CORROSION EVALUATION FOR ABSORPTION – BASED CO₂ CAPTURE PROCESS USING SINGLE AND BLENDED AMINES

A Thesis

Submitted to the Faculty of Graduate Studies and Research

In Partial Fulfillment of the Requirements

For the Degree of

Master of Applied Science

In Process Systems Engineering

University of Regina

By

Prakashpathi Gunasekaran

Regina, Saskatchewan

September, 2012

Copyright 2012: Prakashpathi Gunasekaran
Prakashpathi Gunasekaran, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *Corrosion Evaluation for Absorption - Based CO2 Capture Process Using Single and Blended Amines*, in an oral examination held on September 11, 2012. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

External Examiner:  Dr. Farshid Torabi, Petroleum Systems Engineering

Supervisor:         Dr. Amornvadee Veawab, Environmental Systems Engineering

Committee Member:  Dr. Sahid Azam, Environmental Systems Engineering

Committee Member:  Dr. Adisorn Aroonwilas, Industrial Systems Engineering

Chair of Defense:  Dr. Doug Durst, Faculty of Social Work
ABSTRACT

One of the major problems associated with the amine-based carbon dioxide (CO₂) capture process is corrosion of process components, which results in unexpected downtime, production loss, and even major fatalities. Most of the published corrosion literature is on conventional monoethanolamine (MEA) solvent, and there have been very few corrosion studies conducted on other single amines like methyldiethanolamine (MDEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP), and some blended amines. Although there has been extensive research conducted on the kinetics of concentrated piperazine (PZ) as an attractive solvent for the CO₂ absorption process, no corrosion studies have been conducted for this solvent.

This work investigated the corrosion of construction materials including carbon steel (CS1018) and stainless steels (SS304 and SS316) in the CO₂ capture process, using various types of CO₂ absorption solvents. The tested solvents included MEA, DEA, MDEA, AMP, PZ, and their blends. A series of laboratory corrosion tests was carried out using electrochemical techniques (DC-cyclic potentiodynamic polarization and AC-impedance measurement) and weight loss technique to establish an engineering corrosion database for the CO₂ capture process. Experimental conditions were chosen to be CO₂ saturation and 80°C for most experiments. The electrochemical results show that the corrosivity order of CS1018 for the single amine systems was MEA > AMP > DEA > PZ > MDEA. The corrosion rates in MEA and AMP systems were almost double those of the PZ and MDEA systems. The passivation of carbon steel in the DEA system was more compact and less porous than those in the MDEA, PZ, MEA, and AMP systems. The
corrosive effects of process contaminants, i.e., thiosulfate, oxalate, sulfite, and chloride, on corrosion rate were observed in all amine systems. The presence of thiosulfate reduced the corrosion rate of carbon steel in the MEA system, whereas the presence of oxalate increased the corrosion rate in all tested single amines. Two corrosivity behaviours were found in the presence of sulfite and chloride. In the presence of sulfite, the corrosion rate of carbon steel was increased in the MEA, DEA, MDEA, and PZ systems, but decreased in the AMP system. In the presence of chloride, the corrosion rate increased only in the MDEA system, but decreased in the MEA, DEA, AMP, and PZ systems. In addition to single amines, five different blended amines were also tested for their corrosiveness. The results show that the corrosivity trend of CS1018 in blended amine systems was MEA-PZ ≥ MEA-AMP ≥ MEA-MDEA > MDEA-PZ > AMP-PZ. The stainless steel materials (SS316 and/or SS304) offered great resistance to corrosion in all amine systems. For example, the corrosion rates were very low, in the range of 0.006 - 0.036 mmpy, which is well below the standard acceptable corrosion rate (0.07 mmpy). Conductivity of the solution was found to correlate well with corrosion rate in both single and blended amine systems. The weight loss results show that after 28 days, the corrosivity order of CS1018 in single amine systems was MEA > DEA > PZ > AMP ≈ MDEA. The corrosion products deposited over carbon steel were found to be iron carbonate (FeCO₃) and iron oxide (Fe₃O₄).
ACKNOWLEDGEMENTS

I wish to express my heartfelt gratitude to my supervisor Dr. Amornvadee Veawab, whose constant guidance, support, and suggestions have encouraged and motivated me to successfully complete my research work. She has always fostered a positive research environment throughout my research work and provided me the freedom to take up new problems and steered me in the proper direction. I would also like to thank Dr. Adisorn Aroonwilas for his help in setting up my experiments and for his valuable suggestions for my research work. Financial support from the Faculty of Graduate Studies and Research at the University of Regina and Natural Sciences and Engineering Research Council (NSERC) is also gratefully acknowledged.

I would like to express my deepest gratitude to my dad and mom, Mr. Gunasekaran and Mrs. Amutha for their love, encouragement, and their understanding. They have been my role models, my mentors, and have given me everything in my life. I take this opportunity to thank my dearest brother Baskaran for encouraging me, believing in me, and being my moral support in all of my endeavours. I would like to extend special thanks to my best buddies Suresh, Ameer, Neelu, Ezhiyil, Rengarajan, Balaji, Karthi, Ranga, Krishna, Nambi and my colleagues for their constant support and interest in my research work.

Finally, I wish to extend my sincere gratitude to my dearest friend, Hariprakash, for making me what I am today.
# TABLE OF CONTENTS

Abstract

Acknowledgement

Table of Contents

List of Tables

List of Figures

Nomenclature

## 1. INTRODUCTION

1.1 CO₂ Absorption process

1.2 Absorption solvents

1.3 Corrosion problems

1.4 Research motivation, objectives and scope

## 2. LITERATURE REVIEW AND FUNDAMENTALS

2.1 Amine-CO₂ absorption mechanism

2.2 Principles of Corrosion

2.2.1 Corrosion of materials

2.2.2 Electrode potential

2.2.3 Exchange current density

2.2.4 Polarization

2.2.4.1 Polarization characteristics

2.2.5 Mixed potential theory
2.2.6 Potentiodynamic anodic polarization 31
2.2.7 Pourbaix diagram 33
2.2.8 Electrochemical Impedance Spectroscopy 37
  2.2.8.1 Principles of EIS technique 37
  2.2.8.2 Impedance analysis 38
  2.2.8.3 Constant phase element model 43
2.3 Theoretical methods for corrosion inhibitor studies 44
  2.3.1 Quantitative Structure Activity Relation (QSAR) 44
  2.2.2 Hard and Soft Acid and Base Theory (HSAB) 46

3 CORROSION EXPERIMENTS

3.1 Electrochemical experiments 48
  3.1.1 Solution preparation 48
  3.1.2 Specimen preparation 49
  3.1.3 Experimental setup 51
  3.1.4 Experimental procedure 55
  3.1.5 Validation of experimental setup and procedure 56
  3.1.6 Data analysis 56
3.2 Weight loss experiments 62
  3.2.1 Specimen and solution preparation 62
  3.2.2 Experimental setup 62
  3.2.3 Experimental procedure 65
  3.2.4 Specimen cleaning procedure 65
  3.2.5 Data analysis 68
3.3 Surface analysis

4 RESULTS AND DISCUSSION

4.1 General corrosion behaviour of CS1018 in aqueous amine-CO₂ environments
   4.1.1 Effect of solution temperature
   4.1.2 Effect of CO₂ loading of solution

4.2 Comparative corrosiveness of single amines
   4.2.1 Non contaminated amines
     4.2.1.1 Reasons for comparative corrosiveness
     4.2.1.2 Passive film analysis
   4.2.2 Contaminated amines
     4.2.2.1 Effect of thiosulfate
     4.2.2.2 Effect of oxalate
     4.2.2.3 Effect of sulfite
     4.2.2.4 Effect of chloride

4.3 Comparative corrosiveness of blended amines

4.4 Corrosion correlation

4.5 Corrosion resistance of stainless steel

4.6 Weight loss experiments
   4.6.1 Surface analysis
   4.6.2 Amine degradation during experiment

5 CONCLUSIONS AND FUTURE WORK

5.1 Conclusion
5.2 Recommendations for future work 189

REFERENCES 191
LIST OF TABLES

Table 1.1 Molecular structures of amines used in gas treating 5
Table 1.2 Merits and demerits of various amine absorption solvents 6
Table 1.3 Summary of plant experiences on corrosion in acid gas treating plants 8
Table 1.4 Literature reference for laboratory corrosion studies in amine-based absorption process 14
Table 1.5 Literature information on corrosion studies in amine-based absorption process 15
Table 3.1 Summary of the chemical reagents used in the experiments 50
Table 3.2 Chemical compositions of the tested specimens 53
Table 4.1 Tested parameters and conditions for corrosion experiments 70
Table 4.2 Summary of pH, conductivity, and electrochemical parameters for different amine systems 72
Table 4.3 Equivalent circuit element values that best fitted with the impedance data for carbon steel corrosion in MEA system at different temperature 77
Table 4.4 Impedance fitted parameters for various amines at CO₂ saturation and 80°C 90
Table 4.5 Quantum chemical indices obtained using PM6 computation 95
Table 4.6 Calculated parameters from quantum calculation results 98
Table 4.7 Summary of pH, conductivity, and electrochemical parameters 116
for CS1018 in different amine systems in presence of 10,000 ppm process contaminants

Table 4.8  Summary of pH, conductivity, and electrochemical parameters for CS1018 in blended amine systems

Table 4.9  Summary of pH, conductivity, and electrochemical parameters for SS304 and SS316 in different amine systems
LIST OF FIGURES

Figure 1.1 Process flow diagram of the amine-based CO₂ capture unit for coal fired power plant flue gases 3

Figure 2.1 Electrochemical reactions occurring during the corrosion of iron in de-aerated acid solution 26

Figure 2.2 Polarization characteristics (a) Activation polarization showing Tafel behaviour (b) Cathodic concentration polarization showing limiting current density and (c) Combined polarization 29

Figure 2.3 Polarization of two half cell reactions for zinc in acid solution 32

Figure 2.4 Anodic polarization curve showing active-passive behaviour 34

Figure 2.5 Pourbaix diagram for Fe-H₂O system at 25°C 36

Figure 2.6 Equivalent circuit model for an electrical double layer 40

Figure 2.7 Nyquist plot corresponding to equivalent circuit 40

Figure 2.8 Nyquist plot and equivalent circuit model with diffusion component circuit 42

Figure 2.9 Bode plots 42

Figure 3.1 A sketch of specimen used for electrochemical corrosion experiment 52

Figure 3.2 Electrochemical corrosion setup (a) A schematic diagram and (b) A photograph 54

Figure 3.3 Validation of potentiodynamic polarization experiments using ASTM G5-94 (2004) standards 57
Figure 3.4  Validation of impedance experiments using ASTM G106-89 (2010) 58
(a) Nyquist plot (b) Bode plot- Phase angle vs Frequency
(c) Bode plot- Impedance magnitude vs Frequency

Figure 3.5  Tafel extrapolation method 59

Figure 3.6  Cyclic potentiodynamic polarization curves (a) No pitting (b) pitting 61

Figure 3.7  A sketch of the weight loss specimen 63

Figure 3.8  Weight loss setup (a) A schematic diagram and (b) A photograph 64

Figure 3.9  Mass loss of corroded specimens resulting from repetitive cleaning cycles 67

Figure 4.1  Effect of temperature (a) polarization behaviour and (b) corrosion rate of CS1018 in 5.0 kmol/m$^3$ MEA at 0.20 mol CO$_2$/mol amine loading 71

Figure 4.2  Effect of temperature on (a) Nyquist plot and (b) Bode-phase angle plot for CS1018 in 5.0 kmol/m$^3$ MEA at 0.20 mol CO$_2$/mol amine loading 74

Figure 4.3  Equivalent circuit model for fitting impedance results obtained for CS1018 tested in 5.0 kmol/m$^3$ MEA solution at 0.20 mol CO$_2$/mol amine loading condition 76

Figure 4.4  Nyquist plot for CS1018 in 5.0 kmol/m$^3$ MEA solution at 0.20 mol CO$_2$/mol amine loading condition at 80°C drawn from experimental and fitted data 76

Figure 4.5  Arrhenius plot (log C.R Vs 1/T) 80

Figure 4.6  Effect of CO$_2$ loading on polarization behaviour of CS1018 in 81
5.0 kmol/m$^3$ MEA solution (a) 40°C and (b) 80°C

**Figure 4.7** Effect of CO$_2$ loading on impedance behaviour of CS1018 in 5.0 kmol/m$^3$ MEA solution (a) 40°C and (b) 80°C

**Figure 4.8** Corrosion behaviour of CS1018 in single amine systems at 80°C and CO$_2$ saturation (5.0 kmol/m$^3$ of MEA, DEA, MDEA, and PZ; 4.0 kmol/m$^3$ of AMP) (a) polarization behaviour and (b) corrosion rate

**Figure 4.9** Cyclic polarization curves of CS1018 in 5.0 kmol/m$^3$ amine solutions at CO$_2$ saturation and 80°C (a) DEA and (b) PZ

**Figure 4.10** SEM images of CS1018 (a) fresh specimen before test (b) corroded specimen in DEA system and (c) corroded specimen in PZ system (highlighted area indicating pits)

**Figure 4.11** Impedance behaviour of CS1018 in single amine systems at 80°C and CO$_2$ saturation (5.0 kmol/m$^3$ of MEA, DEA, MDEA and PZ; 4.0 kmol/m$^3$ of AMP) (a) Nyquist plot and (b) Charge transfer resistance (R$_{ct}$)

**Figure 4.12** Equivalent circuit model for the dissolution of CS1018 in amine solution

**Figure 4.13** Nyquist plot for CS1018 in 5.0 kmol/m$^3$ MEA solution at CO$_2$ saturation and 80°C drawn from experimental and fitted impedance data

**Figure 4.14** Effect of solution pH on corrosion rate of CS1018 in various amine systems at CO$_2$ saturation & 80°C (5.0 kmol/m$^3$ of MEA, DEA,
MDEA and PZ; 4.0 kmol/m$^3$ of AMP)

Figure 4.15  Corrosion behaviour of CS1018 in 5.0 kmol/m$^3$ PZ solution at various CO$_2$ loadings and 80°C (a) polarization behaviours (b) Nyquist plot and (c) Bode-phase plot

Figure 4.16  Active-passive polarization behaviour of CS1018 in various aqueous amine-CO$_2$ systems at CO$_2$ saturation and 80°C

Figure 4.17  Pourbaix diagram for carbon steel in various amine systems at CO$_2$ saturation and 80°C (a) MEA-CO$_2$-H$_2$O (b) DEA-CO$_2$-H$_2$O (c) PZ-CO$_2$-H$_2$O and (d) MDEA-CO$_2$-H$_2$O at CO$_2$ saturation and 80°C (created from OLI corrosion analyzer)

Figure 4.18  Nyquist plot for CS1018 in secondary passive region in 4.0 kmol/m$^3$ AMP solution at CO$_2$ saturation & 80°C showing capacitive loop followed by Warburg impedance

Figure 4.19  Nyquist plot for CS1018 in secondary passive region for all amine systems at CO$_2$ saturation & 80°C (5.0 kmol/m$^3$ of MEA, DEA, MDEA and PZ; 4.0 kmol/m$^3$ of AMP)

Figure 4.20  Equivalent circuit model for the dissolution of carbon steel at the passive zone

Figure 4.21  Nyquist plot for CS1018 in DEA system at passive zone with fitted impedance data

Figure 4.22  Randle’s plot corresponding to the Nyquist plots obtained at passive region for all amine systems

Figure 4.23  Warburg coefficient ($\sigma_w$) for CS1018 at passive region for all
amine systems

Figure 4.24 SEM images of CS1018 obtained at the passive region in various amines at CO$_2$ saturation and 80°C (a) DEA (b) MDEA (c) PZ (d) MEA and (e) AMP

Figure 4.25 Corrosion behaviour of CS1018 in 5.0 kmol/m$^3$ MEA solution at CO$_2$ saturation and 80°C with and without 10,000 ppm sodium thiosulfate (a) polarization behaviours (b) Nyquist plots and (c) Bode-phase plots

Figure 4.26 Effect of 10,000 ppm oxalate on (a) polarization behaviour and (b) corrosion rate of CS1018 in various amines

Figure 4.27 Localized corrosion behaviour of CS1018 in aqueous PZ-CO$_2$ system in presence of 10,000 ppm oxalate

Figure 4.28 Polarization behaviour of CS1018 in various amines with and without 10,000 ppm oxalate (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA

Figure 4.29 Effect of 10,000 ppm oxalate on (a) Nyquist plots and (b) charge transfer resistance of CS1018 in various amines

Figure 4.30 Impedance behaviour of CS1018 in various amines with and without 10,000 ppm oxalate (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA

Figure 4.31 Effect of 10,000 ppm sodium sulfite on (a) polarization behaviour and (b) corrosion rate of CS1018 in various amines

Figure 4.32 Polarization behaviour of CS1018 in various amines with and
without 10,000 ppm sulfite (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA

Figure 4.33  Localized corrosion behaviour of CS1018 in aqueous amine-CO\textsubscript{2} systems in presence of 10,000 ppm sulfite (a) MEA (b) AMP (c) DEA and (d) PZ

Figure 4.34  SEM image of corroded specimen in 5.0 kmol/m\textsuperscript{3} MEA solution at CO\textsubscript{2} saturation & 80°C in presence of 10,000 ppm sulfite, showing crater like pits at different magnification (a) 1000 X and (b) 1500 X

Figure 4.35  The photographic image of CS1018 in MEA-CO\textsubscript{2}-H\textsubscript{2}O system with 10,000 ppm sodium sulfite, showing the (a) presence of black coloured layer at the initial stages of experiment (b) presence of rusty surface on anodic polarization during the experiment

Figure 4.36  Photographic image of tested specimens in AMP-CO\textsubscript{2}-H\textsubscript{2}O and DEA-CO\textsubscript{2}-H\textsubscript{2}O system with 10,000 ppm Na\textsubscript{2}SO\textsubscript{3} taken after the experiment, showing the presence of adsorbed black layer

Figure 4.37  Surface analysis of corroded specimen in AMP-CO\textsubscript{2}-H\textsubscript{2}O system with 10,000 ppm Na\textsubscript{2}SO\textsubscript{3} (a) SEM image and (b) EDS analysis (with elements wt %)

Figure 4.38  Effect of 10,000 ppm sulfite on (a) Nyquist plots and (b) Charge transfer resistance of CS1018 in various amines

Figure 4.39  Impedance behaviour of CS1018 in various amines with and without 10,000 ppm sulfite (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA
Figure 4.40  Effect of 10,000 ppm chloride on (a) polarization behaviour and (b) corrosion rate of CS1018 in various amines

Figure 4.41  Polarization behaviour of CS1018 in various amines with and without 10,000 ppm chloride (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA

Figure 4.42  Effect of 10,000 ppm chloride on (a) Nyquist plots and (b) charge transfer resistance of CS1018 in various amines

Figure 4.43  Impedance behaviour of CS1018 in various amines with and without 10,000 ppm chloride (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA

Figure 4.44  Localized corrosion behaviour of CS1018 in aqueous amine-CO$_2$ systems in presence of 10,000 ppm chloride (a) DEA and (b) PZ

Figure 4.45  Pitting corrosion of CS1018 specimen in aqueous DEA-CO$_2$ system in presence of 10,000 ppm NaCl (a) photographic image showing scattered pits during experiment (b) SEM image showing scattered pits (100 X magnification) and (c) SEM image showing pit depth (1000 X magnification)

Figure 4.46  Polarization behaviour of CS1018 in blended amine systems under 5.0 kmol/m$^3$ (1:1 molar ratio) concentration at CO$_2$ saturation & 40°C (a) polarization curves and (b) corrosion rate

Figure 4.47  Impedance behaviour of CS1018 in blended amine systems under 5.0 kmol/m$^3$ (1:1 molar ratio) concentration at CO$_2$ saturation & 40°C (a) Nyquist plots and (b) charge transfer resistance
Figure 4.48  Polarization behaviour of CS1018 in blended amine systems under 146
5.0 kmol/m$^3$ (1:1 molar ratio) concentration at CO$_2$ saturation & 
80°C (a) polarization curves and (b) corrosion rate

Figure 4.49  Localized corrosion behaviour of CS1018 in blended amine 
147
systems under 5.0 kmol/m$^3$ (1:1 molar ratio) concentration at CO$_2$
saturation & 80°C (a) MEA-PZ and (b) MEA-MDEA blends

Figure 4.50  Impedance behaviour of CS1018 in blended amine systems under 
148
5.0 kmol/m$^3$ (1:1 molar ratio) concentration at CO$_2$ saturation & 
80°C (a) Nyquist plots and (b) charge transfer resistance

Figure 4.51  Polarization behaviour of CS1018 in blended amine systems and 
150
their precursors under CO$_2$ saturation and at 80°C (a) MEA-PZ (b) 
MEA-AMP (c) MEA-MDEA (d) MDEA-PZ and (e) AMP-PZ

Figure 4.52  Corrosion comparison between the precursors and the blended 
151
amine (a) corrosion rate and (b) charge transfer resistance

Figure 4.53  Correlation plot for corrosion rate of CS1018 with properties of 
155
amine solution in all tested amine systems including single and 
blended amines (a) pH (b) Conductivity (c) CO$_2$ loading (mol CO$_2$/ 
/mol amine) without PZ data (d) CO$_2$ loading (mol CO$_2$/mol amine) 
with PZ data and (e) CO$_2$ loading (mol CO$_2$/mol alkalinity) 
with all corrosion data

Figure 4.54  Corrosion behaviour of CS1018, SS304 and SS316 in 5.0 kmol/m$^3$ 
157
MEA solution at CO$_2$ saturation & 80°C (a) polarization behaviours 
(b) Nyquist plot
Figure 4.55  Corrosion behaviour of SS304 in various amines at CO$_2$ saturation and 80°C (5.0 kmol/m$^3$ of MEA, DEA, MDEA & PZ; and 4.0 kmol/m$^3$ of AMP) polarization behaviours and (b) Nyquist plot.

Figure 4.56  Corrosion behaviour of SS304 in various amines at CO$_2$ saturation and 80°C in presence of 10,000 ppm NaCl (5.0 kmol/m$^3$ of MEA, DEA, MDEA & PZ; and 4.0 kmol/m$^3$ of AMP) (a) polarization behaviours and (b) Nyquist plot.

Figure 4.57  Polarization behaviour of SS304 in various amines with and without 10,000 ppm NaCl (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA.

Figure 4.58  Comparison of weight loss corrosion rate of CS1018 in all amines at CO$_2$ saturation and 80°C (MEA, DEA, AMP, MDEA - 5.0 kmol/m$^3$ and AMP - 4.0 kmol/m$^3$).

