysis reported in this work revealed that the iron sulfides developed in the surface of steel during corrosion in acidic thiosulfate-containing solutions are the same as those reported for hydrogen sulfide solutions [2-4] or elemental sulfur suspensions [5]. However, it might be argued that there could have been changes in the structure and composition of the film after removing it from the solution, where it came in contact with air. In-situ analysis of the solution near the corroding steel could
reveal whether the estimations of surface concentration of hydrogen sulfide reported here are accurate and could also provide quantitative and qualitative data of intermediate or secondary products of the reduction of thiosulfate to hydrogen sulfide. This information could be used to determine the actual mechanism of transformation of thiosulfate to hydrogen sulfide.

The rate limiting process during corrosion fatigue is not completely clear. The value of the high frequency slope in several solutions suggested that diffusion of hydrogen could be the rate controlling step. This mechanism would predict a plateau at the frequency where hydrogen would have diffused through the entire length of the fracture process zone in half a cycle. However, such plateau was not observed in specimens tested in air after being charged with hydrogen. Corrosion fatigue crack growth rate measurements at different temperatures and frequencies could be useful for estimating the activation energy of the rate limiting step, and identifying the exact mechanism at each frequency range.

Comparison of fatigue crack growth rates performed in situ and in air, where crack tip hydrogen charging was not possible, suggested that bulk hydrogen charging would be enough to explain the rate of fatigue crack growth in solutions saturated with hydrogen sulfide. However, this was not confirmed for less aggressive solutions. The rate of hydrogen charging at the crack tip could be affected by the local pH, potential, concentration of species and the cracking of films during load cycles. Measurements of crack tip electrochemistry in corrosion fatigue and air tests after hydrogen charging in
less aggressive environments could extend the knowledge about the relative importance of crack tip charging vs. bulk hydrogen charging.

The rate of fatigue crack growth that could be obtained with thiosulfate solutions was near that measured in a solution saturated with an H₂S/N₂ mixture with a partial pressure of H₂S equal to 0.56 kPa. This was consistent with the rate of hydrogen permeation measured in these solutions. A possible way of increasing the rate of hydrogen permeation in thiosulfate solutions could be the use of a cathodic potential. Potentiodynamic curves presented in chapter 4 predicted an increase in hydrogen sulfide and hydrogen evolution currents with cathodic potential. The rate of film formation, which is related to corrosion and affects negatively hydrogen absorption, is also expected to decrease. However, a secondary effect of the cathodic potential would be a decrease in crack tip blunting and crack closure, two effects that can affect the value of the plateau at low frequency.

In this work, the thiosulfate containing environment was continuously bubbled with N₂ at a fixed flow rate in all the experiments. In thermodynamics terminology, this corresponds to an open system. This was to help to maintain a slight overpressure in the cell that would compensate the intrinsic minor leaks of the system, minimizing air contamination. It was shown in Chapter 3 that there was a steady state in the hydrogen sulfide concentration in the surface of the steel, in the bulk and in the vapor. Another option could have been to work with a closed system, after an initial N₂ deareation. It is expected that in this situation concentrations of hydrogen sulfide at the steel surface, solution and vapor would increase over time until reaching equilibrium with the
thiosulfate in solution. Equilibrium values in the closed system are expected to be larger than the steady state values in the open system, and probably more concentrated hydrogen sulfide solutions could be simulated. The ratio of volume of solution over exposed area of steel would still have to be large enough so that increase in pH due to steel corrosion would not be an issue. The complication with this approach is that all cells must have improved seals, so that air contamination would not be an issue over the time required for completion of the experiments.

It was discussed in this work that crack closure and crack tip blunting were possible process that retarded fatigue crack growth rate at low frequency. It was not possible to discuss on the relative importance of those effects for the solutions containing hydrogen sulfide or thiosulfate. Crack length was monitored in this work by the direct potential current drop technique, but another possibility could be the compliance technique. Compliance is the inverse of the load vs. displacement slope normalized by elastic modulus and specimen thickness [6]. Crack closure is produced by the opening force produced by premature contact of crack surfaces during the unloading cycles. This opening force can be detected by the point in the unloading cycle where the load vs. displacement curve departs from linearity, and the effective stress intensity factor range could be calculated, $\Delta K_{\text{eff}}$. The crack closure effect contribution of the environment could be subtracted from the $da/dN$ vs. frequency plot by normalizing the crack growth rate by the $da/dN$ value in air at $\Delta K_{\text{eff}}$. 
6.3. References


235


236


55. Hornlund, E., et al., *Hydrogen diffusivities and concentrations in 520M carbon steel under cathodic protection in 0.5M NaCl and the effect of added sulphite,*