Figure 4.59  Photographic image of (a) fresh specimen, and tested specimens withdrawn after 28 days (b) MEA (c) DEA (d) PZ (e) AMP and (f) MDEA.

Figure 4.60  Fresh CS1018 specimen (a) SEM image (Magnification – 500 X) and (b) EDS analysis with Wt% of the element.

Figure 4.61  Surface analysis of the CS1018 specimen tested in 5.0 kmol/m$^3$ MEA solution at CO$_2$ saturation and 80°C, removed after 28 days (a) XRD spectra (b) SEM image (Magnification - 1000X) and (c) EDS analysis.

Figure 4.62  Surface analysis of the CS1018 specimen tested in 5.0 kmol/m$^3$
DEA solution at CO$_2$ saturation and 80°C, removed after 28 days
(a) XRD spectra (b) SEM image (Magnification - 1000X) and
(c) EDS analysis

Figure 4.63 Surface analysis of the CS1018 specimen tested in 5.0 kmol/m$^3$ PZ solution at CO$_2$ saturation and 80°C, removed after 28 days
(a) XRD spectra (b) SEM image (Magnification - 1000X) and
(c) EDS analysis

Figure 4.64 Surface analysis of the CS1018 specimen tested in 4.0 kmol/m$^3$ AMP solution at CO$_2$ saturation and 80°C, removed after 28 days
(a) XRD spectra (b) SEM image (Magnification - 1000X) and
(c) EDS analysis

Figure 4.65 Surface analysis of the CS1018 specimen tested in 5.0 kmol/m$^3$ MDEA solution at CO$_2$ saturation and 80°C, removed after 28 days (a) XRD spectra (b) SEM image (Magnification – 1000X) and (c) EDS analysis

Figure 4.66 SEM image of CS1018 (after chemical cleaning) tested in DEA system showing localized corrosion behaviour (a) 250 X (b) 500 X

Figure 4.67 Microscopic image (Magnification – 50 X) of corrosion products over CS1018 surface immersed in 5.0 kmol/m$^3$ PZ at CO$_2$ saturation and 80°C (a) after 7 days (b) after 14 days

Figure 4.68 Photographic image of corroded specimen (before chemical cleaning) in AMP system taken after 28 days (a) undisturbed
passive layer and (b) specimen with peeled off passive layer

Figure 4.69 Photographic image of SS304 (left) and CS1018 (right) specimen tested with MEA system (a) Before immersion and (b) After 28 days

Figure 4.70 Fresh SS304 specimen (a) SEM image (Magnification – 500 X) and (b) EDS analysis

Figure 4.71 Surface analysis of SS304 surface immersed in 5.0 kmol/m$^3$ MEA at CO$_2$ saturation and 80°C, after 28 days (a) SEM image (Magnification - 500X) and (b) EDS analysis

Figure 4.72 Weight loss solution of MEA system tested with SS304 (left corrosion cell) and CS1018 (right corrosion cell) (a) Day 1 and (b) Day 28

Figure 4.73 Weight loss solution of DEA system (a) Day 1 (b) Day 28

Figure 4.74 Weight loss solution of PZ system (a) Day 1 (b) Day 28

Figure 4.75 Weight loss solution of AMP system (a) Day 1 (b) Day 28

Figure 4.76 Weight loss solution of MDEA system (a) Day 1 (b) Day 28
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Electron affinity (eV)</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AMP</td>
<td>2-Amino-2-methyl-1-propanol</td>
</tr>
<tr>
<td>(a_{\text{oxid}})</td>
<td>Activity of oxidized species</td>
</tr>
<tr>
<td>(a_{\text{red}})</td>
<td>Activity of reduced species</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance (farad)</td>
</tr>
<tr>
<td>(C_{\text{dl}})</td>
<td>Double layer capacitance ((\mu\text{F/cm}^2))</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant phase element</td>
</tr>
<tr>
<td>CR</td>
<td>Corrosion rate</td>
</tr>
<tr>
<td>CS</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>(^0\text{C})</td>
<td>Degree Centigrade</td>
</tr>
<tr>
<td>D</td>
<td>Density (g/cm(^3))</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
</tr>
<tr>
<td>E</td>
<td>Electrode potential (V)</td>
</tr>
<tr>
<td>(E_0)</td>
<td>Standard electrode potential (V)</td>
</tr>
<tr>
<td>(E_a)</td>
<td>Activation energy (J/mol)</td>
</tr>
<tr>
<td>(E_b)</td>
<td>Breakdown potential or pitting potential (V)</td>
</tr>
<tr>
<td>(E_{\text{corr}})</td>
<td>Corrosion potential (V)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>$E_{\text{HOMO}}$</td>
<td>Highest occupied molecular orbital energy (eV)</td>
</tr>
<tr>
<td>$E_{\text{LUMO}}$</td>
<td>Lowest unoccupied molecular orbital energy (eV)</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>$E_{\text{pp}}$</td>
<td>Primary passivation potential (V)</td>
</tr>
<tr>
<td>$E_{\text{rev}}$</td>
<td>Equilibrium potential (or Reversible potential) (V)</td>
</tr>
<tr>
<td>$E_{\text{rp}}$</td>
<td>Repassivation potential (V)</td>
</tr>
<tr>
<td>EW</td>
<td>Equivalent weight (g/equivalent)</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>Energy gap (eV)</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant (96,500 coulombs per equivalent)</td>
</tr>
<tr>
<td>f</td>
<td>Frequency (Hz)</td>
</tr>
<tr>
<td>HSAB</td>
<td>Hard and Soft Acid and Base</td>
</tr>
<tr>
<td>HSS</td>
<td>Heat stable salts</td>
</tr>
<tr>
<td>I</td>
<td>Ionization potential (eV)</td>
</tr>
<tr>
<td>$i_0$</td>
<td>Equilibrium exchange current density ($\text{A/cm}^2$)</td>
</tr>
<tr>
<td>$i_a$</td>
<td>Anodic current density ($\text{A/cm}^2$)</td>
</tr>
<tr>
<td>$i_c$</td>
<td>Cathodic current density ($\text{A/cm}^2$)</td>
</tr>
<tr>
<td>$i_{\text{corr}}$</td>
<td>Corrosion current density ($\text{A/cm}^2$)</td>
</tr>
<tr>
<td>$i_{\text{crit}}$</td>
<td>Critical current density ($\text{A/cm}^2$)</td>
</tr>
<tr>
<td>$i_L$</td>
<td>Limiting current density ($\text{A/cm}^2$)</td>
</tr>
<tr>
<td>$i_{\text{pass}}$</td>
<td>Passivation current density ($\text{A/cm}^2$)</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
</tr>
<tr>
<td>$K_c$</td>
<td>Carbamate stability constant (m$^3$/kmol)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>MDEA</td>
<td>Methyl diethanolamine</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>mmpy</td>
<td>Millimetre per year</td>
</tr>
<tr>
<td>mpy</td>
<td>Mils per year</td>
</tr>
<tr>
<td>n</td>
<td>Phase shift</td>
</tr>
<tr>
<td>n_e</td>
<td>Number of equivalents exchanged</td>
</tr>
<tr>
<td>ΔN</td>
<td>Number of electron transferred</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>PAR</td>
<td>Princeton Applied Research</td>
</tr>
<tr>
<td>PM6</td>
<td>Parameterized model number 6</td>
</tr>
<tr>
<td>PZ</td>
<td>Piperazine</td>
</tr>
<tr>
<td>Q_{al}</td>
<td>Adsorbed layer capacitance (μF/cm²)</td>
</tr>
<tr>
<td>Q_{dl}</td>
<td>Proportional factor of double layer capacitance (μF/cm²)</td>
</tr>
<tr>
<td>Q_{f}</td>
<td>Film capacitance (μF/cm²)</td>
</tr>
<tr>
<td>QSAR</td>
<td>Quantitative Structure Activity Relationship</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant (JK⁻¹mol⁻¹)</td>
</tr>
<tr>
<td>R_{al}</td>
<td>Adsorbed layer resistance (ohm cm²)</td>
</tr>
<tr>
<td>R_{ct}</td>
<td>Charge transfer resistance (ohm cm²)</td>
</tr>
<tr>
<td>R_P</td>
<td>Polarization resistance (ohm cm²)</td>
</tr>
<tr>
<td>R_s</td>
<td>Solution resistance (ohm cm²)</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress corrosion cracking</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
</tbody>
</table>
SS  Stainless steel
W  Warburg impedance (ohm cm$^2$)
WE  Working electrode
Wt%  Weight percent
XRD  X-ray Powder Diffraction
Z  Impedance (ohm cm$^2$)
Z$'$  Real impedance (ohm cm$^2$)
Z$''$  Imaginary impedance (ohm cm$^2$)

**Greek Letters:**

$\beta_a$  Anodic Tafel slope (mV/decade of current density)
$\beta_b$  Cathodic Tafel slope (mV/decade of current density)
$\eta$  Overpotential (V)
$\eta_{act}$  Activation polarization (V)
$\eta_{conc}$  Concentration polarization (V)
$\eta_H$  Hardness (eV)
$\eta_T$  Combined polarization (V)
$\theta$  Phase angle (degree)
$\sigma$  Softness (eV)
$\sigma_w$  Warburg coefficient (ohm cm$^2$ s$^{-1/2}$)
$\tau$  Relaxation time (s) or Time constant
$\chi$  Electronegativity (eV)
$\mu$  Dipole moment (debye)
1. INTRODUCTION

A report submitted by the Intergovernmental Panel on Climate Change (IPCC) concludes that human activities result in the production of greenhouse gases (GHGs) such as carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4}), chlorofluorocarbons (CFCs), and nitrous oxide (N\textsubscript{2}O) that significantly contribute to global warming (IPCC, 1990). Among the GHGs, CO\textsubscript{2} is the major contributor to global warming as it contributes to almost 60\% of the greenhouse gas effect (Houghton, 1997). The main anthropogenic CO\textsubscript{2} emission sources are flue gases from coal-fired power plants, cement manufacturing plants, and oil refineries. The Energy Information Administration (EIA), within the U.S. Department of Energy (DOE), estimated that approximately 83\% of the GHG emissions in the U.S are generated from combustion and non-fuel uses (e.g., solvents for paints, printing inks) of fossil fuels (coal, petroleum, and natural gas) (EIA, 2006c). To reduce CO\textsubscript{2} emissions, carbon capture and sequestration (CCS) is considered an effective strategy and immediate technological solution (Figueroa et al., 2008). The incorporation of a CO\textsubscript{2} removal unit to an existing coal-fired power plant is a viable option for short- to medium-term interventions to reduce CO\textsubscript{2} emissions into the atmosphere from large-point sources (Alie et al., 2005). With post-combustion CO\textsubscript{2} capture, it is possible to recover 85 – 95\% of CO\textsubscript{2} from fossil fuel emissions (Marion et al., 2001).

1.1 CO\textsubscript{2} Absorption process

The removal of acid gases such as CO\textsubscript{2} and hydrogen sulfide (H\textsubscript{2}S) from gas streams by an amine-based absorption process is an important process in natural gas
industries, oil refineries, and petrochemical plants. The amine-based absorption process became popular in the 1930s and has been used successfully ever since. Recently, this process has been explored for capturing CO$_2$ from industrial flue gas streams emitted particularly from coal fired power plants.

A process diagram for a typical amine-based CO$_2$ capture unit is shown in Figure 1.1. The flue gas from the power plant is initially passed into the direct contact cooler where the temperature of the flue gas, which is above 100°C, is brought down close to 40°C in order to increase the absorption efficiency. The flue gas is then transported by a gas blower to the absorber to overcome the pressure drop caused by the absorber. The flue gas stream entering the bottom of the absorber is counter-currently contacted with the lean amine solution flowing down from the absorber top. The CO$_2$ from the gas stream is absorbed into the lean amine solution through reversible chemical reactions. The treated gas from the absorber top passes through a water wash unit to recover the volatile amine component and eventually is released to the atmosphere. The amine solution leaves the absorber bottom as rich amine solution loaded with CO$_2$. It is then sent through the heat exchanger, where the rich amine solution is pre-heated by the lean amine solution from the stripper bottom. The rich solution is then fed to the top of the stripper where its temperature is further elevated to 100–120°C by heat from the reboiler. This results in the reversal of the chemical equilibrium between the amine and CO$_2$. The stripped CO$_2$ along with water vapour leaves the stripper and enters the overhead condenser. The condensed water is recycled back to the stripper and the produced CO$_2$ gas is compressed for transportation and storage. The lean amine solution is cooled by the heat exchanger before reaching the absorber for the next cycle of CO$_2$ absorption.
Figure 1.1: Process flow diagram of the amine-based CO$_2$ capture unit for coal-fired power plant flue gas
1.2 Absorption solvents

A wide variety of absorption solvents has been used since the advent of acid gas absorption technology. Amines are the most used solvents in the acid gas treating units. These amines are broadly classified into primary (e.g., monoethanolamine (MEA), diglycolamine (DGA)), secondary (e.g., diethanolamine (DEA), diisopropanolamine (DIPA), and piperazine (PZ)), tertiary (e.g., triethanolamine (TEA), methyl diethanolamine (MDEA)), and sterically hindered amines (e.g., 2-amino-2-methyl-1-propanol (AMP), 2–piperidine ethanol (PE)) based on the number of substitutions on the nitrogen atom. Their molecular structures are given in Table 1.1. The solvents like MEA, DEA, and MDEA have proved to be of major commercial interest for gas purification processes (Kohl and Nielsen, 1997). MEA remains the most widely-used solvent, and estimates are that in 1990, it comprised 40% of the solvent market share (Dupart et al., 1993). PZ is a cyclic diamine and is generally used in small concentrations as a promoter or an activating agent with other amines due to its relatively high rate of reaction with CO₂. In recent years, the use of PZ alone as an absorption solvent for CO₂ capture has been investigated by several researchers (Bishnoi and Rochelle, 2000; Derks et al., 2006; Samanta and Bandyopadhyay, 2007; Kadiwala et al., 2010). The kinetic studies on CO₂ absorption using concentrated PZ (8 m) have revealed its rapid rate of CO₂ absorption, higher resistant to thermal degradation, lower oxidation degradation rate, and lower equivalent work requirement for stripping when compared to 7 m MEA (Freeman et al., 2010). Each absorption solvent has its own merits and drawbacks (Table 1.2), both of which have to be considered in selecting a suitable solvent for the CO₂ capture process.
### Table 1.1: Molecular structures of amines used in gas treating

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary Amine</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Monoethanolamine (MEA)</td>
<td>(a) OH-CH₂-CH₂-NH₂</td>
</tr>
<tr>
<td></td>
<td>Diglycolamine (DGA)</td>
<td>(a) OH-CH₂-CH₂-O-CH₂-CH₂-NH₂</td>
</tr>
<tr>
<td><strong>Secondary Amine</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diethanolamine (DEA)</td>
<td>(a) OH-CH₂-CH₂-NH</td>
</tr>
</tbody>
</table>
|                             | Diisopropanolamine (DIPA)      | (a) OH
|                             |                                | CH₃-CH-CH₂-NH         |
|                             |                                | CH₂-CH-CH₂-OH         |
|                             | Piperazine (PZ)                | (b) HN
|                             |                                | NH                   |
| **Tertiary Amine**          |                                |                     |
|                             | Triethanolamine (TEA)          | (a) OH-CH₂-CH₂-N-CH₂-CH₂-OH |
|                             | Methyldiethanolamine (MDEA)    | (a) OH-CH₂-CH₂-N-CH₃ |
| **Sterically Hindered Amine** | 2-amino-2 methyl-1-propanol (AMP) | (a) CH₃
|                             |                                | OH-CH₂-C-NH₂CH₃      |
|                             | 2-Piperidine ethanol (PE)      | (a) N
|                             |                                | CH₂-CH₂-OH           |
Table 1.2: Merits and drawbacks of various amine absorption solvents

<table>
<thead>
<tr>
<th>Amine</th>
<th>Merit</th>
<th>Demerit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>➢ Rapid reaction rate with CO₂ than AMP, DEA and MDEA (^{(a),(g)})</td>
<td>➢ High enthalpy of reaction and hence higher regeneration energy requirement (^{(a)})</td>
</tr>
<tr>
<td></td>
<td>➢ Low cost compared to other primary and secondary amines (^{(a),(b)})</td>
<td>➢ More vapourization loss due to its high vapour pressure (^{(a)})</td>
</tr>
<tr>
<td></td>
<td>➢ Ease of reclamation (^{(a)})</td>
<td>➢ High amine degradation by sulfur dioxide (SO₂), Nitrogen dioxide (NO₂) and Oxygen (O₂) in flue gas (^{(c)})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ High equipment corrosion rate</td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>➢ Lower solvent regeneration energy than MEA</td>
<td>➢ Reclaiming process requires vacuum distillation (^{(a)})</td>
</tr>
<tr>
<td></td>
<td>➢ Moderate cost</td>
<td>➢ Involve in irreversible reactions with COS, CO₂ which results in the formation of corrosive degradation products (^{(a),(d)})</td>
</tr>
<tr>
<td></td>
<td>➢ Less vapourization loss due to its low vapour pressure (^{(a)})</td>
<td></td>
</tr>
<tr>
<td>Methyl diethanolamine (MDEA)</td>
<td>➢ Lower energy requirement for solvent regeneration process than MEA and DEA</td>
<td>➢ Lower CO₂ absorption rate (^{(e)})</td>
</tr>
<tr>
<td></td>
<td>➢ Higher CO₂ absorption capacity than MEA and DEA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>➢ Less volatile than MEA and DEA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>➢ Not degrade readily (^{(a)})</td>
<td></td>
</tr>
<tr>
<td>2-amino-2-methyl-1- propanol (AMP)</td>
<td>➢ CO₂ absorption capacity is twice that of any primary or secondary amines.</td>
<td>➢ Lower reaction kinetic rate with CO₂ than MEA</td>
</tr>
<tr>
<td></td>
<td>➢ Lower energy requirement for solvent regeneration than MEA (^{(f)})</td>
<td>➢ CO₂ removal efficiency lower than MEA (^{(b)})</td>
</tr>
<tr>
<td></td>
<td>➢ Much faster reaction rate with CO₂ than MDEA (^{(b),(f)})</td>
<td>➢ High volatility than PZ</td>
</tr>
<tr>
<td></td>
<td>➢ More stable and its degradation resistance is higher than MEA(^{(i)})</td>
<td></td>
</tr>
<tr>
<td>Piperazine (PZ)</td>
<td>➢ Faster kinetics with CO₂ than MEA and DEA (^{(j)})</td>
<td>➢ 2-3 times more expensive than MEA</td>
</tr>
<tr>
<td></td>
<td>➢ High absorption capacity than MEA (^{(k)})</td>
<td>➢ Narrow solubility window</td>
</tr>
<tr>
<td></td>
<td>➢ Higher resistance to thermal and oxidative degradation than MEA (^{(k)})</td>
<td></td>
</tr>
</tbody>
</table>

\(^{(a)}\) – Kohl and Nielsen, 1997; \(^{(b)}\) – Gabrielsen et al., 2007; \(^{(c)}\) – Yang et al., 2008; \(^{(d)}\) – Dawodu and Meisen, 1992; \(^{(e)}\) – Sartori et al., 1983; \(^{(f)}\) – Sakwattanapong et al., 2009; \(^{(g)}\) – Chowdhury et al., 2011; \(^{(h)}\) – Choi et al., 2009; \(^{(i)}\) – Lepaumier et al., 2009; \(^{(j)}\) – Bishnoi and Rochelle, 2000; \(^{(k)}\) – Freeman et al., 2010;
In recent years, the use of aqueous blended amines has been proposed and used for acid gas absorption processes. The blended amines are designed to take advantage of the desirable properties from the parent amines. The blended amines that combine the high rate of CO₂ reaction of the primary or secondary amines with the low heat of reaction of tertiary amines are considered as the more attractive alternatives for the CO₂ capture process. Several studies focusing on blended amines involving PZ, AMP, MEA, MDEA and other solvents have been reported in the literature. For example, there has been significant interest in aqueous mixtures containing amines and PZ activator for the CO₂ absorption process. The BASF activated MDEA process involves 2.5 to 4.5 kmol/m³ MDEA solution containing up to 0.8 kmol/m³ PZ as the promoter (Appl et al., 1980). A number of other studies included PZ activated MDEA (Xu et al., 1992; Bishnoi and Rochelle, 2002; Ali and Aroua, 2004; Closmann et al., 2009), MEA-PZ blend (Dang et al., 2003; Dugas and Rochelle, 2009), DEA-PZ blend (Mondal, 2009), AMP-PZ blend (Sun et al., 2005, Samanta et al., 2009; Yang et al., 2010; Dash et al., 2011), and blends containing N-MDEA-PZ-Sulfolane (Jenab et al., 2005).

1.3 Corrosion problems

Corrosion in amine-based gas treating plants is a serious operating problem that has long been reported in the literature. As seen from the summary of plant experience on corrosion in Table 1.3, various types of corrosion occur in amine-based gas treating plants, i.e. general corrosion, galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, erosion corrosion, and stress corrosion cracking (SCC). The most susceptible areas to corrosion are the bottoms of the absorbers, the regenerators, pumps
Table 1.3: Summary of plant experiences on corrosion in acid gas treating plants

<table>
<thead>
<tr>
<th>Reference</th>
<th>Plant type</th>
<th>Solvent</th>
<th>Acid gas</th>
<th>Corrosion type</th>
<th>Corrosive area</th>
<th>Corrosion causes</th>
<th>Corrosion mitigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dingman et al., 1966</td>
<td>Gas treating plant</td>
<td>MEA</td>
<td>CO₂, H₂S</td>
<td>Erosion corrosion</td>
<td>Rich/lean heat exchanger</td>
<td>Acid gas flashing</td>
<td>-NA-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Regenerator</td>
<td>High solution velocity</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Solid contamination</td>
<td></td>
</tr>
<tr>
<td>William et al., 1968</td>
<td>Steel plant</td>
<td>MEA</td>
<td>CO₂</td>
<td>General corrosion</td>
<td>Reboiler tubes</td>
<td>Amine degradation products and other impurities</td>
<td>-NA-</td>
</tr>
<tr>
<td>Smith and Younger, 1972</td>
<td>Gas treating unit</td>
<td>DEA</td>
<td>CO₂, H₂S</td>
<td>Erosion corrosion, Stress corrosion cracking</td>
<td>Rich/lean heat exchanger</td>
<td>Solution contamination</td>
<td>-NA-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Regenerator</td>
<td>High liquid flow velocity</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Reboiler vapour line</td>
<td>Chloride ion evolution from gasket material</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SCC in Heat exchanger plate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schmeal et al., 1978</td>
<td>Gas treating plant</td>
<td>Sulfinol</td>
<td>CO₂, H₂S</td>
<td>Pitting corrosion</td>
<td>Absorber bottom below 5th tray</td>
<td>Acid gas flashing</td>
<td>-NA-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(DIPA + Sulfolane)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hall and Barron, 1981</td>
<td>Gas treating plant</td>
<td>DEA</td>
<td>-NA-</td>
<td></td>
<td></td>
<td>Reboiler bundle</td>
<td>-NA-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rich/lean heat exchanger</td>
<td></td>
</tr>
<tr>
<td>Krawczyk et al., 1984</td>
<td>Natural gas purification</td>
<td>MEA</td>
<td>CO₂</td>
<td>General corrosion</td>
<td>Hot lean circuit</td>
<td>Corrosion inhibitor (Ammonium thiocyanate)</td>
<td>-NA-</td>
</tr>
<tr>
<td>Dupart et al., 1993</td>
<td>Ammonia plant</td>
<td>MEA to formulated MDEA</td>
<td>CO₂</td>
<td>Intergranular corrosion</td>
<td>Heat affected zone of 304 stainless steel (SS) stripper shell welds</td>
<td>Sensitization of the SS from fabrication techniques used in vessel</td>
<td>-NA-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A correct weld procedure was incorporated and the affected welds repaired</td>
<td>-NA-</td>
</tr>
<tr>
<td>Dupart et al., 1993</td>
<td>Gas treating plant</td>
<td>Formulated MDEA</td>
<td>CO₂, H₂S</td>
<td>Pitting corrosion</td>
<td>Erosion corrosion</td>
<td>Circulating pump suction strainer</td>
<td>CO₂ flashing</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Ammonia plant</td>
<td>MEA to formulated MDEA</td>
<td>CO₂</td>
<td>Erosion corrosion</td>
<td>Bottom of amine contactor</td>
<td>Turbulent interaction between the inlet gas and liquid surface</td>
<td>Eroded area filled with a metal impregnated epoxy</td>
<td></td>
</tr>
<tr>
<td>Ammonia plant</td>
<td>MEA</td>
<td>CO₂</td>
<td>General corrosion</td>
<td>Galvanic corrosion</td>
<td>Bottom of amine contactor</td>
<td>Corrosion mechanism penetrated the protective passive film in vapour region at the contactor bottom</td>
<td>Liquid level in the contactor was maintained above the inlet gas distributor</td>
</tr>
<tr>
<td>Natural gas treatment plant</td>
<td>Formulated MDEA</td>
<td>CO₂</td>
<td>Pitting corrosion</td>
<td>Erosion corrosion</td>
<td>Carbon steel tray decks</td>
<td>Shell side of the heat exchanger</td>
<td>Booster pump impeller and case</td>
</tr>
<tr>
<td>Hay et al., 1996</td>
<td>Gas Treating plant, Alberta, Canada</td>
<td>MDEA</td>
<td>CO₂, H₂S</td>
<td>Crevice Corrosion</td>
<td>Stress corrosion cracking</td>
<td>SS Heat exchanger plates in gasket groove area</td>
<td>Synergistic sulfide – halide attack</td>
</tr>
<tr>
<td>Russell et al., 1997</td>
<td>CO₂ removal plant, Michigan, US</td>
<td>MDEA</td>
<td>CO₂, H₂S</td>
<td>Pitting corrosion</td>
<td>Lower section of amine contactor in 304 SS tray</td>
<td>Presence of Chloride in feed gas stream</td>
<td>Presence of sulfides from trace H₂S</td>
</tr>
<tr>
<td>Source</td>
<td>Location</td>
<td>Amines</td>
<td>CO₂, H₂S</td>
<td>Corrosion Types</td>
<td>Observations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------------------------</td>
<td>--------</td>
<td>----------</td>
<td>------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DeHart et al., 1999</td>
<td>CO₂ recovery plant, MA, England</td>
<td>MEA</td>
<td>CO₂</td>
<td>Galvanic corrosion, Uniform corrosion, Vapour distribution tray in absorber shell, Around manway in stripper</td>
<td>Wet CO₂ corrosion, Presence of degradation product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Addington et al., 2000</td>
<td>Acid gas scrubbing unit, Sulfiban</td>
<td>MEA</td>
<td>CO₂, H₂S and HCN</td>
<td>General corrosion, In 316 SS reboiler tubes, Regeneration tower, Rich / lean amine exchanger tube</td>
<td>Presence of high level of formate HSS, High reboiler tube temperature, above 160°C, Installation of manual reclaimer level control, Addition of antifoam agent, Decreasing the saturated steam temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Howard and Sargent, 2001</td>
<td>Gas treating plant, Texas</td>
<td>MDEA</td>
<td>CO₂, H₂S</td>
<td>Cavitation corrosion, Amine circulation pump, Level control valve, Suction nozzle</td>
<td>Oxygen contamination leading to HSS formation, majorly bicine, Use of oxygen scavenger or inhibitor, Addition of caustic soda to neutralize bicine, Ion exchange reclamation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Safruddin et al., 2003</td>
<td>Amine unit of LNG plant, Badak, Indonesia</td>
<td>MEA</td>
<td>CO₂</td>
<td>Erosion corrosion, Absorber vessel wall in the gaps between support rings and vessel wall</td>
<td>Improper installation of sealing gasket, New support rings permanently welded to the vessel wall</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulger et al., 2005</td>
<td>Gas treating, Alberta, Canada</td>
<td>Sulfinol-D Process</td>
<td>CO₂, H₂S</td>
<td>Pitting corrosion, General corrosion</td>
<td>Reclamation, 304 L SS material installed in vapour and liquid return line</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Zahrani and Al-Luqman, 2006</td>
<td>Gas treating plant, , Dhahran, Saudi Arabia</td>
<td>DGA</td>
<td>CO₂, H₂S</td>
<td>Erosion Corrosion, Pitting corrosion, Stress corrosion</td>
<td>High fluid velocity, Amine degradation, Reclamation control valve, Steam line in reboiler and reclaimer, Reclaimer tube, High fluid velocity in level control valve, High steam line velocity, High chloride, Maintaining the fluid velocity as per API 571 recommendation. Maintaining chloride level</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kermani et al., 2007</td>
<td>Acid gas removal unit, DAS island</td>
<td>K₂CO₃</td>
<td>CO₂, H₂S</td>
<td>Cracking</td>
<td>Uniform corrosion</td>
<td>Condenser bundle</td>
<td>Hydriding</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------------------</td>
<td>-------</td>
<td>--------</td>
<td>----------</td>
<td>------------------</td>
<td>---------------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Localized wall loss</td>
<td>Baffle plate holes</td>
<td>Removal of protective Titanium oxide layer due to high velocity of stream</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fretting corrosion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moore et al., 2008</td>
<td>Gas treating plant, Dhahran, KSA</td>
<td>ADIP</td>
<td>CO₂, H₂S</td>
<td>General corrosion</td>
<td>Thermosyphon reboiler made of carbon steel</td>
<td>Poor design of amine sump pit allowing oxygen ingress and, hence, amine degradation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
valves, and reboiler bundles, where the acid gas loading and temperature are high (DuPart et al., 1993).

The corrosion in gas treating plants has major impacts on plant economics and safety of plant personnel. The plant economics are negatively impacted by the losses of revenue due to unscheduled downtime, production losses, reduced equipment life, and the cost for repair of the corroded process components. A corrosion cost analysis in gas treating plants (Tems and Al-Zahrani, 2006) estimated that 25% of the maintenance budget was committed to corrosion control. For the safety of the plant personnel, two catastrophic incidents that took place in amine units due to stress corrosion cracking in the 1980s can be given here as examples. One such incident was reported to be the cracking of a tank at the ambient temperature at a U.K. refinery that used MEA as an absorption solvent. The second, and most serious incident, was the rupture of an MEA contactor tower at a U.S. refinery that claimed the lives of 17 people and resulted in extensive property damage (Richert et al., 1989).

Corrosiveness of the amine solutions loaded with CO$_2$ depends on process parameters, such as type and concentration of amines, rich amine flashing, temperature, oxygen ingression, amine degradation products, solution turbulence, and solution contamination. Besides these, plant design, plant metallurgy, poor operating practices, and improper fabrication can also lead to severe corrosion. In most cases, proper plant design, use of corrosion inhibitors, use of corrosion-resistant materials, and incorporation of corrosion monitoring techniques such as Non-Destructive Examination (NDE) remain effective corrosion control strategies.
1.4 Research motivation, objectives, and scope

According to Herzog and Vukmirovic (1999), the integration of amine-based CO\(_2\) capture units with coal-fired power plants will impose an energy penalty of 20% (reduction in power output), which has a major effect on overall costs. Thus, the present CO\(_2\) capture technology demands the need for cost effective solvents. Selection of solvents for post-combustion capture considers properties of the solvents as well as tradeoffs between different properties. Such properties are reaction kinetics with CO\(_2\), CO\(_2\) absorption capacity, heat of reaction with CO\(_2\), energy requirement for solvent regeneration, solvent solubility, vapour pressure, cyclic CO\(_2\) absorption capacity, environmental impacts, economics, and operational difficulties such as degradation of solvent, corrosion, and foaming. The major costs associated with corrosion damage and corrosion control can be minimized by selecting suitable solvent systems that entail minimum corrosion difficulties.

Laboratory corrosion experiments can provide useful information for screening suitable absorption solvent. However, the availability of laboratory corrosion studies for these amine solvents is limited. As seen from Table 1.4, most of the literature is only on MEA, and few studies exist for other single and blended solvents. Moreover, the available corrosion data were observed from different test environments using different corrosion measurement techniques (weight loss or electrochemical methods). From Table 1.5, only one study (Veawab et al., 1999) involves comparative corrosion analysis of various amines under identical test conditions. It involves electrochemical corrosion tests on four different single amines (MEA, DEA, MDEA, and AMP). This study (like others), however, does not provide much information on the reasons for the corrosivity
Table 1.4: Literature references for laboratory corrosion studies in amine-based absorption process

<table>
<thead>
<tr>
<th>Absorption solvent</th>
<th>Number of lab corrosion studies</th>
<th>Literature Reference</th>
</tr>
</thead>
</table>
| MEA                | 12                              | Froning and Jones (1958)  
|                    |                                 | Kittel et al. (2009, 2010)  
|                    |                                 | Kladkaew et al. (2009, 2011)  
|                    |                                 | Hamah-Ali et al. (2011)  
| DGA                | 1                               | Guo et al. (1998)  
| DEA                | 3                               | Chakma and Melsen (1986)  
|                    |                                 | Veawab et al. (1999)  
|                    |                                 | Garcia-Arriaga et al. (2010)  
| MDEA               | 4                               | Rooney et al. (1996)  
|                    |                                 | Guo et al. (1999)  
|                    |                                 | Khorrami et al. (2008)  
|                    |                                 | Duan et al. (2010)  
| PZ                 | 0                               | -  
| Blended solvents   | 4                               | Dupart et al. (1999)  
|                    |                                 | Veawab et al. (1999 & 2009)  
|                    |                                 | Eustaquio-Rincon et al. (2008)  

14
Table 1.5: Literature information on corrosion studies in amine-based absorption process

<table>
<thead>
<tr>
<th>Reference</th>
<th>Solvent</th>
<th>Gas</th>
<th>Experimental condition</th>
<th>Methodology</th>
<th>Results</th>
</tr>
</thead>
</table>
| Kladkaew et al., 2011 | MEA    | CO₂-SO₂ - O₂ | ✓ In presence of inhibitor  
 ✓ Amine concentration → 7.0 kmol/m³  
 ✓ Substrate → CS 1020  
 ✓ CO₂ loading → 0.50 mol / mol  
 ✓ Temperature → 353 K  
 ✓ O₂ content → 6%  
 ✓ SO₂ concentration → 0-204 ppm | Electrochemical technique – Potentiodynamic polarization. | ✓ CO₂ loading had the strongest impact on corrosion rate over SO₂ & O₂ content  
 ✓ Inhibitor C showed the highest inhibition efficiency of 95%. |
| Hamah-Ali et al., 2011 | MEA    | CO₂    | ✓ In presence of inhibitor ([bmim][DCA] → 0.1 to 1.0 M  
 ✓ Amine concentration → 2 & 4 M  
 ✓ Substrate → Carbon steel  
 ✓ CO₂ loading → 0.55 mol/mol  
 ✓ Temperature → 40, 60, 80°C  
 ✓ Scan rate → 0.9 mV/s  
 ✓ Frequency range → 0.1 Hz – 100 kHz  
 ✓ Voltage amplitude → 5 mV | Electrochemical techniques - EIS and cyclic polarization | ✓ Presence of inhibitor decreased both anodic and cathodic reaction and, hence, the corrosion rate, without changing reaction mechanism.  
 ✓ Inhibition efficiency decreased with increase in temperature. |
| Duan et al., 2010 | MDEA   | CO₂    | ✓ Amine concentration → 50 wt%  
 ✓ Substrate → CS (ASTM A36)  
 ✓ CO₂ content → 12%  
 ✓ O₂ content → 6%  
 ✓ Temperature → 50°C  
 ✓ HSS → 15000 ppm  
 ✓ Scan rate → 0.160 mV/s  
 ✓ Frequency range → 10 kHz – 10 mHz  
 ✓ Voltage amplitude → 10 mV | Electrochemical techniques - LPR, EIS and cyclic polarization. | ✓ The corrosivity order is MDEA/CO₂/O₂/HSS > MDEA/CO₂/O₂ > MDEA/CO₂.  
 ✓ The corrosion morphology of carbon steel in presence of O₂ and HSS showed uniform corrosion with preferential dissolution of ferrite. |
<table>
<thead>
<tr>
<th>Study</th>
<th>Amine Concentration</th>
<th>CO₂ Loading</th>
<th>Substrate</th>
<th>O₂ Content</th>
<th>Temperature</th>
<th>Scan Rate</th>
<th>Electrochemical Technique</th>
<th>Differences in the Corrosive Factor</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kittel et al., 2010</td>
<td>20, 30, 40 wt%</td>
<td>0.5 mol/mol</td>
<td>CS</td>
<td>5%</td>
<td>80°C</td>
<td>10 mV/min</td>
<td>Polarization</td>
<td>Between acid gas treatment and CO₂ capture were discussed.</td>
<td>Temperature and CO₂ loading are the most significant factor controlling corrosion.</td>
</tr>
<tr>
<td>Veawab et al., 2009</td>
<td>5.0, 6.2, 7.0, 8.7 kmol/m³</td>
<td>0.20, 0.40, 0.58 &amp; 0.63 mol/mol</td>
<td>CS1018 &amp; SS306</td>
<td>6% &amp; 5.6%</td>
<td>40 &amp; 80°C</td>
<td>10 mV/min</td>
<td>Polarization</td>
<td>The blended MEA / PZ was more corrosive than MEA solution at identical concentration range.</td>
<td></td>
</tr>
<tr>
<td>Kittel et al., 2009</td>
<td>30 wt%</td>
<td>0.0 – 0.5 mol/mol</td>
<td>CS1018 &amp; SS306</td>
<td>6% &amp; 5.6%</td>
<td>303 – 353 K</td>
<td>0-100%</td>
<td>Polarization</td>
<td>Lowest corrosion in the cool parts of the unit and highest corrosion in hottest part was observed.</td>
<td></td>
</tr>
<tr>
<td>Kladkaew et al., 2009</td>
<td>1.0 - 7.0 kmol/m³</td>
<td>0.0 – 0.5 mol/mol</td>
<td>CS1020</td>
<td>0-100%</td>
<td>303 – 353 K</td>
<td>0-204 ppm</td>
<td>Polarization</td>
<td>Presence of SO₂ in the flue stream results in increased hydrogen ion concentration and, hence, the higher corrosion rate.</td>
<td></td>
</tr>
</tbody>
</table>

**Electrochemical Technique**
- Polarization
- Cyclic Potentiodynamic polarization
- Field Study by 1) Weight loss coupons for the Castor pilot plant 2) Corrosometer probes in ITC system.
- Presence of SO₂ in the flue stream results in increased hydrogen ion concentration and, hence, the higher corrosion rate.
- CO₂ loading had the strongest impact on corrosion rate over SO₂ & O₂ content.
<table>
<thead>
<tr>
<th>Study</th>
<th>Solution</th>
<th>CO₂</th>
<th>Factors</th>
<th>Methods</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veawab et al., 2008</td>
<td>MEA</td>
<td>CO₂</td>
<td>Amine concentration → 5.0, 7.0, 9.0 kmol/m³</td>
<td>Electrochemical technique – Cyclic Potentiodynamic polarization</td>
<td>Increase in temperature, acid gas loading, solution concentration, solution velocity results in higher corrosion rate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Substrate → CS 1018</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂ loading → 0.20 &amp; 0.55 mol / mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temperature → 40 &amp; 80°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O₂ partial pressure → 0.0, 5.07, 10.13 kPa</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Scan rate → 0.60 V/h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Khorrami et al., 2008</td>
<td>Activated MDEA</td>
<td>CO₂</td>
<td>Amine concentration → 10, 27 and 37 wt %</td>
<td>Electrochemical techniques - Potentiodynamic polarization and AC impedance test.</td>
<td>Passive layer formed in 10 wt% a-MDEA was less stable compared to 37 wt %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Substrate → Carbon steel</td>
<td></td>
<td>Corrosion process at projection potential in passive region is diffusion controlled, and it is independent of passive region</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂ loading → CO₂ saturation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temperature → 50, 65 &amp; 80°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Scan rate → 0.5 mV/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Frequency range → 10⁻³ – 10⁻⁵ Hz</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Voltage amplitude → 5 mV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rincon et al., 2008</td>
<td>DEA, MDEA, and its blends</td>
<td>CO₂ and H₂S</td>
<td>Amine concentration → 15-60 wt%</td>
<td>Weight loss method using Semistatic weight loss test apparatus</td>
<td>H₂S contributes most to the corrosion process.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Substrate → CS 1010</td>
<td></td>
<td>Higher the mass % of MDEA in the MDEA/DEA blend, lower the corrosion rate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temperature → 393.15 K</td>
<td></td>
<td>Corrosion rate increases with amount of H₂S in the amine solution.</td>
</tr>
<tr>
<td>Veawab et al., 2006</td>
<td>MEA</td>
<td>CO₂</td>
<td>Amine concentration → 5.0 kmol/m³</td>
<td>Electrochemical techniques – Tafel plot, LPR, potentiodynamic polarization</td>
<td>Oxalate was found to be more corrosive, followed by malonate and formate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Substrate → CS 1018 &amp; SS304</td>
<td></td>
<td>Stainless steel was least affected by presence of HSAS.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂ loading → 0.20 mol / mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temperature → 80°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>In presence of heat stable salts</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Scan rate → 0.60 V/h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veawab et al., 2005</td>
<td>MEA</td>
<td>CO₂</td>
<td>In presence of Inhibitor</td>
<td>Electrochemical technique –</td>
<td>NaVO₃ inhibitor provided 96% inhibition efficiency without any</td>
</tr>
<tr>
<td>Study</td>
<td>Amines</td>
<td>CO₂ Loading</td>
<td>CO₂ Saturation</td>
<td>Temperature (°C)</td>
<td>O₂ Content (%)</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------------------</td>
<td>-------------</td>
<td>----------------</td>
<td>------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Veawab et al., 2002</td>
<td>MEA</td>
<td>CO₂</td>
<td>-NA -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veawab et al., 1999</td>
<td>MEA, DEA, MDEA, AMP, and blended system.</td>
<td>CO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veawab et al., 1999</td>
<td>AMP and MEA</td>
<td>CO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guo et al., 1999</td>
<td>MDEA</td>
<td>CO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Study</td>
<td>Amine</td>
<td>CO₂/H₂S</td>
<td>Parameters</td>
<td>Techniques</td>
<td>Corrosion Mechanism</td>
</tr>
<tr>
<td>-----------------------</td>
<td>--------</td>
<td>---------</td>
<td>------------</td>
<td>------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Guo et al., 1998</td>
<td>DGA</td>
<td>CO₂</td>
<td>Amine conc. → 0.1, 1, 5.0 M</td>
<td>Electrochemical techniques - Potentiodynamic polarization and AC impedance test</td>
<td>The anodic dissolution mechanism depends upon DGA concentration and temperature. At 100°C, corrosion product film observed at low concentration (0.1 &amp; 1 M) but not at high concentration (5 M)</td>
</tr>
<tr>
<td>Rooney et al., 1996 &amp; 1997</td>
<td>MDEA</td>
<td>CO₂ &amp; H₂S</td>
<td>Amine conc. → 50 wt %</td>
<td>Weight loss coupon method</td>
<td>Oxalic acid with MDEA more corrosive than any other anions. Increase in temperature from 180°F to 250°F resulted in increase in corrosivity of solution. In vapour state, anions like formic acid, malonic acid, and sodium thiosulfate induced higher corrosion rate.</td>
</tr>
<tr>
<td>Chakma et al., 1986</td>
<td>DEA</td>
<td>CO₂</td>
<td>Amine conc. → 30–60 wt%</td>
<td>Potentiodynamic Polarization (25°C) and Weight – Loss tests(100°C)</td>
<td>HEOD - the degradation compound primarily responsible for corrosion. Pitting behaviour was observed with DEA and HEOD system</td>
</tr>
<tr>
<td>Froning et al., 1958</td>
<td>MEA</td>
<td>CO₂ and H₂S</td>
<td>Amine conc. → 10 &amp; 20 wt%</td>
<td>Weight loss method</td>
<td>In presence of CO₂-H₂S mixture, the corrosion rate was primarily controlled by amount of H₂S.</td>
</tr>
</tbody>
</table>
differences among the tested amines and does not cover the effect of process contaminants on corrosion behaviour. Although many speculations on the possible corroding agents have been put forth in the available literature for amine-CO$_2$-H$_2$O environments, such knowledge remains inconclusive, and there are no theoretical analyses to explain the differences in corrosivity among different amines. Moreover, as mentioned in Section 1.2, although many blended amine systems have been used for gas treating and being studied for CO$_2$ capture applications, few corrosion studies were carried out for this blended amine system.

The overall objectives of this work are, therefore, to provide extensive corrosion information on commonly used plant construction materials (carbon steel and stainless steel) in various amine-based CO$_2$ absorption solvents. The specific objectives are: 1) to provide a corrosion engineering database of both single and blended amines that are commonly used and/or have potential to serve as absorption solvents and 2) to gain knowledge and understanding of comparative corrosiveness of various amines. To achieve these objectives, a large number of corrosion experiments was carried out using electrochemical and weight loss techniques. The tested solvents were MEA, DEA, MDEA, AMP, PZ and their blends. The corrosion behaviours in the presence of process contaminants including thiosulfate, oxalate, sulfite, and chloride were tested. This research implements a comprehensive evaluation in following sequence:

Task 1: Corrosion evaluation of CS1018 in single amine systems

Task 2: Comparative corrosion analysis of single amine systems by considering quantity of corroding agents and by using corrosion inhibitor principles (Quantitative Structure Activity Relationship (QSAR) studies, and Hard
and Soft Acid and Base (HSAB) theory)

Task 3: Passive behaviour analysis of CS1018 in single amine systems

Task 4: Corrosion evaluation of CS1018 in single amine systems in the presence of process contaminants

Task 5: Corrosion evaluation of CS1018 in blended amine systems

Task 6: Corrosion resistance testing of stainless steels (SS304 and SS316) in single amine systems

Task 7: Weight loss corrosion test of CS1018 and SS304 in single amine systems
2. LITERATURE REVIEW AND FUNDAMENTALS

2.1 Amine-CO\textsubscript{2} absorption mechanism

In an amine-based CO\textsubscript{2} capture unit, the amine absorption solvents are mixed with water to form active solution, and that will react with the inlet gas stream to remove CO\textsubscript{2}. In case of primary amine (MEA) or secondary amine (DEA), the reaction mechanism is that it absorbs CO\textsubscript{2} as amine-carbamate. Two different absorption mechanisms have been proposed, which are Zwitterion (Caplow, 1968 and Danckwerts, 1979) and Termolecular (Crooks and Donnellan, 1989) mechanisms. Zwitterion mechanism is a two step process in which amine reacts with CO\textsubscript{2} to form an intermediate Zwitterion in the first step followed by the deprotonation of Zwitterion by the base present in the system, resulting in carbamate formation. Termolecular mechanism is a single step process where the reaction product between the amine, CO\textsubscript{2}, and the base will be in the form of a loosely-bound encounter complex. In this mechanism, the formation of the bond between amine and CO\textsubscript{2} and the proton transfer takes place simultaneously.

Zwitterion reaction mechanism is the generally accepted reaction mechanism between amine and CO\textsubscript{2}. Reactions involved in CO\textsubscript{2} absorption using aqueous MEA solution are given below (Danckwerts, 1979):

\[ \text{Water ionization} \quad 2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \quad (2.1) \]
\[ \text{Hydrolysis and ionization of CO}_2 \quad 2\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \quad (2.2) \]
\[ \text{Dissociation of bicarbonate} \quad \text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \quad (2.3) \]
\[ \text{Zwitterion formation} \quad \text{RNH}_2 + \text{CO}_2 \leftrightarrow \text{RNH}_2^+\text{COO}^- \quad (2.4) \]
\[ \text{Carbamate formation} \quad \text{RNH}_2^+\text{COO}^- + \text{B} \rightarrow \text{RNHCOO}^- + \text{BH} \quad (2.5) \]
Carbamate reversion \[ \text{RNHCOO}^- + \text{H}_2\text{O} \leftrightarrow \text{RNH}_2 + \text{HCO}_3^- \] (2.6)

Bicarbonate formation \[ \text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^- \] (2.7)

The overall CO$_2$ absorption mechanism with MEA and DEA can be written as:

For MEA \[ \text{CO}_2 + 2\text{RNH}_2 \leftrightarrow \text{RNHCOO}^- + \text{RNH}_3^+ \] (2.8)

For DEA \[ \text{CO}_2 + 2\text{R}_2\text{NH} \leftrightarrow \text{R}_2\text{NCOO}^- + \text{R}_2\text{NH}_2^+ \] (2.9)

where RNHCOO$^-$ and R$_2$NCOO$^-$ are their respective carbamates and RNH$_3^+$ and R$_2$NH$_2^+$ are their respective protonated amines. The stoichiometry of the reaction limits the amount of CO$_2$ that can be absorbed, and the maximum amount is 0.50 mole of CO$_2$ per mole of amine. The Zwitterion mechanism is also applied to the CO$_2$ absorption using PZ solvent (Derks et al., 2006). It involves the reaction of CO$_2$ with PZ to form a zwitterion intermediate (PZH$^+\text{COO}^-$), which is subsequently deprotonated by a base present in the system, resulting in piperazine carbamate (PZCOO$^-$) and protonated PZ (PZH$^+\text{). Since}$ piperazine is a diamine, it can involve multiple reactions with CO$_2$ and favours formation of protonated piperazine carbamate (H$^+\text{PZCOO}^-$) and piperazine dicarbamate (PZ(COO$^-$)$_2\text{), as shown in the equations below (Bishnoi and Rochelle, 2000).}$

\[ \text{CO}_2 + \text{PZ} + \text{H}_2\text{O} \leftrightarrow \text{PZCOO}^- + \text{H}_3\text{O}^+ \] (2.10)

\[ \text{H}_3\text{O}^+ + \text{PZCOO}^- \leftrightarrow \text{H}_2\text{O} + \text{H}^+\text{PZCOO}^- \] (2.11)

\[ \text{PZCOO}^- + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{PZ (COO}^-\text{)}_2 + \text{H}_3\text{O}^+ \] (2.12)

In the case of a tertiary amine like MDEA, it does not react with CO$_2$ directly to form any carbamates. The CO$_2$ reaction can only occur after the CO$_2$ dissolves in the water to form a bicarbonate ion (Danckwerts, 1979). Thus, the maximum stoichiometric absorption of CO$_2$ with MDEA can reach up to one mole of CO$_2$ per mole of amine. The overall CO$_2$ absorption mechanism with MDEA can be written as:
\[ \text{RN} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{R}_3\text{NH}^+ + \text{HCO}_3^- \quad (2.13) \]

For AMP, the absorption mechanism is similar to that of MDEA. Though it undergoes carbamate formation, its high instability results in the hydrolysis of carbamate compound (Reaction 2.14) to form bicarbonate and free amine.

\[ \text{RNHCOO}^- + \text{H}_2\text{O} \leftrightarrow \text{RNH}_2 + \text{HCO}_3^- \quad (2.14) \]

Thus, the overall reaction of AMP with CO\(_2\) can be written as:

\[ \text{RNH}_2 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{RNH}_3^+ + \text{HCO}_3^- \quad (2.15) \]

A certain amount of carbamate hydrolysis occurs with all types of amine, so that even with MEA or DEA, the CO\(_2\) loadings greater than 0.50 mol CO\(_2\)/mol amine are feasible (Sartori and Savage, 1983). The extent to which carbamate hydrolysis occurs is determined by its carbamate stability constant (K\(_c\)).

### 2.2 Principles of Corrosion

#### 2.2.1 Corrosion of materials

Corrosion is an electrochemical process that results in the destructive attack of metal due to its reaction with the environment. The corrosion cell is composed of an anode, cathode, electrolyte, and metallic pathway. The anode is an electrode from which electrons leave the cell, and the cathode is an electrode from which electrons enter the cell. The basic anodic reaction with every corrosion process is the oxidation of a metal to its ion or metal dissolution (Reaction 2.16). There are several cathodic reactions possible within the corrosion environment, and the most common reactions are reduction of hydrogen ions or hydrogen evolution reactions and oxygen reduction reactions. The
hydrogen evolution reaction is represented in Reaction 2.17, and Reaction 2.18 represents the overall corrosion mechanism.

At anodic site: \[ \text{Fe} (s) \rightarrow \text{Fe}^{2+} (aq) + 2e^- \quad (2.16) \]

At cathodic site: \[ 2\text{H}^+ (aq) + 2e^- \rightarrow \text{H}_2 (g) \quad (2.17) \]

Overall reaction: \[ \text{Fe} (s) + 2\text{H}^+ (aq) \rightarrow \text{Fe}^{2+} (aq) + \text{H}_2 (g) \quad (2.18) \]

Figure 2.1 illustrates the simple corrosion mechanism of iron immersed in a de-aerated acid solution showing both anodic and cathodic reactions. Metal ions (Fe$^{2+}$) from the anodic site leave the metal lattice (Reaction 2.16), and the electrons left behind travel through the metallic path to the cathodic site and take part in the reduction reaction (Reaction 2.17). Thus, corrosion can be defined as simultaneous transfer of charge and mass across a metal/solution interface.

### 2.2.2 Electrode potential

When a metal is immersed in an electrolyte, there exists a metal/solution interface resulting in an electrical double layer. The charge on the metal side of the interface is balanced by the distribution of ions in the solution side of the interface. This electrical double layer leads to the development of potential difference across the interface and is commonly referred to as electrode potential. The factors that affect the electrode potential are the nature of the metal, the chemical nature of the aqueous solution, the presence of oxide films on the metal surface, the presence of adsorbed gases on the metal surface, and the presence of mechanical stress on the metal surface (McCafferty, 2010). This electrode potential can be measured with the help of a standard reference electrode, as it is impossible to measure the absolute electrode potential. The Standard Hydrogen Electrode
**Figure 2.1:** Electrochemical reactions occurring during the corrosion of iron in de-aerated acid solution
(SHE) is universally accepted as a standard reference electrode. Some of the other reference electrodes include the Saturated Calomel Electrode, Silver/Silver Chloride Electrode, etc.

2.2.3 Exchange current density

Exchange current density is a characteristic of a reversible electrode reaction. It is the current density associated with the electrode at equilibrium. Consider the following reversible reaction of a hydrogen electrode:

$$2H^+ + 2e^- \leftrightarrow H_2$$ (2.19)

At equilibrium conditions, the free energy of activation for the $H^+$ reduction (forward) and $H_2$ oxidation (backward) reactions are located at the same level, and, hence, both the reaction rates are equal. Thus, at equilibrium conditions, no net current flows. The relationship between the exchange reaction rate and the current density can be stated from Faraday’s law (Equation 2.20).

$$r_{oxid} = r_{red} = \frac{i_0 a}{nF}$$ (2.20)

where $r_{oxid}$ and $r_{red}$ are the equilibrium oxidation and reduction rate (g/cm$^2$/s); $i_0$ is the equilibrium exchange current density (A/cm$^2$); $n$ denotes the number of equivalent electrons exchanged; $F$ is Faraday’s constant (96,500 coulombs per equivalent); and ‘a’ is the atomic weight (grams). In other words, the exchange current density ($i_0$) is the rate of oxidation and reduction reactions at an equilibrium electrode expressed in terms of current density. The value of exchange current density of a given metal varies with electrolyte type, concentration of electrolyte, purity of the metal and surface cleanliness.
2.2.4 Polarization

Electrochemical polarization or polarization is the deviation of electrode potential from its equilibrium value on application of an external current. The magnitude of deviation is defined as overpotential (\( \eta \)), which is the difference between the applied voltage and the equilibrium potential (\( E_{\text{rev}} \)) of the electrode in that particular electrolyte. Both anodes and cathodes can be polarized. Anodic polarization involves removal of electrons from the metal surface, resulting in the displacement of electrode potential in the positive direction so that the electrode acts more anodic. In cathodic polarization, electrons are supplied to the metal surface, making the electrode potential (E) negative to the equilibrium potential so that the electrode acts more cathodic.

2.2.4.1 Polarization characteristics

Polarization can be categorized into different types: activation, concentration, and combined polarization. Activation polarization is the set of electrochemical processes that are controlled by the slow step in the reaction sequence at the metal/electrolyte interface. For activation polarization, the relationship between the current density and overpotential is given as Equations 2.21 and 2.22, and its characteristics are shown in Figure 2.2-a.

\[
\eta_a = \pm \beta_a \log \frac{i_a}{i_0} \quad \text{(for anodic branch)} \tag{2.21}
\]

\[
\eta_c = \pm \beta_c \log \frac{i_c}{i_0} \quad \text{(for cathodic branch)} \tag{2.22}
\]

Equations 2.21 and 2.22 are called Tafel equations. The terms \( \beta_a \) and \( \beta_c \) are the slopes for the anodic and cathodic polarization and are termed as the \( \beta \) slope or Tafel constant expressed in mV/decade; \( i_a \) and \( i_c \) are anodic and cathodic current densities (A/cm\(^2\)).
Figure 2.2: Polarization characteristics (a) Activation polarization showing Tafel behaviour, (b) Cathodic concentration polarization showing limiting current density, and (c) Combined polarization (Redrawn from Jones, 1992)
Concentration polarization refers to the polarization that occurs when the corrosion process is controlled by the mass transfer of chemical species to, or from, the electrode surface. It occurs when the interfacial concentration of reducible species is small and approaches zero due to a relatively high reduction rate at the interface. At this stage, the corrosion rate is determined by the limiting rate called the limiting current density \( i_L \), which represents the maximum reduction rate possible for the corroding system. It is expressed as:

\[
i_L = \frac{D_Z n F C_B}{\delta}
\]  \hspace{1cm} (2.23)

where \( D_Z \) = diffusivity of chemical species, \( Z \); \( n \) = number of equivalents exchanged; \( F \) = Faraday’s constant (96,500 coulombs/equivalent); \( \delta \) = thickness of concentration gradient; and \( C_B \) = bulk concentration of chemical species. The equation for the concentration polarization \( \eta_{conc} \) can be defined as:

\[
\eta_{conc} = \frac{2.3 R T}{nF} \log \left( 1 - \frac{i}{i_L} \right)
\]  \hspace{1cm} (2.24)

where \( R \) = gas constant; \( T \) = temperature; and \( i \) = current density. The characteristics of concentration polarization are illustrated in Figure 2.2-b. The concentration polarization becomes apparent only when the net current density approaches the limiting current density \( i_L \), and it remains unaltered irrespective of change in polarization magnitude.

The combined polarization is a sum of activation and concentration polarization and can be expressed as in Equation 2.25. The combined polarization (Figure 2.2-c) shows only the cathodic branch, since for the anodic branch, the polarization is primarily governed by the activation process due to the abundance of metal atoms at the surface.

\[
\eta_t = \eta_{act} + \eta_{conc}
\]  \hspace{1cm} (2.25)
2.2.5 Mixed potential theory

In a corrosion process, there exist a number of oxidation and reduction reactions that take place simultaneously on the corroding metal surface. Thus, the metal can be treated as a mixed electrode that is in contact with two or more oxidation-reduction systems. Consider a two half cell reaction when zinc is immersed in hydrochloric acid:

\[ \text{Zn} \leftrightarrow \text{Zn}^{2+} + 2e^- \tag{2.26} \]
\[ 2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2 \tag{2.27} \]

Each reactions has its corresponding reversible potential \( E_{Zn/Zn^{2+}} \) and \( E_{H^+/H_2} \) and exchange current density \( i_{0,Zn/Zn^{2+}} \) and \( i_{0,H^+/H_2} \) as shown in the Figure 2.3. Although the reversible potentials for each half cell reaction are different in the environment, they proceed to the common potential or mixed potential, where the total rate of oxidation reactions is equal to the total rate of reduction reactions. Here, both anodic and cathodic currents are equal and the net current is zero. This steady state mixed potential is known as corrosion potential \( E_{corr} \) (also open circuit potential), and the current density corresponding to the corrosion potential is called the corrosion current density \( i_{corr} \).

2.2.6 Potentiodynamic anodic polarization

Anodic polarization occurs when a potential more positive than the corrosion potential \( E_{corr} \) is applied on the metal sample with the help of an external power source (Sastri, 2001). At this condition, the anodic current predominates, and the cathodic current becomes negligible. Similarly, in cathodic polarization, the cathodic current predominates over the anodic current. Potentiodynamic polarization curves are obtained by plotting the logarithm of the current response as a function of applied potential. This
Figure 2.3: Polarization of two half cell reactions for zinc in acid solution (Redrawn from Jones, 1992)
plot can provide an abundance of useful information, such as the ability of the metal to spontaneously passivate in the corroding environment, the potential range over which the metal remains under passive condition, and the corrosion current in the passive region.

A typical potentiodynamic anodic polarization curve with active, passive, and transpassive behaviour is shown in Figure 2.4. The first part of the curve is called the active region, where the metal undergoes corrosion with the increase in applied potential in the positive direction, until it reaches point B. At point B, the passive layer formation initiates, and the corresponding potential and current density are termed as primary passive potential ($E_{pp}$) and critical current density ($i_{crit}$), respectively. Beyond $E_{pp}$, the corrosion current starts decreasing as the passive layer becomes stable, and it eventually reaches the passivation current density ($i_{pass}$). On further increase in potential, the breakdown of passive film occurs at D, resulting in higher current density. This region is called the transpassive region, and the corresponding potential is the breakdown potential or pitting potential ($E_b$). The increase in the current density might also be due to the evolution of oxygen by the breakdown of water in the electrolyte (McCafferty, 2010).

### 2.2.7 Pourbaix diagram

A Pourbaix diagram is the plot drawn between potential and pH, which represents the stability of a metal as a function of electrode potential and pH of the electrolyte. This diagram provides useful thermodynamics information such as predicting the spontaneous direction of the reactions and also the information about the environmental conditions where the corrosion attacks can be prevented or reduced (Fontana, 2005). Three possible states of metallic material are described in the Pourbaix diagram: immunity, passivation,
Figure 2.4: Anodic polarization curve showing active-passive behaviour

(Redrawn from Jones, 1992)
and corrosion region. A typical Pourbaix diagram for the Fe-H₂O system is represented in Figure 2.5. In the immunity region, the metal is immune to corrosion attack; in the passive region, the metal has a tendency to be coated with an oxide or hydroxide film, depending upon the environment. In the corrosion region, the metal is stable as ionic soluble products and, thus, favours corrosion attack. The lines in the diagram are constructed with the help of the Nernst equation, as shown in Equation 2.28.

\[ E = E_0 + 2.3 \frac{RT}{nF} \log \frac{a_{\text{oxid}}}{a_{\text{red}}} \]  

(2.28)

where \( E \) = Electrode potential (volt); \( E_0 \) = Standard electrode potential (volt); \( R \) = gas constant; \( T \) = absolute temperature; \( n \) = number of electrons transferred; \( F \) = Faraday constant; \( a_{\text{oxid}} \) = activity of oxidized species; and \( a_{\text{red}} \) = activity of reduced species. The horizontal lines represent the electron transfer reaction (Reaction 2.29) and are independent of pH. The vertical lines are independent of potential and represent a non-electron transfer reaction (Reaction 2.30). The sloping lines in the diagram represent the reactions (Reaction 2.31) that are dependent on both pH and electrode potential.

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{Fe}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_2 + 2\text{H}^+ \\
\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2e^- \leftrightarrow 2\text{Fe}^{2+} + 3\text{H}_2\text{O}
\]

(2.29)  

(2.30)  

(2.31)

Besides these, there are two additional dotted lines, a and b, where line ‘a’ represents the hydrogen evolution reaction (Reaction 2.32 – 2.33) and line ‘b’ represents the oxygen evolution reaction (Equation 2.34).

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \\
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \\
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- 
\]

(2.32)  

(2.33)  

(2.34)
Figure 2.5: Pourbaix diagram for Fe-H₂O system at 25°C (Adapted from Revie and Uhlig, 2008)
2.2.8 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) also known as AC impedance technique can determine a wealth of electrochemical kinetics and mechanistic information when applied to a corrosion system (Sastri, 2001). This technique consists of perturbing the electrochemical system by superimposing a small sinusoidal AC signal (10-20 mV) over the range of frequencies. The response will be a sinusoidal current signal with the same frequency with changes in amplitude and phase angle. The relationship between the applied sinusoidal potential and the resulting current is known as the impedance (Sastri, 2001). It has several advantages over DC polarization techniques. AC impedance involves very small excitation amplitudes and remains as a non-destructive technique. The electrochemical system is perturbed to a very minimum extent when compared to the DC technique. This technique provides valuable information like double layer capacitance and can be used to study the metal/solution interface, oxide films, and the corrosion performance of organic coatings on metals (McCafferty, 2010).

2.2.8.1 Principles of EIS technique

EIS is based on Ohm’s law, according to which, resistance (R') of an electrical circuit is defined as the ratio between voltage (E) and current (I).

\[ R' = \frac{E}{I} \]  \hspace{1cm} (2.35)

The resistance is the ability of a circuit element to resist the flow of electrical current, and such a circuit element is called a resistor. For an ideal resistor, the resistance value is independent of the frequency, and the AC current and the voltage signal that pass through the resistor are in phase with each other. The impedance (Z) is equivalent to the
resistance-current-potential relationship of a DC circuit and is used for complex circuit
behaviour with one or more circuit elements. In other words, impedance is resistance to
the flow of an AC current \( Z = E/I \). When an electrochemical system is perturbed by an
applied AC signal, the system relaxes to a new steady state and the time required for this
process is called the time constant or relaxation time \( \tau \) (McCafferty, 2010). The
relaxation time \( \tau \) is given as

\[
\tau = R'C
\]

(2.36)

where \( \tau \) is in seconds; \( R' \) is resistance in ohms; and \( C \) is capacitance in farads. On
perturbing the electrochemical system, each electrode/electrolyte interface will undergo a
unique response. It facilitates many fundamental processes such as electron transfer
within the electrode, at the electrode/electrolyte interface, and from a charged species.
This rate of charge transfer depends on the resistance of the electrolyte, electrode, and on
the rate of reaction occurring at the interface. Upon analyzing this transient response, it is
possible to extract many of electrochemical properties with a single measurement.

2.2.8.2 Impedance analysis

The AC electrical circuit involved in an electrochemical system is analyzed by
utilizing complex number principles. Thus, the impedance of the electrochemical system
is expressed in terms of real \( Z'(\omega) \) and imaginary \( Z''(\omega) \) components (Jones, 1992).

\[
Z(\omega) = Z'(\omega) + Z''(\omega)
\]

(2.37)

where \( \omega = 2\pi f \) and \( f \) is frequency expressed in cycles per second (hertz). The impedance
behaviour of an electrode can be expressed in one or both of the two graphical
representations called the Nyquist plot and Bode plot. The Nyquist plot is an impedance
plane plot of an imaginary $Z''(\omega)$ component (or capacitive component of the impedance) as a function of the real $Z'(\omega)$ component (or resistive component of the impedance). A Bode plot is an alternative method of displaying the impedance data in which the absolute impedance ($|Z|$) and the phase angle ($\theta$) of the resultant waveform are plotted against the frequency (Sastri, 2001). Since these plots are the representations of the electrical circuit elements at the metal/electrolyte interface, understanding their circuit arrangement gives a clear picture of the interface.

The equivalent circuit model representing the metal/electrolyte interface is shown in Figure 2.6. This represents a common circuit model and is called a Randles cell. The electric circuit elements are arranged in such a way to represent the actual electrochemical process occurring at the metal/electrolyte interface. The polarization resistance ($R_p$) and double layer capacitance ($C_{dl}$) constitutes a parallel component and is in series with solution resistance ($R_s$). In general, each circuit element responds differently to the applied AC sinusoidal potential. When applied to a pure resistor, the current and potential waveforms would be in phase and differ only in amplitude (Sastri, 2001). The impedance of a resistor is independent of frequency, and it has only a real component. For a capacitor, the current response to a sinusoidal potential involves a $-90^\circ$ phase shift (Jones, 1992), and their impedance decreases as the frequency is raised.

A typical Nyquist plot for the illustrated equivalent circuit model is represented in Figure 2.7. The electrochemical parameters such as solution resistance ($R_s$), polarization resistance ($R_p$) or charge transfer resistance ($R_{ct}$), and double layer capacitance ($C_{dl}$) can be extracted from a Nyquist plot. The solution resistance is obtained from the point where the impedance curve meets the real axis in the high frequency region. The point where
Figure 2.6: Equivalent circuit model for an electrical double layer

(Redrawn from McCafferty, 2010)

\[ \omega_{\text{max}} = \frac{1}{R_p C_{dl}} \]

Figure 2.7: Nyquist plot corresponding to equivalent circuit

(Redrawn from McCafferty, 2010)
the impedance curve meets the real axis at the low frequency region corresponds to \((R_S + R_P)\), from which the \(R_P\) or \(R_{ct}\) can be calculated. The electrochemical reaction rate can be calculated from \(R_P\), as the corrosion rate is inversely proportional to the polarization resistance. The information about the film formation mechanism on electrodes, adsorption and desorption processes, and integrity of organic coatings can be obtained from measured capacitance (Sastri, 2001). From the shape of the Nyquist plot, one can determine the number of time constants involved in the electrochemical reaction. Each semicircle in the Nyquist plot is characteristic of a time constant associated with an electrochemical process. The Nyquist plot for the corrosion process, which includes mass transfer diffusion effects, is illustrated in Figure 2.8. The corrosion process is considered diffusion controlled when the movement of reactants and products to and from the metal surface remains as a rate determining step. In this case, the equivalent circuit model (Figure 2.8) must include an additional resistive element in the circuit called the Warburg impedance \((W)\). From the Nyquist plot, this Warburg impedance is evidenced as a 45° straight line to the axis at the low frequency end. The major shortcoming of the Nyquist plot is that the frequency dependency of impedance cannot be observed from the plot.

A graphical representation of Bode plots is shown in Figure 2.9. Unlike the Nyquist plot, frequency information can be explicitly viewed from a Bode plot. From the figure, the solid curve represents a Bode impedance plot and the dotted curve represents a Bode phase angle plot. In the Bode impedance curve, the resistances appear as horizontal lines and the capacitances appear as slanted lines (McCafferty, 2010). The value of \(C_{dl}\) can be extracted from both the Bode plots. Other advantages of Bode plots are that the frequency break points associated with each time constants can be distinctly viewed.
Figure 2.8: Nyquist plot and equivalent circuit model with diffusion component circuit

(Redrawn from McCafferty, 2010)

Figure 2.9: Bode plots (Redrawn from Sastri, 2001)
The Bode magnitude plot has a slope value of -1 for a simple kinetic controlled electrochemical reaction. The diffusion process in the electrochemical reaction is indicated by a slope of -1/2 or -1/4 in a Bode magnitude plot.

2.2.8.3 Constant phase element model

Although an electrochemical double layer with a metal/electrolyte interface looks identical to an electrical capacitor, their behaviours are not identical. The impedance spectra (Nyquist plot) for a practical electrode system will often show depressed semicircles (capacitive loops) with their centres below the real axis. This phenomenon is termed as the dispersion effect, which makes the electrochemical double layer behave as a non-ideal capacitor due to its surface heterogeneity. The double layer can be considered as an ideal capacitor only when the electrode surface is smooth and uniform. Thus, a constant phase element (CPE), \( Q_{dl} \), is used in the equivalent circuit instead of an ideal capacitor \( (C_{dl}) \) to account for the depression of semicircle. It differs only by the exponent factor used in the impedance expression of a capacitor \( (Z = 1/ (j\omega C_{dl})) \). The impedance of CPE is calculated using the following equation:

\[
Z_{CPE} = \frac{1}{Q_{dl}(j\omega)^n},
\]

where \( Z_{CPE} \) is the impedance of CPE, \( Q_{dl} \) is the proportional factor, \( j \) is \( \sqrt{-1} \), \( \omega = 2\pi f \), and ‘n’ is an exponent factor that takes a value between 0 and 1 and characterises the phase shift. Thus, the circuit element ‘\( C_{dl} \)’ in Figure 2.6 can be replaced with ‘\( Q_{dl} \)’ to represent the actual process taking place at the electrode surface. The CPE may be interpreted as a different electronic component based on the ‘n’ value. When \( n=1 \), the CPE acts as an ideal capacitor. Also, it represents a resistor when \( n=0 \) and an inductor when \( n= -1 \) and a
Warburg response when n=0.5.

2.3 Theoretical methods for corrosion inhibitor studies

2.3.1 Quantitative Structure Activity Relation (QSAR)

Quantum chemical method based on QSAR has proven to be useful in the determination of molecular structure and also in elucidating the electronic structure and reactivity of a compound (Kraka et al., 2000). Quantum chemical methods are significant in the study of electrochemistry and provide useful information about the structure and behaviour of corrosion inhibitors. In general, the addition of an inhibitor molecule to a corroding system favours the adsorption of the inhibitor over the metal surface, leading to the formation of a metal complex (Sastri, 2001). From the literature, most of the corrosion inhibitors are organic compounds that have hetero atoms and functional groups that facilitate the adsorption of the inhibitor over the metal surface. Several works have been done on the theoretical prediction of the corrosion inhibition efficiency of organic inhibitors based on quantum chemical calculations (Vosta and Eliásek, 1971; Chakrabarti, 1984; Costa and Lluch, 1984; Sayos, 1986; 2004; El Issami et al., 2007).

The prominent quantum chemical parameters of a compound are atomic charges, molecular orbital energies, dipole moment, and energy (Gece, 2008). Each parameter has its own significance in determining the reactivity or interaction between species. A number of semi-empirical methods have been developed including MNDO (modified neglect of diatomic overlap), AM1 (Austin model 1), PM3 (parameterized model number 3), and PM6 (parameterized model number 6) to perform quantum calculations. The quantum chemical indices such as the energy of the highest occupied molecular orbital
(E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE), the dipole moment (μ), and the ionization potential (I) can be extracted from quantum calculations.

The highest occupied molecular orbital (HOMO) is the orbital that could act as an electron donor, and the lowest unoccupied molecular orbital (LUMO) is the orbital that could act as electron acceptor (Gece, 2008). According to frontier molecular orbital theory, the formation of a transition state results from the interaction occurring between the frontier orbitals (HOMO and LUMO) of the reacting compounds. From the quantum studies on corrosion inhibition, the energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency of the molecule to donate electrons, and this energy is directly related to ionization potential of the molecule. Thus, a higher value of E_{HOMO} indicates a better tendency towards the donation of electrons to acceptor molecules with low energy or an empty molecular orbital. It favours the adsorption of molecules on the metal surface and, hence, has higher inhibition efficiency (Gece, 2008). On the other hand, the energy of the lowest unoccupied molecular orbital (E_{LUMO}) indicates the tendency of the molecule to accept electrons, and this energy is directly related to electron affinity. Therefore, the lower the value of E_{LUMO}, more probable it is that the molecule will accept electrons (Gece, 2008).

The energy gap of the molecule is given by the difference between E_{LUMO} and E_{HOMO} (ΔE= E_{LUMO} - E_{HOMO}). The energy difference or energy gap (ΔE) is another important parameter, and it determines the reactivity of inhibitor molecules in terms of their adsorption on a metal surface (Obi-Egbedi et al., 2011). The lower the ΔE value, the higher the reactivity of the inhibitor molecules, as the energy required for electron
removal from the last occupied orbital will be low, resulting in greater inhibition efficiency (Gece, 2009). This energy difference can also be related to the softness or hardness of the molecule. In general, soft molecules are more reactive than hard molecules. A larger energy gap indicates high stability for the molecule in a chemical reaction and, hence, a hard molecule. A smaller energy gap represents easier polarizability and, hence, a soft molecule. The other important quantum parameter is dipole moment (µ). Dipole moment is the measure of polarity of a polar covalent bond (Gece, 2008). In general, molecules have such dipole moment due to the non-uniform distribution of positive and negative charge on various atoms. A lower dipole moment favours the accumulation of a molecule on the surface (Khalil, 2003). From all the quantum chemical indices, the adsorption property of the species based on its molecular structure can be derived.

2.3.2 Hard and Soft Acid and Base Theory (HSAB)

According to Pearson’s hard and soft acid and base theory, hard acids tend to bind with hard bases and soft acids tend to bind with soft bases. The characteristic properties of a hard acid (electron acceptor) or a hard base (electron donor) are small atomic radius, a highly effective nuclear charge, and low polarizability. Conversely, the softness of an acid or base is characterized by a large atomic radius, a low effective nuclear charge, high polarizability, and low electronegativity (Sastri, 2001). The hard and soft acid and base (HSAB) concept can be applied in establishing the corrosion inhibition properties of a given compound. Based on the HSAB principle (Sastri, 2001), the inhibitors can be described as hard (PO$_4^{3-}$), soft (RSH, RS’, R$_3$P), or borderline inhibitors (C$_6$H$_5$NH$_2$).
The parameters including hardness and softness of the molecule, electron affinity, ionization energy, electronegativity, and the number of electrons transferred can be obtained from the calculated quantum chemical indices using the QSAR method. These parameters can provide information on the relative hardness/or softness of the species. Ionization potential (I) and electron affinity (A) are related to \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \), as shown in the following equations:

\[
I = -E_{\text{HOMO}} \quad (2.39)
\]

\[
A = -E_{\text{LUMO}} \quad (2.40)
\]

These calculated parameters can be related to electronegativity (\( \chi \)) and absolute hardness (\( \eta \)) using the equations below:

\[
\chi = \frac{(I + A)}{2} \quad (2.41)
\]

\[
\eta = \frac{(I - A)}{2} \quad (2.42)
\]

Global softness (\( \sigma \)) can be calculated from the hardness value as shown below:

\[
\sigma = \frac{1}{\eta} \quad (2.43)
\]

The number of electrons transferred (\( \Delta N \)) from adsorbed molecules to metal atoms can be calculated from the following equation:

\[
\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{amine}}}{2(\eta_{\text{Fe}} + \eta_{\text{amine}})} \quad (2.44)
\]

where \( \chi_{\text{Fe}} \) and \( \chi_{\text{amine}} \) are the absolute electronegativity of iron and amine studied and \( \eta_{\text{Fe}} \) and \( \eta_{\text{amine}} \) represent the absolute hardness of the iron and amines. Similar to quantum indices, these parameters can also be utilized for determining the interactions between reacting species and the metal surface.
3. CORROSION EXPERIMENTS

This work employs two corrosion measuring techniques, i.e., electrochemical and weight loss, to reveal the corrosiveness of various amines on carbon steel and stainless steel. The electrochemical technique involves short-term exposure of test specimens in a given process environment to obtain the corrosion rate and electrokinetic information of the tested specimen. The weight loss technique involves long-term exposure of the specimen in a given process environment to obtain the long-term corrosion rate and metal surface information. The information relevant to the corrosion experiments, which includes the experimental setup, experimental procedure, solution preparation, specimen preparation, sample analyses, and data analyses, are provided in the following sections.

3.1 Electrochemical experiments

3.1.1 Solution preparation

The electrochemical experiments were carried out using five different types of amines that are commonly used and being studied for their uses in CO₂ capture applications, i.e., MEA, DEA, MDEA, AMP, and PZ. Since their service concentrations in gas treating applications are 32 wt% (≈ 5.25 kmol/m³) MEA, 25 – 30 wt% (≈ 2.43 – 2.95 kmol/m³) DEA, and 43 – 53 wt% (≈ 3.66 – 4.50 kmol/m³) MDEA (Kohl and Nielsen, 1997), amine concentration of 5.0 kmol/m³ was chosen for all tested amines except AMP, for corrosiveness comparison purpose. By nature, aqueous AMP solutions crystallize under CO₂-saturated conditions at higher amine concentrations. Hence, in this work, a concentration of 4.0 kmol/m³ of AMP solution was tested, instead of a 5.0
kmol/m³ solution. The aqueous amine solutions were prepared by diluting the amine reagents with deionized water, and their concentrations were determined by titration with a 1.0 N standard hydrochloric acid (HCl) solution using methyl orange as an indicator. All tested amine solutions were loaded with dissolved CO₂ to achieve a desired CO₂ loading by purging CO₂ gas (Praxair, research grade, ON) into the amine solution. The CO₂ loading measurements were done as per the Association of Official Analytical Chemists (AOAC) method by titrating with 1.0 N HCl solution using a Chittick apparatus (Horeitz, 1975).

In some experiments, process contaminants, including thiosulfate, oxalate, sulfite, and chloride, were added to the amine solution to study their effects on corrosion. Oxalate was made up by administering its respective acid form of anion, i.e., oxalic acid, in the prepared amine solutions. Thiosulfate, sulfite, and chloride were prepared by dissolving its respective salt forms, i.e. sodium thiosulfate, sodium sulfite, and sodium chloride into the amine solutions. The tested concentration of the process contaminant was 10,000 ppm, representing actual ranges of the process contaminant present in the service amine solution. Purities of all the chemicals used are summarized in Table 3.1.

### 3.1.2 Specimen preparation

Carbon steel 1018 (CS1018) and stainless steel 304 and 316 (SS304 and SS316) were chosen as the specimen materials since they are common materials for process equipment and pipings in gas treating plants and are also recommended for post combustion CO₂ capture processes (Billingham et al., 2011). In addition, stainless steel 430 (SS430) was used for validating the experimental setup and procedures, as
Table 3.1: Summary of the chemical reagents used in the experiments

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Absorption solvent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoethanolamine (C_2H_7NO)</td>
<td>Sigma Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Diethanolamine (C_4H_11NO_2)</td>
<td>Sigma Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Methyl Diethanolamine (C_5H_13NO_2)</td>
<td>Sigma Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>2-Amino-2-methyl-1-propanol (C_4H_11NO)</td>
<td>Sigma Aldrich</td>
<td>95%</td>
</tr>
<tr>
<td>Piperazine (C_4H_10N_2)</td>
<td>Sigma Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td><strong>Process contaminant</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxalic acid (H_2C_2O_4)</td>
<td>Sigma Aldrich</td>
<td>98%</td>
</tr>
<tr>
<td>Sodium thiosulfate (Na_2S_2O_3)</td>
<td>Sigma Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Sodium sulfite (Na_2SO_3)</td>
<td>Fisher Scientific</td>
<td>99.3%</td>
</tr>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>EMD</td>
<td>99%</td>
</tr>
<tr>
<td><strong>Titration chemicals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl orange (C_{14}H_{14}N_3NaO_5S)</td>
<td>Sigma Aldrich</td>
<td>0.1%</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl)</td>
<td>Fisher Scientific</td>
<td>1.000 ± 0.005 N</td>
</tr>
<tr>
<td><strong>ASTM standardization solution</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphuric acid (H_2SO_4)</td>
<td>BDH</td>
<td>95-98%</td>
</tr>
<tr>
<td><strong>Degreasing solvent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol (CH_3OH)</td>
<td>Fisher Scientific</td>
<td>99.9%</td>
</tr>
</tbody>
</table>
recommended by the ASTM standard. All tested specimens were cylindrical in shape with a height of 0.80 cm, outside diameter of 1.20 cm, and center hole diameter of 0.60 cm, as shown in Figure 3.1. Their chemical compositions are given in Table 3.2. Before the tests, the specimens were prepared by wet grinding with 600-grit silicon carbide (SiC) papers using deionized water and then were degreased with high purity methanol and dried with hot air in accordance with the ASTM G1-03 (2003) standard.

3.1.3 Experimental setup

The experiments were conducted using an electrochemical corrosion setup, illustrated in Figure 3.2. The setup consisted of two main components, the 100 ml jacketed microcell with three electrode assembly (Model 636 ring-disk electrode assembly, Princeton Applied Research (PAR), USA) and a computer-controlled potentiostat (Basic Electrochemical System, PAR, USA) with a corrosion analyzer, namely PowerCORR & PowerSINE Corrosion software (PAR, USA). Within the microcell, specimens (CS1018, SS304, SS316 and SS430) with a surface area of 3.02 cm² served as the working electrodes (WE), while silver/silver chloride (Ag/AgCl) and platinum (Pt) were used as the reference electrode (RE) and the counter electrode (CE), respectively. The microcell was equipped with a gas supply system consisting of CO₂ and nitrogen (N₂) cylinders and gas flow meters, a water-cooled condenser to minimize vapourization loss of test solutions, and the heater-circulator to control the temperature of the test solution within ± 1.0°C of the desired temperature. In addition, for each experiment, a pH meter (pH510 series, USA) with ± 0.01 accuracy, and a conductivity meter (YSI 3200) with ± 0.1% accuracy were used for pH and conductivity.
Figure 3.1: A sketch of a specimen used for electrochemical corrosion experiments
Table 3.2: Chemical compositions of the tested specimens

<table>
<thead>
<tr>
<th>Types of specimen</th>
<th>Chemical composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel 1018</td>
<td>C - 0.175</td>
</tr>
<tr>
<td></td>
<td>Mn - 0.750</td>
</tr>
<tr>
<td></td>
<td>Fe - balance</td>
</tr>
<tr>
<td>Stainless steel 304</td>
<td>C – 0.052</td>
</tr>
<tr>
<td></td>
<td>Cu – 0.449</td>
</tr>
<tr>
<td></td>
<td>Mo – 0.325</td>
</tr>
<tr>
<td></td>
<td>Cr – 18.163</td>
</tr>
<tr>
<td></td>
<td>Mn – 1.698</td>
</tr>
<tr>
<td></td>
<td>N – 0.045</td>
</tr>
<tr>
<td></td>
<td>Ni – 8.215</td>
</tr>
<tr>
<td></td>
<td>S – 0.01</td>
</tr>
<tr>
<td></td>
<td>P – 0.035</td>
</tr>
<tr>
<td></td>
<td>Si – 0.277</td>
</tr>
<tr>
<td></td>
<td>Fe - balance</td>
</tr>
<tr>
<td>Stainless steel 316</td>
<td>C – 0.022</td>
</tr>
<tr>
<td></td>
<td>Cu – 0.41</td>
</tr>
<tr>
<td></td>
<td>Mo – 2.02</td>
</tr>
<tr>
<td></td>
<td>Cr – 16.35</td>
</tr>
<tr>
<td></td>
<td>Mn – 1.42</td>
</tr>
<tr>
<td></td>
<td>N – 0.062</td>
</tr>
<tr>
<td></td>
<td>Ni – 10.05</td>
</tr>
<tr>
<td></td>
<td>S – 0.022</td>
</tr>
<tr>
<td></td>
<td>P – 0.038</td>
</tr>
<tr>
<td></td>
<td>Si – 0.40</td>
</tr>
<tr>
<td></td>
<td>Co – 0.18</td>
</tr>
<tr>
<td></td>
<td>Fe - balance</td>
</tr>
<tr>
<td>Stainless Steel 430</td>
<td>Al - 0.014</td>
</tr>
<tr>
<td></td>
<td>C - 0.046</td>
</tr>
<tr>
<td></td>
<td>Co - 0.030</td>
</tr>
<tr>
<td></td>
<td>Cr -16.280</td>
</tr>
<tr>
<td></td>
<td>Cu - 0.120</td>
</tr>
<tr>
<td></td>
<td>Mn - 0.410</td>
</tr>
<tr>
<td></td>
<td>Mo - 0.020</td>
</tr>
<tr>
<td></td>
<td>Ni - 0.140</td>
</tr>
<tr>
<td></td>
<td>P - 0.023</td>
</tr>
<tr>
<td></td>
<td>S - 0.05</td>
</tr>
<tr>
<td></td>
<td>Si – 0.420</td>
</tr>
<tr>
<td></td>
<td>Sn – 0.020</td>
</tr>
<tr>
<td></td>
<td>V – 0.050</td>
</tr>
<tr>
<td></td>
<td>Fe - balance</td>
</tr>
</tbody>
</table>
Figure 3.2: Electrochemical corrosion setup

(a) A schematic diagram and (b) A photograph (Original in colour)
measurements, respectively. Both the pH and conductivity meters were calibrated regularly with the standard solutions.

3.1.4 Experimental procedure

The microcell cell was charged with 100 cm$^3$ of the prepared amine solution. The test solution was purged with CO$_2$ at a constant flow rate (2.0 cm$^3$/min) throughout the experiment to maintain CO$_2$ saturation or was purged with either N$_2$ or a mixture of N$_2$ and CO$_2$ to maintain the required CO$_2$ loading (0.20, 0.30, 0.50 mol CO$_2$/mol amine). The temperature of the solution was gradually raised and maintained at a set value by circulating hot water through the outer jacket of the microcell. Once the temperature of the solution was within ± 1.0°C of the set temperature, the solution samples were taken from the microcell for the solution analysis of amine concentration, CO$_2$ loading, pH, and conductivity.

After this solution analysis, three electrodes (WE, RE and CE) were assembled into the microcell. All electrical connections were established between the electrodes and the potentiostat. The open circuit potential (OCP) of the specimen against the reference electrode was recorded until reaching the steady state potential value. At the steady state potential, impedance measurements were performed at a frequency range from 10 kHz to 10 mHz and a sinusoidal voltage amplitude of ±10 mV. After the impedance measurements, a potentiodynamic cyclic polarization scan was carried out with a scan rate of 0.166 mV/s. All the experimental data, impedance curves, and polarization curves were recorded and stored in the data acquisition system. When the experiment was complete, a sample of the solution was taken again to measure pH, conductivity, amine
3.1.5 Validation of experimental setup and procedure

Prior to the experiments, the experimental setup and procedures were validated for both potentiodynamic polarization and impedance measurements by conforming to ASTM G5-94 (2004) and ASTM G106-89 (2010) standards. Stainless steel 430 was used as the working electrode for both measurements for validation purpose. The ASTM polarization test was conducted using 1.0 N sulfuric acid (H₂SO₄) solution at 30.0 ± 1.0°C. The ASTM impedance test was carried out in 0.495 M sodium sulfate (Na₂SO₄) solution containing 0.005 M H₂SO₄ at 30.0 ± 1.0°C. The microcell was de-aerated by purging N₂ gas at a flow rate of 150 cm³/min for 60 minutes prior to the immersion of the tested specimen. The results obtained were then compared with the ASTM reference bands generated from a number of laboratories. Figures 3.3 and 3.4 illustrate that the obtained results fall within the ASTM reference bands, thereby conforming to ASTM standards and validating the experimental setup and procedures.

3.1.6 Data Analysis

a) Tafel plot

From the potentiodynamic polarization experiment, a plot of log i (log current density) as a function of potential was obtained. The Tafel extrapolation method was employed to estimate the corrosion current density (iₜₐ₇) from the polarization curve. The extrapolation of linear portion (± 250 mV from OCP) of the anodic and cathodic curves to the OCP (Figure 3.5) provides an estimate of iₜₐ₇, which can be translated to corrosion...
Figure 3.3: Validation of potentiodynamic polarization experiments using ASTM G5-94 (2004) standard
Figure 3.4: Validation of impedance experiments using ASTM G106-89 (2010)

(a) Nyquist plot  (b) Bode plot- Phase angle vs Frequency  (c) Bode plot- Impedance magnitude vs Frequency
Figure 3.5: Tafel extrapolation method (Redrawn from Jones, 1992)
rate in mmpy as expressed below:

\[ CR = \frac{3.27 \times 10^{-3} \times i_{\text{corr}} \times EW}{D} \]  

(3.1)

where CR is the corrosion rate (mmpy), \(i_{\text{corr}}\) is the corrosion current density (µA/cm²), EW is the equivalent weight of carbon steel specimen (g/equivalent), and D is the density of the specimen (g/cm³).

b) **Potentiodynamic cyclic polarization**

Potentiodynamic cyclic polarization curves provide kinetics information including corrosion current density \(i_{\text{corr}}\), critical current density \(i_{\text{crit}}\), primary passivation potential \(E_{\text{pp}}\), passivation current density \(i_{p}\), and breakdown potential (or pitting potential) \(E_{b}\). By conducting a reverse polarization scan, the tendency of occurrence of pitting corrosion under a given test condition was identified. A reverse scan that lies to the left of the forward scan (negative hysteresis) suggests no pitting tendency (Figure 3.6-a), whereas a reverse scan that lies to the right of the forward scan (positive hysteresis) suggests pitting tendency (Figure 3.6-b). The other factor that determines the extent of pitting corrosion is repassivation or protection potential \(E_{\text{rp}}\). The potential at which the hysteresis loop is completed during the reverse scan after the propagation of pitting corrosion is called the repassivation potential \(E_{\text{rp}}\). The more positive \(E_{\text{rp}}\), or the closer to the pitting potential, the less likely the propagation of pitting corrosion.

c) **Impedance measurement**

The impedance parameters, including solution resistance \(R_s\), charge transfer resistance \(R_{ct}\), and double layer capacitance \(C_{dl}\), were extracted from a Nyquist plot.
Figure 3.6: Cyclic potentiodynamic polarization curves (a) No pitting (b) Pitting

(Redrawn from Srinivasan, 2006)
Charge transfer resistance was obtained from the diameter of the semicircle in Nyquist plot. The double layer capacitance ($C_{dl}$) was calculated using the frequency attained at the maximum of the semicircle, ($F_{max}$) and $R_{ct}$, with the help of Equation (3.2).

$$C_{dl} = \frac{1}{2\pi F_{max} R_{ct}}$$  \hspace{1cm} (3.2)

where $C_{dl}$ is in $\mu$F/cm$^2$, $F_{max}$ is in Hz, and $R_{ct}$ and $R_s$ are in ohm cm$^2$. In analysing the compactness of the passive layer formed on the specimen in each system, Warburg coefficients ($\sigma_w$) were compared. $\sigma_w$ is in $\Omega$.cm$^2$/s$^{0.5}$ and was obtained from the slope of Randle’s plot ($\text{Re}Z$ Vs $\frac{1}{\omega^{0.5}}$). The ZSimpWin V3.10 software program from PAR, which is based on non-linear least squares, was employed to establish the equivalent circuit model and to fit the impedance data obtained from the experiments.

3.2 Weight loss experiments

3.2.1 Specimen and solution preparation

Carbon steel 1018 and stainless steel 304 specimens were used for the weight loss experiments. The specimens were flat and rectangular in shape with the dimensions of 1.0 inch height, 1.0 inch width, and 0.125 inch thickness (Figure 3.7). The tested specimens were 600 grit surface finished, and the amine solutions were prepared in a similar manner to that of the electrochemical experiments.

3.2.2 Experimental setup

The setup used for the weight loss experiments is shown in Figure 3.8. The setup consisted of two jacketed cylindrical glass corrosion cells covered with a metal lid. Each
Figure 3.7: A sketch of the weight loss specimen
Figure 3.8: Weight loss setup (a) A schematic diagram and (b) A photograph

(Original in colour)
glass cell was equipped with a gas dispenser, a thermometer, a water cooled condenser, and a glass specimen hook. The desired solution temperature was achieved by circulating hot water through the outer jackets of the glass cells with the help of the heater-circulator. Depending on the test conditions, the required gas, such as CO\textsubscript{2}, was purged into the test solution. Vapourization loss of the test solution was minimized by means of the water-cooled condenser provided for each corrosion cell. A sampling port per each cell was provided for solution analysis.

### 3.2.3 Experimental procedure

The test solution saturated with CO\textsubscript{2} was transferred to the weight loss corrosion cells. The tested specimens were weighed with the microbalance to an accuracy of ± 0.10 mg. Each weighed specimen was hung on the glass specimen hook attached to the corrosion cell. The thermometer was placed in each corrosion cell, and the condenser was fitted to the metal lid. Once the water temperature reached 80°C, the hot water was circulated through the outer jacket of each glass cell. The CO\textsubscript{2} gas was purged into the solution throughout the experiment to maintain the CO\textsubscript{2} saturation. The solution concentration, CO\textsubscript{2} loading, pH, and conductivity were regularly monitored throughout the experiments. The corroded specimens were removed from the corrosion cell at specific time intervals (7, 14, 21, and 28 days) and then cleaned using the ASTM procedure explained in section 3.2.4. The specimens were then weighed to determine the weight loss and corrosion rate.
3.2.4 Specimen cleaning procedure

ASTM standard G1-03 (2003) was followed to clean the specimens after testing and to remove any corrosion products that might form on the metal surface without significant removal of the base metal. This procedure comprised both mechanical and chemical cleaning. In the mechanical cleaning, the specimen was initially washed under running tap water. Loose bulky corrosion products were removed using a non-metallic bristle by brushing lightly over the specimen. The specimens were then dried with air and weighed. In cases in which the corroded specimens were covered with tenacious corrosion products, sequential mechanical and chemical cleanings were carried out. The chemical cleaning involved repeated immersions of the specimens in the specific cleaning solution recommended by ASTM G1-03 (2003) for the removal of corrosion products with minimal dissolution of any base metal. For iron and steel, the cleaning solution was a mixture of 1000 cm³ hydrochloric acid (HCl), 20 g antimony trioxide (Sb₂O₃), and 50 g stannous chloride (SnCl₂). The immersion time was 1.0 minute per cycle, and the immersion temperature was 25°C. The cleaning cycles were repeated on specimens a number of times, and the mass loss of the specimen after each cycle was determined. For stainless steel specimens, the recommended cleaning solution was 100 ml nitric acid (HNO₃) made up to 1000 ml with reagent water. The immersion time was 2.0 minutes per cycle, and the immersion temperature was 60°C. The mass loss was then plotted against the number of cleaning cycles as shown in Figure 3.9. Two lines AB and BC were obtained. Point B, which was the intersection of the two lines, represents the mass loss due to corrosion.
Figure 3.9: Mass loss of corroded specimens resulting from repetitive cleaning cycles
3.2.5 Data analysis

The corrosion rate was calculated from the resulting mass loss obtained from Figure 3.9 by using the following equation:

\[
CR = \frac{K \times W}{A \times T \times D}
\] (3.3)

where \( CR \) is the corrosion rate in mmpy, \( K \) is \( 8.76 \times 10^4 \) (constant for converting units of \( CR \)), \( W \) is the mass loss in g, \( A \) is the area in cm\(^2\), \( T \) is the time of exposure in hours, and \( D \) is the density of metal in g/cm\(^3\). This equation assumes that the obtained mass loss is due to general corrosion, not localized corrosion such as pitting or intergranular corrosion.

3.3 Surface analysis

The surface analyses of the specimens from both electrochemical and weight loss experiments were carried out to characterize corrosion products or passive film and reveal any localized corrosion that might occur on the specimen. X-ray Powder Diffraction (XRD) spectra for the specimens were recorded on a Bruker Discover diffractometer using nickel-filtered Cu K\(\alpha\) (0.154056 nm) as the radiation source. The presence of crystalline phases over metal surface was identified through comparison with the reference data from the International Centre for Diffraction Data (ICDD) files. Scanning electron microscopy (SEM) images were captured using a JSM-5600 (JEOL, USA) microscope. The elemental mapping of the microscopic images was performed with Energy-dispersive X-ray Spectroscopy (EDS) using an EDAX Genesis 7000 model.
4. RESULTS AND DISCUSSION

This chapter presents and discusses the experimental results on corrosion of carbon steel 1018 (CS1018) and stainless steel 304 (SS304) materials in various single and blended amines obtained through electrochemical and weight loss tests. The effects of process contaminants on the corrosion behaviour of various amines are also discussed. The corrosion database generated will help in the selection of proper amine systems suitable for carbon capture processes in terms of minimum corrosion difficulties. All tested parameters and conditions are presented in Table 4.1.

4.1 General corrosion behaviour of CS1018 in aqueous amine-CO₂ environments

The corrosivity of carbon steel in aqueous amine-CO₂ environments is typically influenced by process parameters. The parametric effect on corrosion was tested by carrying out the electrochemical corrosion experiments described in Chapter 3. MEA was chosen as a representative for CO₂ absorption solvents due to its common use in gas treating plants, as well as in post-combustion CO₂ capture units. The process parameters of interest are solution temperature and CO₂ loading of solution.

4.1.1 Effect of solution temperature

Corrosion behaviour of CS1018 in 5.0 kmol/m³ MEA aqueous solution containing a CO₂ loading of 0.20 mol/mol was experimentally evaluated at three different solution temperatures: 40, 60, and 80°C. The results in Figure 4.1 and Table 4.2 show that the solution temperature significantly affects corrosion behaviour and rate. As the solution temperature increases, both anodic and cathodic polarization curves (Figure 4.1-a) shift to
**Table 4.1:** Tested parameters and conditions for corrosion experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test Condition</th>
</tr>
</thead>
</table>
| Specimen                                       | Carbon steel 1018  
Stainless steel 304  
Stainless steel 316                                                                                                                                          |
| Absorption solvents                            | Monoethanolamine (MEA)  
Diethanolamine (DEA)  
Methyl Diethanolamine (MDEA)  
2-amino-2-methyl 1-propanol (AMP)  
Piperazine (PZ)  
MEA- PZ  
MEA-MDEA  
MEA- AMP  
MDEA - PZ  
AMP - PZ |
| Amine concentration (kmol/m³)                  | 4.0 & 5.0                                                                                                                                                  |
| CO₂ Loading (mol CO₂ /mol amine)               | 0.20, 0.30, 0.50 & CO₂ saturation*                                                                                                                         |
| Solution temperature (°C)                      | 40, 60, 80                                                                                                                                                 |
| Mixing ratio of blended solvents (mol : mol)   | 1:1                                                                                                                                                        |
| Process contaminants                            | 10,000 ppm  
(Thiosulfate, oxalate, sulfite, and chloride)                                                                                                                                                   |

*CO₂ saturation loading (mol CO₂ /mol amine) at 80°C and 5.0 kmol/m³ amine concentration:

- MEA - 0.53 mol/mol
- DEA - 0.40 mol/mol
- MDEA - 0.14 mol/mol
- PZ – 0.82 mol/mol

*CO₂ saturation loading (mol CO₂ /mol amine) at 80°C and 4.0 kmol/m³ amine concentration:

- AMP – 0.51 mol/mol
Figure 4.1: Effect of temperature on (a) polarization behaviour and (b) corrosion rate of CS1018 in 5.0 kmol/m³ MEA at 0.20 mol CO₂/mol amine loading.
Table 4.2: Summary of pH, conductivity, and electrochemical parameters for different amine systems

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental Conditions</th>
<th>pH</th>
<th>σ (mS/cm)</th>
<th>βa (mV/decade)</th>
<th>βc (mV/decade)</th>
<th>Ecorr (mV)</th>
<th>Icorr (µA)</th>
<th>Corrosion rate (mpy)</th>
<th>Rct (ohm cm²)</th>
<th>Cdl(µF/cm²)</th>
<th>Pitting Tendency</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>5.0 kmol/m³, 80°C, 0.53 mol/mol</td>
<td>8.48±0.03</td>
<td>48.47±1.40</td>
<td>123.20±12.00</td>
<td>71.12±4.94</td>
<td>-749.14±0.50</td>
<td>1027.00±3.00</td>
<td>4.17±0.02</td>
<td>74.94±2.38</td>
<td>269.92±8.57</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³, 40°C, 0.64 mol/mol</td>
<td>8.21±0.07</td>
<td>39.32±0.55</td>
<td>160.84±5.81</td>
<td>107.71±15.31</td>
<td>-734.76±10.00</td>
<td>435.60±20.00</td>
<td>1.69±0.07</td>
<td>212.49±1.02</td>
<td>397.13±1.05</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³, 40°C, 0.20 mol/mol</td>
<td>10.51±0.03</td>
<td>20.54±0.23</td>
<td>102.39±0.80</td>
<td>52.03±1.30</td>
<td>-835.60±7.00</td>
<td>54.03±3.00</td>
<td>0.08±0.02</td>
<td>862.51±0.56</td>
<td>408.45±1.18</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³, 60°C, 0.20 mol/mol</td>
<td>10.09±0.02</td>
<td>24.58±0.40</td>
<td>109.16±0.28</td>
<td>57.95±1.70</td>
<td>-819.46±1.00</td>
<td>177.80±1.20</td>
<td>0.27±0.02</td>
<td>388.06±7.20</td>
<td>341.58±8.60</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³, 80°C, 0.20 mol/mol</td>
<td>9.95±0.01</td>
<td>26.16±0.04</td>
<td>114.15±1.70</td>
<td>67.21±0.15</td>
<td>-801.42±2.00</td>
<td>475.30±6.00</td>
<td>0.62±0.02</td>
<td>119.66±8.77</td>
<td>707.85±9.10</td>
<td>No</td>
</tr>
<tr>
<td>DEA</td>
<td>5.0 kmol/m³, 80°C, 0.40 mol/mol</td>
<td>8.41±0.04</td>
<td>14.59±0.31</td>
<td>103.98±5.12</td>
<td>69.33±1.22</td>
<td>-748.45±0.60</td>
<td>610.40±8.20</td>
<td>2.37±0.03</td>
<td>156.94±0.54</td>
<td>333.85±1.16</td>
<td>Yes</td>
</tr>
<tr>
<td>MDEA</td>
<td>5.0 kmol/m³, 80°C, 0.14 mol/mol</td>
<td>8.85±0.07</td>
<td>4.76±0.52</td>
<td>100.57±1.00</td>
<td>91.36±3.20</td>
<td>-768.04±0.76</td>
<td>230.35±0.35</td>
<td>0.89±0.02</td>
<td>295.38±3.08</td>
<td>459.96±2.02</td>
<td>No</td>
</tr>
<tr>
<td>AMP</td>
<td>4.0 kmol/m³, 80°C, 0.51 mol/mol</td>
<td>8.95±0.13</td>
<td>25.66±0.20</td>
<td>110.71±3.38</td>
<td>67.99±1.00</td>
<td>-744.13±12.00</td>
<td>801.55±20.50</td>
<td>3.11±0.08</td>
<td>92.34±1.21</td>
<td>375.25±3.15</td>
<td>No</td>
</tr>
<tr>
<td>PZ</td>
<td>5.0 kmol/m³, 80°C, 0.82 mol/mol</td>
<td>8.46±0.03</td>
<td>14.19±0.06</td>
<td>135.85±8.40</td>
<td>77.33±10.50</td>
<td>-755.00±0.30</td>
<td>423.25±4.20</td>
<td>1.64±0.02</td>
<td>243.16±2.17</td>
<td>347.07±2.98</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³, 80°C, 0.50 mol/mol</td>
<td>9.63±0.01</td>
<td>15.36±0.21</td>
<td>100.87±5.63</td>
<td>67.36±3.26</td>
<td>-783.17±9.32</td>
<td>122.20±8.20</td>
<td>0.47±0.03</td>
<td>530.47±10.62</td>
<td>412.75±0.47</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³, 80°C, 0.30 mol/mol</td>
<td>10.03±0.03</td>
<td>14.05±0.12</td>
<td>94.91±0.60</td>
<td>51.90±0.70</td>
<td>-811.69±5.00</td>
<td>86.29±2.40</td>
<td>0.33±0.01</td>
<td>898.91±5.10</td>
<td>631.18±3.58</td>
<td>No</td>
</tr>
</tbody>
</table>

σ = conductivity; βa = anodic Tafel slope; βc = cathodic Tafel slope; Ecorr = corrosion potential; Icorr = corrosion current; Rct = charge transfer resistance; Cdl = double layer capacitance.
the positive direction of current densities. This suggests that increasing the solution temperature enhances both the rate of iron dissolution and rate of oxidizing agent reduction, thereby inducing a greater corrosion rate (Figure 4.1b). The enhancement of the rate of oxidizer reduction is a result of the increase in dissociation rate of protonated alkanolamine ion (RNH$_3^+$) and bicarbonate ion (HCO$_3^-$) in the bulk MEA solution from increasing the temperature, as shown in Reactions 4.1- 4.2 (Danckwerts et al., 1967).

\[
\text{RNH}_3^+ \leftrightarrow \text{RNH}_2 + \text{H}^+ \quad (4.1)
\]

\[
\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \quad (4.2)
\]

where RNH$_2$ and CO$_3^{2-}$ denote primary amine and carbonate ion respectively. This is evident by the increase in hydrogen ion (H$^+$) concentration or the decrease in solution pH (Table 4.2). The cyclic polarization curves of all tested temperatures exhibit negative hysteresis, indicating no pitting tendency on the metal surface.

In addition to the polarization results, the impedance results also show a similar increasing trend of corrosion rate as a result of the increasing solution temperature. As illustrated in Table 4.2, charge transfer resistance (R$_{ct}$) decreases with solution temperature, causing the corrosion rate to increase. From the Nyquist plot (Figure 4.2-a) two depressed semicircles (two time constants) can be observed at high and medium frequency ends, which indicates that the corrosion mechanism is controlled by two processes. The high frequency semicircle reflects the adsorption of chemical species taking place at the metal surface, and the semicircle at the medium frequency region is attributable to the charge transfer process at the double layer. The diameter of the medium frequency semicircle decreases with temperature, indicating the decrease in R$_{ct}$ and corresponding increase in corrosion rate. From the Bode-phase plot (Figure 4.2-b),
Figure 4.2: Effect of temperature on (a) Nyquist plot and (b) Bode – phase angle plot for CS1018 in 5.0 kmol/m³ MEA at 0.20 mol CO₂/mol amine loading
the presence of two time constants can be observed as two distinct peaks, one each at the
high and medium frequency regions for all the temperatures.

The reason for the appearance of two capacitive loops (semicircles) under this test
condition could be due to the adsorption of free amine over the carbon steel surface,
facilitating the formation of an adsorbed layer. The availability of high free amine
concentration in 0.20 mol CO₂/mol amine solution can possibly favour adsorption
process. A similar kind of amine adsorption over the steel surface that offers corrosion
inhibition has been reported in the literature (Lin et al., 2002; Garcia-Arriaga et al.,
2010). Since amine has a functional groups with hetero atoms (N and O atoms with lone
pairs of electrons), these groups can act as adsorption centre and possibly take part in the
adsorption process, offering corrosion protection. The type of adsorption can be either
physical or chemical adsorption.

The impedance results were interpreted in terms of an equivalent circuit (Gao and
Liang, 2007; Morad, 2007; Garcia-Arriaga et al., 2010) shown in Figure 4.3. The
parameters of interest, such as solution resistance (Rₛ), charge transfer resistance (Rₜ),
double layer capacitance (Qₜ), adsorbed layer resistance (Rₐ), and adsorbed layer
capacitance (Qₐ) can be extracted from the equivalent circuit. The Nyquist plot obtained
at 40°C, fitted to the equivalent circuit, is shown in Figure 4.4, and the extracted
parameters for all the conditions are presented in Table 4.3.

From Table 4.3, the value of nₐ was found in the range of 0.79-0.88, which
indicates that the adsorbed film over the carbon steel surface was inhomogeneous. The
resistance (Rₐ) associated with the adsorbed film increased with increasing the
temperature from 40 to 60°C, which suggests the possibility of chemical adsorption, as it
Figure 4.3: Equivalent circuit model for fitting impedance results obtained for CS1018 tested in 5.0 kmol/m³ MEA solution at 0.20 mol CO₂/mol amine loading condition.

Figure 4.4: Nyquist plot for CS1018 in 5.0 kmol/m³ MEA solution at 0.20 mol CO₂/mol amine loading condition at 80°C drawn from experimental and fitted data.
Table 4.3: Equivalent circuit element values that best fitted with the impedance data for carbon steel corrosion in MEA system at different temperature

<table>
<thead>
<tr>
<th>Fitted parameters</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Solution resistance, $R_s$ (ohm cm$^2$)</td>
<td>7.66</td>
</tr>
<tr>
<td>Adsorbed layer resistance, $R_{al}$ (ohm cm$^2$)</td>
<td>61.7</td>
</tr>
<tr>
<td>Adsorbed layer capacitance, $Q_{al}$:</td>
<td></td>
</tr>
<tr>
<td>$Y_{al} \times 10^{-4}$ (ohm$^{-1}$cm$^{-2}$sec$^{n}$)</td>
<td>3.8</td>
</tr>
<tr>
<td>phase, $n_{al}$</td>
<td>0.88</td>
</tr>
<tr>
<td>Charge transfer resistance, $R_{ct}$ (ohm cm$^2$)</td>
<td>771.1</td>
</tr>
<tr>
<td>Double layer capacitance, $Q_{dl}$:</td>
<td></td>
</tr>
<tr>
<td>$Y_{dl} \times 10^{-4}$ (ohm$^{-1}$cm$^{-2}$sec$^{n}$)</td>
<td>6.16</td>
</tr>
<tr>
<td>phase, $n_{dl}$</td>
<td>0.44</td>
</tr>
</tbody>
</table>
is favoured at higher temperature. However, the $R_{al}$ value at 80°C is lower than at 60°C. Similarly, the adsorbed layer capacitance ($Q_{al}$) decreased on increasing the temperature from 40 to 60°C. This suggests that on increasing the temperature, more MEA molecules were adsorbed by displacing the water molecules, thereby increasing the thickness of the double layer and decreasing the capacitance value. However, the $Q_{al}$ value at 80°C was higher than at 60°C. Thus, no specific trend can be observed from the impedance fit results, and it does not give a clear picture of the type of adsorption involved. The possibility of both the type of adsorption (physiosorption and chemisorption) by organic inhibitor molecules has also been reported in the literature (Noor and Al-Moubaraki, 2008; Mayanglambam et al., 2011). The charge transfer resistance ($R_{ct}$) increased from 89.3 to 771.1 ohm cm$^2$ on lowering the temperature, which confirms the corrosion trend established from the polarization results.

From the experimental results (Figure 4.1-b), Arrhenius behaviour was observed over the measured range of temperature, as the corrosion rate of carbon steel in aqueous MEA-CO$_2$ solution increased with temperature. The activation energy ($E_a$), required for the corrosion of CS1018 in 5.0 kmol/m$^3$ MEA aqueous solution with 0.20 mol CO$_2$/mol amine loading can be calculated using the logarithmic form of the Arrhenius equation (Equation 4.3).

$$\log C.R = \log A - \left( \frac{E_a}{2.303 \times R \times T} \right)$$  \hspace{1cm} (4.3)

where $C.R$ is the corrosion rate (mmpy), $A$ is the Arrhenius pre exponential factor, $E_a$ is the activation corrosion energy (J/mol), $R$ is the universal gas constant (J/ K mol), and $T$ is the absolute temperature (K). From Equation 4.3, the plot of log $C.R$ Vs (1/T) should yield a straight line with a slope of (-$E_a$/2.303 R) from which the activation energy can be
calculated. Figure 4.5 shows the Arrhenius plot, and the value of $E_a$ was found to be 45.57 kJ/mol. This $E_a$ can be used to predict the performance of any corrosion inhibitors in this system. The activation energy in the presence of an inhibitor should be higher than the $E_a$ value obtained for an uninhibited system. The $E_a$ value and the Arrhenius equation can also be used to predict the corrosion rate of carbon steel in the MEA-based CO$_2$ absorption process (at similar concentrations and CO$_2$ loading) at the temperatures where experimental data cannot be produced, i.e. temperature exceeding 80°C.

### 4.1.2 Effect of CO$_2$ loading of solution

To determine the effect of CO$_2$ loading of solution on the corrosiveness of the system, experiments were conducted at CO$_2$ saturated conditions at 40 and 80°C. The corrosion results were compared with the results obtained at lower CO$_2$ loading (0.20 mol CO$_2$/mol amine) conditions at similar test temperatures. Under saturated conditions, the CO$_2$ loading was in the range of 0.63±0.02 and 0.53±0.01 mol CO$_2$/mol amine at 40 and 80°C, respectively.

The polarization results in Figure 4.6 show that an increase in CO$_2$ loading shifts the polarization curve to higher current densities in both anodic and cathodic branches, indicating a greater corrosion current density and corrosion rate. As presented in Table 4.2, for example at 80°C, the corrosion rate increased from 1.85 to 4.17 mmpy on increasing the CO$_2$ loading from 0.20 mol CO$_2$/mol amine to CO$_2$ saturation. This increase in corrosion rate is a result of the increase in oxidizer concentration with CO$_2$ loading, which in turn can accelerate the corrosion process. The concentration of the oxidizer species depends on the amount of CO$_2$ present in the amine solution. The
Figure 4.5: Arrhenius plot (log C.R Vs 1/T)

![Arrhenius plot](image)
Figure 4.6: Effect of CO\textsubscript{2} loading on polarization behaviour of CS1018 in 5.0 kmol/m\textsuperscript{3} MEA solution (a) 40°C and (b) 80°C
increase in oxidizer concentration is evidenced by the higher cathodic current densities at saturated conditions (Figure 4.6). The wide difference in the critical current densities ($i_{\text{crit}}$) between the two loading conditions can also be seen from the polarization curves, indicating the highly corrosive nature of amine solution at rich loading conditions. No localized corrosion behaviour was observed from the cyclic polarization curve.

The Nyquist plots obtained at two different CO$_2$ loadings are illustrated in Figure 4.7, and the impedance data are presented in Table 4.2. The charge transfer resistance ($R_{\text{ct}}$) at lower CO$_2$ loading is higher than at saturated conditions at both temperatures, which confirms the polarization results. As explained in the previous section, the adsorption of free amine over carbon steel surface occurs with the aqueous amine-CO$_2$ system. The extent to which the adsorption takes place is determined by the availability of free amine and the temperature. With CO$_2$ saturated amine solution, the concentration of free amine is less compared to 0.20 mol CO$_2$/mol amine solution. Thus, the adsorption process might not be favoured much at saturated conditions. The Nyquist plots obtained for saturated conditions at 40°C and 80°C (Figure 4.7) show a high frequency semicircle, which is due to the charge transfer process, followed by a small indistinct capacitive loop (diffusion tail) at the low frequency end. This low frequency loop could exist due to the minimum adsorption of free amine over the metal surface at saturated conditions. On the other hand, for the amine solution with 0.20 mol CO$_2$/mol amine loading, two distinct time constants (two capacitive loops, one each at the high and medium frequency regions) can be observed, indicating more amine absorption processes taking place at the surface. This suggests that the adsorption process gets suppressed in amine solutions with rich CO$_2$ loading.
Figure 4.7: Effect of CO$_2$ loading on impedance behaviour of CS1018 in 5.0 kmol/m$^3$ MEA solution (a) 40°C and (b) 80°C
4.2 Comparative corrosiveness of single amines

4.2.1 Non-contaminated amines

The corrosion behaviours of CS1018 in various aqueous amine solutions (MEA, DEA, MDEA, AMP, and PZ) were examined by conducting the electrochemical experiments under CO₂ saturation and 80°C. The polarization results in Figure 4.8(a) show that the MEA system exhibits the highest anodic and cathodic current densities, followed by AMP, DEA, PZ, and MDEA. This suggests that rates of metal dissolution and reduction of oxidizers can be ranked as: MEA > AMP > DEA > PZ > MDEA. As a result, the corrosion rate can also be ranked in a similar manner, and the corrosivity order for the tested amines is MEA > AMP > DEA > PZ > MDEA (Figure 4.8-b). This trend of corrosion rate is in a good agreement with what was stated in Kohl and Nielsen (1997) in that the primary amines are more corrosive than the secondary amines, which in turn are more corrosive than tertiary amines.

The cyclic polarization curves in Figure 4.9 show pitting in DEA and PZ systems. However, the pitting tendency was minimal, as its repassivation potential (E_{rp}) was close to the pitting potential (E_{p}). The scanning electron microscopy (SEM) images of the fresh specimen and the corroded specimens tested with DEA and PZ system are given in Figure 4.10. The extent of corrosion damage can be observed from the differences in the surface morphologies of the fresh and tested specimens. The specimen from the DEA system showed signs of cracks, confirming localized corrosion attack, as cracks usually initiate from the pits, while that from the PZ system showed scattered pits, as highlighted in Figure 4.10(c).
Figure 4.8: Corrosion behaviour of CS1018 in single amine systems at 80°C and CO$_2$ saturation (5.0 kmol/m$^3$ of MEA, DEA, MDEA and PZ; 4.0 kmol/m$^3$ of AMP)

(a) polarization behaviour and (b) corrosion rate
Figure 4.9: Cyclic polarization curves of CS1018 in 5.0 kmol/m$^3$ amine solutions at CO$_2$ saturation and 80°C (a) DEA and (b) PZ
Figure 4.10: SEM images of CS1018 (a) fresh specimen before test (b) corroded specimen in DEA system and (c) corroded specimen in PZ system (highlighted area indicating pits) (Original in colour)
From the impedance results, the Nyquist plots (Figure 4.11-a) for MEA, AMP, DEA, and PZ systems show a semicircle (capacitive loop) at the high frequency end with an indistinct capacitive loop at the low frequency end. The high frequency semicircle is due to the charge transfer kinetics and the low frequency loop can be related to amine adsorption or adsorption of the reaction intermediates from the corrosion reaction. For the MDEA system, three time constants can be observed. A high frequency semicircle represents the amine adsorption process, medium frequency semicircle indicates the charge transfer kinetics, and the low frequency loop (diffusion tail) can be related to adsorption process similar to those in other amines. From the charge transfer loops, the MEA system yields the lowest diameter, while the MDEA system yields the highest, and, thus, the charge transfer resistance \( R_{ct} \) can be ranked as \( \text{MEA} < \text{AMP} < \text{DEA} < \text{PZ} < \text{MDEA} \) (Figure 4.11-b and Table 4.2). This indicates that the corrosivity order is: \( \text{MEA} > \text{AMP} > \text{DEA} > \text{PZ} > \text{MDEA} \), which confirms the results of the polarization experiments. The high frequency semicircle of the MDEA system could be due to a high quantity of free amine being available for molecular adsorption onto the metal surface. That is, under the \( \text{CO}_2 \) saturation at 80°C, the \( \text{CO}_2 \) loading of MDEA was 0.14 mol \( \text{CO}_2 \)/mol amine, which was the lowest compared to the other tested amines; thus, high free amine adsorption on to the metal surface can be expected under these conditions.

The impedance results are interpreted in terms of an equivalent circuit, which is shown in Figure 4.12. Since, the capacitive loops at the low frequency end of the Nyquist plot (Figure 4.11-a) were not clear for most of the amines, the most basic equivalent circuit with a single time constant was chosen for the analysis. Figure 4.13 shows the Nyquist plot for the MEA system fitted to the equivalent circuit, and Table 4.4 presents
Figure 4.11: Impedance behaviour of CS1018 in single amine systems at 80°C and CO$_2$ saturation (5.0 kmol/m$^3$ of MEA, DEA, MDEA and PZ; 4.0 kmol/m$^3$ of AMP)

(a) Nyquist plot and (b) Charge transfer resistance ($R_{ct}$)
Figure 4.12: Equivalent circuit model for the dissolution of CS1018 in amine solution

![Equivalent circuit model](image)

Figure 4.13: Nyquist plot for CS1018 in 5.0 kmol/m³ MEA solution at CO₂ saturation and 80°C drawn from experimental and fitted impedance data

![Nyquist plot](image)

Table 4.4: Impedance fitted parameters for various amines at CO₂ saturation and 80°C

<table>
<thead>
<tr>
<th>Amine</th>
<th>Solution Resistance, R_s (ohm cm²)</th>
<th>Charge transfer Resistance, R_{ct} (ohm cm²)</th>
<th>Double layer capacitance, Q_{dl}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CPE, Y_{dl} (ohm⁻¹ cm² sec⁻¹) x 10⁴</td>
<td>n_{dl}</td>
<td></td>
</tr>
<tr>
<td>MEA</td>
<td>2.42</td>
<td>68.97</td>
<td>8.80</td>
</tr>
<tr>
<td>AMP</td>
<td>4.85</td>
<td>121</td>
<td>4.04</td>
</tr>
<tr>
<td>DEA</td>
<td>7.69</td>
<td>138.7</td>
<td>4.82</td>
</tr>
<tr>
<td>PZ</td>
<td>7.96</td>
<td>215.1</td>
<td>5.99</td>
</tr>
<tr>
<td>MDEA</td>
<td>52.75</td>
<td>356.3</td>
<td>4.87</td>
</tr>
</tbody>
</table>
the extracted impedance parameters such as solution resistance ($R_s$), charge transfer resistance ($R_{ct}$), and double layer capacitance ($Q_{dl}$) for all amine systems. It was found that the solution resistance values can be ranked as $\text{MEA} < \text{AMP} < \text{DEA} < \text{PZ} < \text{MDEA}$. This trend is similar to the $R_{ct}$ trend, which, again, indicates the established corrosivity order: $\text{MEA} > \text{AMP} > \text{DEA} > \text{PZ} > \text{MDEA}$. The value of $n_{dl}$ is in the range of 0.77-0.87, representing the inhomogeneous nature of the metal surface in all amine systems.

4.2.1.1 Reasons for comparative corrosiveness

(a) **Quantity of oxidizer (or) corroding agent analysis**

The corrosiveness order obtained for single amine systems can be explained by considering the quantity of corroding agents or oxidizing agents participating in the corrosion process. Based on the literature, the corroding agents in the aqueous amine-CO$_2$ systems are H$_2$O (Veawab and Aroonwilas, 2002), HCO$_3^-$ (Guo et al., 1999; Veawab and Aroonwilas, 2002), protonated amine (Kohl and Nielsen, 1997; Guo et al., 1998), and carbamate ions (Tomoe et al., 1997; Guo et al., 1998). Hydrogen ions (H$^+$) were reported to play an insignificant role in the corrosion process of the aqueous MEA-CO$_2$ systems (Veawab and Aroonwilas, 2002). This is also confirmed by the pH data obtained for each amine system. As seen in Figure 4.14, no direct correlation can be established between pH and corrosion rate. This demonstrates that H$^+$ is not a major oxidizing agent.

As discussed in Chapter 2 (Reactions 2.8-2.9), the overall CO$_2$ absorption reaction with aqueous MEA and DEA solution results in equivalent amounts of carbamate and protonated amine species. Since the CO$_2$ loading for MEA (0.53 mol CO$_2$/mol amine) is greater than DEA (0.40 mol CO$_2$/mol amine) at saturated conditions, the concentration of
Figure 4.14: Effect of solution pH on corrosion rate of CS1018 in various amine systems at CO₂ saturation & 80°C (5.0 kmol/m³ of MEA, DEA, MDEA and PZ; 4.0 kmol/m³ of AMP)
the HCO$_3^-$, carbamate, and protonated amine should be higher in the MEA system. Moreover, the carbamate stability constant ($K_c$) for MEA (12.5 m$^3$/kmol at 40°C) is high compared to DEA (2.0 m$^3$/kmol at 40°C) (Sartori and Savage, 1983). Thus, the concentration of carbamate species can be expected to be higher in MEA system than in DEA system. Hence, MEA is more corrosive than DEA.

The overall CO$_2$ absorption reaction with aqueous MDEA and AMP solution (Reactions 2.13 and 2.15 from Chapter 2) results in equivalent amounts of protonated amine and bicarbonate species. Since, MDEA has the lowest CO$_2$ loading (0.14 mol CO$_2$/mol amine) compared to AMP (0.51 mol CO$_2$/mol amine) at saturated conditions, the concentration of protonated amine and bicarbonate must be less in MDEA system. Hence, AMP would be more corrosive than MDEA. When comparing AMP and DEA systems, the $K_c$ value for AMP (< 0.1 m$^3$/kmol at 40°C) is less than for the DEA system. However, the CO$_2$ loading of the AMP system is high compared to the DEA system. Thus, the AMP system might have a higher concentration of protonated amine and bicarbonate species than the DEA system, inducing a higher corrosion rate.

At 80°C and CO$_2$ saturation, the PZ system exhibited high CO$_2$ solubility (0.82 mol CO$_2$/mol amine) followed by MEA, AMP, DEA, and MDEA, as shown in Table 4.2. Irrespective of high CO$_2$ loading, PZ remains the second least corrosive amine tested. Its carbamate stability constant is comparable to secondary amines like DEA (Bishnoi et al., 2000). Thus, the concentration of carbamate species would be less compared to the MEA system. Among tested amines, PZ is the only cyclic compound with two secondary amine groups, which can involve in multiple reactions with CO$_2$. At CO$_2$ loading greater than 0.60 mol/mol, the protonation of piperazine carbamate (PZCOO$^-$) takes place, resulting in
protonated piperazine carbamate (\(H^+\text{PZCOO}^\cdot\)). The system also favours the formation of piperazine dicarbamate (\(\text{OOCPZCOO}^\cdot\)) from carbamate (Bishnoi et al., 2000). These species might not have actively participated in the corrosion reactions and could be one of the possible reasons for the low corrosiveness of the PZ system.

(b) **Quantum analysis**

From the impedance results obtained for the single amine systems, it is clear that a certain amount of molecular adsorption onto the carbon steel surface takes place in all amine systems. By utilizing Quantitative Structure Activity Relation (QSAR) method, which is based on quantum principles, one can determine the degree of molecular adsorption occurring in each amine system. Since, amines have functional groups with hetero atoms (N and O), which favours the adsorption process (physisorption or chemisorption), quantum analysis has been carried out to explain the corrosion difference existing among tested amines based on the adsorption properties of each amine over the metal surface.

Computation of some of the key quantum chemical parameters such as the highest occupied molecular orbital energy (\(E_{\text{HOMO}}\)), lowest unoccupied molecular orbital energy (\(E_{\text{LUMO}}\)), energy gap (\(\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}\)), ionization potential (I), and dipole moment (\(\mu\)) were carried out using the PM6 (parameterized model number 6) method in the MOPAC 2009 software for Windows. The obtained quantum parameters are presented in Table 4.5. From the table, PZ has the highest \(E_{\text{HOMO}}\), and, thus, it has a greater tendency to donate electrons to the metal atoms. Based on \(E_{\text{HOMO}}\), PZ has the greater adsorption performance and the adsorption order is: PZ > MDEA > DEA > AMP > MEA. This
Table 4.5: Quantum chemical indices obtained using PM6 computation

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$\Delta E$ (eV)</th>
<th>Ionization potential, $I$ (eV)</th>
<th>Dipole moment, $\mu$ (debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>-9.658</td>
<td>2.407</td>
<td>12.065</td>
<td>9.657</td>
<td>0.74</td>
</tr>
<tr>
<td>AMP</td>
<td>-9.599</td>
<td>2.605</td>
<td>12.204</td>
<td>9.599</td>
<td>2.337</td>
</tr>
<tr>
<td>DEA</td>
<td>-9.471</td>
<td>1.945</td>
<td>11.416</td>
<td>9.47</td>
<td>1.411</td>
</tr>
<tr>
<td>MDEA</td>
<td>-9.1</td>
<td>1.946</td>
<td>11.046</td>
<td>9.1</td>
<td>2.016</td>
</tr>
<tr>
<td>PZ</td>
<td>-8.835</td>
<td>2.924</td>
<td>11.759</td>
<td>8.835</td>
<td>0.006</td>
</tr>
</tbody>
</table>
suggests that with more amine adsorption, the PZ system exhibits greater resistance to
corrosion processes by blocking the active sites for corrosion. By comparison, with less
amine adsorption, the MEA system shows the least resistance to corrosion processes.
Thus, the established corrosivity order based on $E_{\text{HOMO}}$ is: MEA > AMP > DEA >
MDEA > PZ. The obtained trend nearly matches with the corrosivity order obtained from
the experiments. The adsorption order in terms of ionization potential matches with the
$E_{\text{HOMO}}$ order, as the ionization potential is directly related to $E_{\text{HOMO}}$. Since PZ has low
ionization energy, it can easily donate electrons and involve greater bond formation with
metal atoms than other amines. The adsorption order in terms of energy gap ($\Delta E$) is given
as MDEA > DEA > PZ > MEA > AMP. Based on the $\Delta E$ value, the corrosivity among
the tested amines can be ranked as AMP > MEA > PZ > DEA > MDEA. Though this
trend does not completely match with the experimental corrosivity order, the general
corrosive trend (Primary amine > Secondary amine > Tertiary amine) can be established.
The value of dipole moment cannot be directly related to the inhibition efficiency, as it
only gives information on accumulation of inhibitor molecules on the surface layer. From
Table 4.8, PZ has the least dipole moment, favouring its accumulation over the metal
surface and resulting in higher adsorption performance.

From the quantum calculations, not all the quantum parameters yielded the similar
adsorption trend. This is due to the fact that the adsorption of corrosion inhibitors onto
the metal surface and further corrosion protection involves complex interactions. Taking
this under consideration, the composite index and a combination of more than one
quantum chemical parameter (regression analysis) need to be considered in determining
the adsorption performance and inhibition efficiency (Khaled et al., 2005; Khalil 2003;
Eddy et al., 2011). However, the established corrosivity trend based on some of the individual quantum parameters coincided somewhat well with the experimental corrosion trends of the single amine systems.

(c) **Hard and Soft Acid Base (HSAB) theory**

Similar to the QSAR method, HSAB theory can be used to predict the adsorption characteristics of amines by considering the hard/soft nature of the tested amines. Metal atoms on oxide free surfaces or any bulk metal are considered to be soft acids (Sastri, 2001), and, thus, they prefer to coordinate with soft bases by strong covalent bond formation. In our case, all amines are bases, but there is no information about their types, hard, soft, or borderline bases. To determine the nature of the studied amines, parameters like electronegativity (χ), absolute hardness (η), global softness (σ), and number of electrons transferred (ΔN) were calculated with the help of parameters obtained from quantum calculations, and the results are presented in Table 4.6.

In general, molecules with sulfur-containing functional groups are considered to be soft bases, and the molecules with nitrogen and oxygen are considered to be hard bases (Revie, 2011). Nitrogen containing functional groups has also been reported to fall under the borderline category (Sastri, 2001). Thus, amines (with O and N) might establish weaker bonds with the iron surface in amine-CO$_2$-H$_2$O systems, as hard-soft (or borderline-soft) interactions are weaker than soft-soft interaction. The information about the softness of the amines relative to each other can be established from the energy gap value. Soft molecules, in general, have low ΔE value. From Table 4.5, the softness order is MDEA > DEA > PZ > MEA > AMP. This order can also be verified from Table 4.6.
Table 4.6: Calculated parameters from quantum calculation results

<table>
<thead>
<tr>
<th>Species</th>
<th>Electro negativity, χ (eV)</th>
<th>Hardness, η (eV)</th>
<th>Softness, σ (eV)</th>
<th>∆N</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>3.62</td>
<td>6.032</td>
<td>0.166</td>
<td>0.28017</td>
</tr>
<tr>
<td>AMP</td>
<td>3.497</td>
<td>6.102</td>
<td>0.164</td>
<td>0.28704</td>
</tr>
<tr>
<td>DEA</td>
<td>3.763</td>
<td>5.708</td>
<td>0.175</td>
<td>0.28355</td>
</tr>
<tr>
<td>MDEA</td>
<td>3.577</td>
<td>5.523</td>
<td>0.181</td>
<td>0.30989</td>
</tr>
<tr>
<td>PZ</td>
<td>2.955</td>
<td>5.879</td>
<td>0.170</td>
<td>0.34402</td>
</tr>
</tbody>
</table>
where MDEA has the highest softness value and AMP the lowest value. Among the tested amines, PZ is the only amine that does not possess an oxygen-containing functional group, and thus can be treated as a separate category from the other amines.

The hardness or softness of a molecule can also be categorized based on its electronegativity ($\chi$) values. For hard bases, the electronegativity ($\chi$) value will be in the range of 3.4 – 4, and for soft bases, it lies between 2.1 and 3.0. From Table 4.6, the $\chi$ value of PZ (2.955 eV) alone falls under the soft category, and, hence, it can be treated as a soft base. Thus, the softness of amines can be ranked as PZ > MDEA > DEA > MEA > AMP. The soft nature of the PZ base makes it different from other amines, favouring stronger adsorption (soft-soft interaction) onto the iron surface and offering greater resistance to corrosion processes. Thus, the corrosivity trend based on softness is AMP > MEA > DEA > MDEA > PZ. From Table 4.6, the number of electrons transferred ($\Delta N$) is highest for the PZ system and lowest for the MEA system. Thus, the adsorption performance based on the $\Delta N$ value is as follows: PZ > MDEA > AMP > DEA > MEA, and, hence, the corrosivity of the amine can be ranked as MEA > DEA > AMP > MDEA > PZ. Since the obtained $\Delta N$ values for all amines is less than 3.6 (Table 4.6), it suggests that the amines studied behave as donors of electrons and the iron surface acts as an acceptor of electrons, favouring the adsorption process (Lukovits et al., 2001).

From the HSAB analysis, the established corrosivity order does not completely match with the experimental corrosivity trend. As explained in the previous section, this is due to the fact that the adsorption process involves complex interactions. Moreover, apart from the amine adsorption process, the presence of corroding agents in the amine solution also determines the corrosiveness of the solution.
From both the quantum and HSAB theories, PZ stands out distinctly from the rest of the amine with its strong adsorption properties. In general, the adsorption of molecules over the metal surface is determined by the electron density of the functional groups, the presence of lone pairs of electrons, π-electron clouds, and aromatic ring systems. Among the tested amines, PZ is the only cyclic compound with two secondary amine groups (two lone pair of electrons from two N atoms). Thus, the adsorption process might involve either one amine group (vertical adsorption) or both amine groups (flat adsorption), and it can establish a stronger bond with the metal surface (Bereket et al., 2003).

In order to explore more on the amine adsorption effect in the PZ system, experiments were conducted at lower CO$_2$ loading (0.30 and 0.50 mol CO$_2$/mol amine) conditions and at 80°C, as free amine (PZ) concentration will be high at lower loadings. The polarization curves obtained at different loading conditions are shown in Figure 4.15(a). The corrosion rate at these loading conditions was much lower when compared to saturated conditions, as presented in Table 4.2. A light-grey-coloured film was visually observed over the carbon steel specimen during and after the experiments with lower loading conditions, while the same was not observed for the saturated conditions. This could be due to greater amine adsorption taking place at lower loading conditions. The presence of two distinct semicircles (capacitive loops) in the Nyquist plot (Figure 4.15-b) and the presence of two distinct peaks in the Bode plot (Figure 4.15-c) for the lower loading conditions can be related to more amine adsorption taking place at the carbon steel surface. For saturated conditions, such a distinct time constant cannot be observed from both the Nyquist and Bode plots. A equivalent circuit model similar to those illustrated in Figure 4.3 can be used to fit these impedance data.
Figure 4.15: Corrosion behaviour of CS1018 in 5.0 kmol/m$^3$ PZ solution at various CO$_2$ loadings and 80°C (a) polarization behaviours (b) Nyquist plot and (c) Bode-phase plot.
4.2.1.2 Passive film analysis

The polarization curves (Figure 4.16) of carbon steel (CS1018) in aqueous amine-CO$_2$ environments show active-passive-transpassive behaviour. Shifting the system potential from the active to passive region helps in preventing corrosion by formation of a passive film on the metal surface. This method of corrosion control is called “anodic protection,” which is proven to be a useful corrosion control technique in strongly acidic and alkaline environments. Prior knowledge about the protectiveness of the passive layer is an essential parameter before designing any such protection method. This section is intended to analyze the nature of the passive layer formed over carbon steel in each amine system.

The presence of iron carbonate (FeCO$_3$) in the passive layer formed over carbon steel in an MDEA-CO$_2$-H$_2$O environment was evidenced from the published literature (Guo et al., 1999; Khorrami et al., 2008). The presence of the FeCO$_3$ species in other amine systems can also be evidenced from the Pourbaix diagram illustrated in Figure 4.17(a–d). From the polarization curves (Figure 4.16), the difference in the passive behaviour of CS1018 in different amine systems can be observed. A projection in the passive layer after the primary passivation was observed with all amine systems before the stable passivation was achieved. With the AMP system, in particular, the projection was heavy, indicating its instability. The protectiveness of the passive layer depends on its compactness and the porosity of the film. It is also determined by the nature and availability of corrosive species within the system. From Figure 4.16, the passivation current densities ($i_p$) vary from amine to amine, with DEA having the lowest and AMP having the highest current density. Thus, the passive layer formed with the DEA system
**Figure 4.16:** Active-passive polarization behaviour of CS1018 in various aqueous amine-CO$_2$ systems at CO$_2$ saturation and 80°C
Figure 4.17: Pourbaix diagram for carbon steel in various amine systems at CO$_2$ saturation and 80$^\circ$C (a) MEA-CO$_2$-H$_2$O (b) DEA-CO$_2$-H$_2$O (c) PZ-CO$_2$-H$_2$O and (d) MDEA-CO$_2$-H$_2$O (created from OLI corrosion analyzer) (Original in colour)
offers greater corrosion protection followed by MDEA, PZ, MEA, and AMP in the presence of its respective corrosion species within the system.

In general, the nature of the passive layer can very well be analyzed by impedance measurements. Impedance measurements were carried out after the projection potential to study the mechanism of iron dissolution through the passive layer and to determine the compactness and the protectiveness of the passive layer formed with each amine system. The Nyquist plot obtained at the secondary passive region for the AMP system is shown in Figure 4.18. Two time constants can be observed from the plot, and similar behaviour can also be seen with all amines, as illustrated in Figure 4.19. The first time constant appears as a small semicircle and is due to the $R_{ct}$ parallel to the $C_{dl}$ for iron dissolution through the passive film. The second time constant exhibits linear behaviour termed as Warburg impedance, and it is due to the diffusion process across the passive layer.

The equivalent circuit model representing the passive system is illustrated in Figure 4.20. The circuit elements are solution resistance ($R_s$), porous film resistance ($R_f$), and charge transfer resistance ($R_{ct}$) in series with the Warburg impedance ($Z_w$ or $W$), film capacitance ($Q_f$), and double layer capacitance ($Q_{dl}$). Two semicircles and a diffusion tail would be expected for the proposed equivalent circuit. However, only one semicircle and one diffusion tail can be found from the obtained Nyquist plot. This might be due to the occurrence of a much smaller corrosion film resistance when compared to the charge transfer resistance. Figure 4.21 shows the Nyquist plot for the DEA system fitted to the equivalent circuit. From the figure, it is evident that the corrosion mechanism in the presence of a passive layer follows almost the same pattern as the established equivalent circuit.
Figure 4.18: Nyquist plot for CS1018 in secondary passive region in 4.0 kmol/m³ AMP solution at CO₂ saturation & 80°C showing capacitive loop followed by Warburg impedance.

Figure 4.19: Nyquist plot for CS1018 in secondary passive region for all amine systems at CO₂ saturation & 80°C (5.0 kmol/m³ of MEA, DEA, MDEA and PZ; 4.0 kmol/m³ of AMP).
**Figure 4.20:** Equivalent circuit model for the dissolution of carbon steel at the passive zone

**Figure 4.21:** Nyquist plot for CS1018 in DEA system at passive zone with fitted impedance data
The Warburg impedance \( Z_w \) depends on the modes of mass transfer within the corrosion cell. In the case of semi-infinite linear diffusion, it is represented as in the equation below:

\[
Z_w = \sigma_w (\omega)^{1/2} (1 - j)
\]  

(4.4)

where \( \sigma_w \) is the Warburg coefficient (ohm cm\(^2\) s\(^{-1/2}\)) and \( \omega = 2\pi f \) (rad.s\(^{-1}\)). The Warburg coefficient \( \sigma_w \) can be found from the slope of the Randle’s diagram (Figure 4.22), which is the plot between both imaginary or real impedance and \( 1/\omega^{0.5} \). The calculated Warburg coefficients are illustrated in Figure 4.23. From the plot, DEA shows a high Warburg coefficient followed by MDEA, PZ, MEA, and AMP, which matches with passivation current density \( (i_p) \) trend as shown in Figure 4.16. In general, a higher coefficient indicates an increase in resistance of the diffusion process at the electrode. This can be related to a thicker and less porous film resulting in a compact passive layer.

The SEM images of CS1018 specimens at the passive zone for all amine systems are presented in Figure 4.24. The SEM image alone does not provide a clear picture of the protectiveness of the film, as this also depends on the corrosive species present within the system. From the image of the DEA passive film (Figure 4.24-a), a thick, continuous film in the form of crystal branches can be observed. In the case of MDEA and PZ (Figures 4.24(b-c)), the passive film formed is thin and compact, as the polishing lines can be seen from both the images. For the MEA system (Figure 4.24-d), the image shows a discontinuous passive layer in the form of flakes over the surface. The passive layer formed with the AMP system (Figure 4.24-e), displays heavy and porous deposits. Due to the size limitation of the electrochemical test specimen, XRD analysis could not be performed to determine the type of corrosion products formed with each amine system.
**Figure 4.22:** Randle’s plot corresponding to the Nyquist plots obtained at passive region for all amine systems

**Figure 4.23:** Warburg coefficient ($\sigma_w$) for CS1018 at passive region for all amine systems
**Figure 4.24**: SEM images of CS1018 obtained at the passive region in various amines at CO$_2$ saturation and 80$^\circ$C (a) DEA (b) MDEA (c) PZ (d) MEA and (e) AMP

(Original in colour)
4.2.2 Contaminated amines

The corrosion behaviour of CS1018 in aqueous amine solutions containing four process contaminants was investigated in this present work. These process contaminants are thiosulfate, oxalate, sulfite, and chloride. Thiosulfate, oxalate, and sulfite are common heat-stable salts (HSS) found within amine units. The common sources for oxalate anions are oxidative degradation of amine, thermal degradation of amine, and acid in the feed gas. Thiosulfate and sulfite are the reaction products of oxidation of sulphur species (SO₂) present in the unit. Moreover, sulfite accumulates in the system if sodium sulfite is added into the solution as an oxygen scavenging agent. Chloride enters into the amine units through make-up water and feed gas. The experimental conditions were set to be similar to non-contaminated amine experiments to facilitate comparative analysis. The following sections provide detailed corrosion behaviour of each process contaminant in the amine solutions.

4.2.2.1 Effect of thiosulfate

The corrosion effect of thiosulfate was initially tested with aqueous MEA solution in the presence of 10,000 ppm sodium thiosulfate (Na₂S₂O₃) at CO₂ saturation and 80°C. The polarization curves with and without sodium thiosulfate are illustrated in Figure 4.25(a). The corrosion potential (Ecorr) of CS1018 shifted towards the noble region, and the surface is readily passivated as the primary passivation potential (Epp) is closer to the corrosion potential. The critical current density (icrit) required for passivation is much lower than a blank system, as evident from Figure 4.25(a), which favours passive layer formation. The formation of the passive layer was visible during the experiment as a
Figure 4.25: Corrosion behaviour of CS1018 in 5.0 kmol/m$^3$ MEA solution at CO$_2$ saturation and 80$^\circ$C with and without 10,000 ppm sodium thiosulfate

(a) polarization behaviours (b) Nyquist plots and (c) Bode-phase plot
black layer covering the tested specimen. This could be due to adsorption of thiosulfate \((S_2O_3^{2-})\) forming a surface complex with the iron surface. Based on HSAB theory, \(S_2O_3^{2-}\) being a soft base (Sastri, 2001), it forms a complex with the iron surface (soft acid) through a strong covalent bond, resulting in a protective passive layer. Thus, in the presence of thiosulfate, the corrosion rate significantly decreases from 4.17 to 0.43 mmpy. However, the passive layer formed is not stable, as a heavy disruption in the passive layer can be observed from the polarization curve. With thiosulfate, no pitting tendency was observed.

The formation of a passive layer in presence of thiosulfate can also be verified from the impedance results. From the Nyquist plot (Figure 4.25-b), two time constants (a small semicircle followed by larger semicircle) can be observed, indicating the presence of a passive layer. The Bode plot (Figure 4.25-c) with two peaks confirms the presence of two time constants within the system. The measured charge transfer resistance (R_{ct}) and all the electrochemical parameters are reported in Table 4.7. Due to the low corrosion rate in the MEA-thiosulfate system, the thiosulfate was not tested with the rest of the studied amines.

### 4.2.2.2 Effect of oxalate

The corrosion behaviour of CS1018 in the presence of 10,000 ppm oxalic acid \((C_2O_4H_2)\) was tested with all amines, since oxalate salts were reported to be corrosive (Rooney et al., 1996 and 1997; Veawab et al., 2006). The polarization curves obtained for all amine systems with oxalic acid are illustrated in Figure 4.26(a). The corrosion results obtained are presented in Figure 4.26(b) and Table 4.7. The results show that the increase
Table 4.7: Summary of pH, conductivity, and electrochemical parameters for CS1018 in different amine systems in presence of 10,000 ppm process contaminants

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental Conditions</th>
<th>Additives</th>
<th>pH</th>
<th>σ (mS/cm)</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>E_corr (mV)</th>
<th>I_corr (µA)</th>
<th>Corrosion rate (mmpy)</th>
<th>$R_{ct}$ (ohm cm$^2$)</th>
<th>$C_{dl}$ (µF/cm$^2$)</th>
<th>Pitting Tendency</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>5.0 kmol/m$^3$, 80°C, &amp; 0.40 mol/mol</td>
<td>sodium thiosulfate 8.41 ± 0.02</td>
<td>46.30 ± 0.01</td>
<td>27.74 ± 0.50</td>
<td>39.77 ± 0.00</td>
<td>-723.84 ± 5.8</td>
<td>111.35 ± 0.15</td>
<td>0.43 ± 0.03</td>
<td>254.33 ± 21.2</td>
<td>14498.34 ± 1195.65</td>
<td>58.44 ± 15.20</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxalic acid 8.32 ± 0.02</td>
<td>45.61 ± 0.06</td>
<td>89.06 ± 3.00</td>
<td>123.34 ± 9.0</td>
<td>-741.22 ± 6.30</td>
<td>1042.00 ± 3.56</td>
<td>4.29 ± 0.02</td>
<td>61.12 ± 2.42</td>
<td>262.25 ± 28.04</td>
<td>319.79 ± 0.95</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium sulfite 8.33 ± 0.01</td>
<td>45.48 ± 1.40</td>
<td>78.93 ± 1.50</td>
<td>86.29 ± 4.30</td>
<td>-708.48 ± 10.40</td>
<td>1213.66 ± 7.00</td>
<td>4.71 ± 0.03</td>
<td>17.44 ± 0.49</td>
<td>11117.48 ± 302.29</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium Chloride 8.36 ± 0.01</td>
<td>58.55 ± 0.10</td>
<td>159.6 ± 6.20</td>
<td>110.70 ± 4.10</td>
<td>-741.27 ± 7.30</td>
<td>999.30 ± 8.50</td>
<td>3.88 ± 0.02</td>
<td>90.12 ± 2.10</td>
<td>581.44 ± 15.20</td>
<td>321.36</td>
<td>Yes</td>
</tr>
<tr>
<td>DEA</td>
<td>5.0 kmol/m$^3$, 80°C, &amp; 0.40 mol/mol</td>
<td>Oxalic acid 8.40 ± 0.02</td>
<td>17.09 ± 0.05</td>
<td>168.08 ± 1.00</td>
<td>130.26 ± 6.00</td>
<td>-754.65 ± 2.00</td>
<td>1042.00 ± 3.56</td>
<td>4.29 ± 0.02</td>
<td>101.74 ± 0.30</td>
<td>1220.55 ± 8.75</td>
<td>321.36</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium sulfite 8.43 ± 0.03</td>
<td>18.35 ± 0.04</td>
<td>105.99 ± 3.04</td>
<td>109.99 ± 5.45</td>
<td>-752.66 ± 2.40</td>
<td>679.50 ± 3.42</td>
<td>2.64 ± 0.02</td>
<td>26.66 ± 1.64</td>
<td>1220.55 ± 8.75</td>
<td>321.36</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium Chloride 8.45 ± 0.01</td>
<td>18.47 ± 0.02</td>
<td>111.02</td>
<td>125.59</td>
<td>-751.22</td>
<td>482.60</td>
<td>1.87</td>
<td>163.05</td>
<td>321.36</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>MDEA</td>
<td>5.0 kmol/m$^3$, 80°C, &amp; 0.14 mol/mol</td>
<td>Oxalic acid 8.75 ± 0.01</td>
<td>5.82 ± 0.03</td>
<td>138.56 ± 20.00</td>
<td>126.97 ± 11.00</td>
<td>-774.48 ± 1.20</td>
<td>682.25 ± 2.20</td>
<td>2.65 ± 0.01</td>
<td>96.11 ± 8.0</td>
<td>436.26 ± 66.76</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium sulfite 8.97 ± 0.02</td>
<td>4.45 ± 0.04</td>
<td>80.56</td>
<td>69.16</td>
<td>-749.19</td>
<td>322.10</td>
<td>1.23</td>
<td>56.89</td>
<td>2387.95</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium Chloride 8.88 ± 0.02</td>
<td>8.85 ± 0.04</td>
<td>106.70 ± 4.00</td>
<td>145.04 ± 2.36</td>
<td>-772.51 ± 1.50</td>
<td>264.90 ± 4.20</td>
<td>1.03 ± 0.02</td>
<td>271.47 ± 5.60</td>
<td>373.11 ± 12.35</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>AMP</td>
<td>4.0 kmol/m$^3$, 80°C, &amp; 0.51 mol/mol</td>
<td>Oxalic acid 8.87 ± 0.02</td>
<td>28.0 ± 0.05</td>
<td>153.01 ± 10.0</td>
<td>80.76 ± 1.30</td>
<td>-784.54 ± 0.13</td>
<td>991.40 ± 3.00</td>
<td>3.85 ± 0.13</td>
<td>80.15 ± 4.16</td>
<td>655.43 ± 33.30</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium sulfite 8.9 ± 0.03</td>
<td>32.68 ± 0.09</td>
<td>80.89 ± 5.11</td>
<td>94.29 ± 1.70</td>
<td>-794.76 ± 1.80</td>
<td>275.45 ± 2.70</td>
<td>1.07 ± 0.01</td>
<td>87.58 ± 7.61</td>
<td>232.48 ± 20.21</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium Chloride 8.93 ± 0.02</td>
<td>32.60 ± 0.05</td>
<td>88.14 ± 2.30</td>
<td>155.59 ± 1.50</td>
<td>-782.91 ± 0.80</td>
<td>720.50 ± 3.30</td>
<td>2.79 ± 0.03</td>
<td>111.02 ± 3.95</td>
<td>293.08 ± 6.86</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>PZ</td>
<td>5.0 kmol/m$^3$, 80°C, &amp; 0.82 mol/mol</td>
<td>Oxalic acid 8.43 ± 0.02</td>
<td>16.73 ± 0.02</td>
<td>191.42 ± 1.40</td>
<td>108.71 ± 0.70</td>
<td>-765.76 ± 9.00</td>
<td>791.35 ± 24</td>
<td>3.07 ± 0.08</td>
<td>111.82 ± 18.43</td>
<td>481.97 ± 81.12</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium sulfite 8.32 ± 0.01</td>
<td>13.04 ± 0.05</td>
<td>91.69</td>
<td>101.79</td>
<td>-742.78</td>
<td>478.70</td>
<td>1.86</td>
<td>31.41</td>
<td>4325.86</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>sodium Chloride 8.40 ± 0.04</td>
<td>19.10 ± 0.05</td>
<td>117.25</td>
<td>91.53</td>
<td>-743.79</td>
<td>388.20</td>
<td>1.51</td>
<td>271.47</td>
<td>331.66</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

$\sigma$ = conductivity; $\beta_a$ = anodic Tafel slope; $\beta_c$ = cathodic Tafel slope; $E_{corr}$ = corrosion potential; $I_{corr}$ = corrosion current; $R_{ct}$ = charge transfer resistance; $C_{dl}$ = double layer capacitance.
Figure 4.26: Effect of 10,000 ppm oxalate on (a) polarization behaviour and (b) corrosion rate of CS1018 in various amines
in corrosion rate was observed in all amine systems but to varying extents. For MEA, AMP, and DEA, there was a slight increase in corrosion rate, whereas for PZ and MDEA, the corrosion rate increased dramatically. The corrosivity order in the presence of oxalate is MEA > AMP > PZ > DEA > MDEA, as seen in Figure 4.26(b). Localized corrosion behaviour was observed only with the PZ system in the presence of oxalic acid (Figure 4.27). However, the pitting tendency was less, as its repassivation potential was close to the pitting potential.

The drastic increases in the corrosion rates with PZ and MDEA systems can be analyzed based on the corrosion mechanism. The presence of oxalic acid might have accelerated the corrosion process either by being directly reduced on the metal surface (George et al., 2004) or the oxalate anion \((\text{C}_2\text{O}_4^{2-})\) can act as a chelating agent for metal cations (Rooney et al., 1996). From the comparative polarization curves (Figure 4.28), the presence of oxalic acid increases the anodic current densities for all amines, with the MDEA and PZ systems experiencing the major increase. The cathodic current density, however, slightly increases. This suggests the iron dissolution process by iron chelation mechanism in the presence of oxalate anion plays a more important role in increasing the corrosivity than the reduction of oxidizing agents. The obtained results indicate that MDEA-oxalate and PZ-oxalate are more corrosive than other amine systems containing oxalate, or the concentration of oxalate anions could have been higher with the PZ and MDEA systems, which resulted in an accelerated corrosion process.

Since oxalic acid is a diprotic acid, it has to donate two protons to form an oxalate anion. The oxalate anion formation can be facilitated by dissociation of oxalic acid in amine solution or by protonation of free amine in the presence of oxalic acid. As the
Figure 4.27: Localized corrosion behaviour of CS1018 in aqueous PZ-CO$_2$ system in presence of 10,000 ppm oxalate
Figure 4.28: Polarization behaviour of CS1018 in various amines with and without 10,000 ppm oxalate (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA
solution is prepared by adding oxalic acid into a CO$_2$-saturated solution, the degree of amine protonation depends on the availability of free amine in the solution. The CO$_2$ loading of aqueous MDEA solution at 80°C and saturated condition is around 0.14 mol CO$_2$/mol amine, which is less than all the other amines. Thus, MDEA solution will possibly have a high free amine concentration compared to the other amines, favouring oxalate anion formation. This could be the possible reason for the drastic increase in corrosion rate in the MDEA system. For the PZ system containing high CO$_2$ loading (0.83 mol/mol), the system might have less free amine and a high protonated amine concentration. However, PZ being a diamine, it has a tendency to involve multiple reactions. For example, addition of oxalic acid might have facilitated protonation of piperazine carbamate to form protonated piperazine carbamate and favour oxalate formation. In this way, the PZ system can enhance the oxalate anion concentration resulting in accelerated corrosion.

The Nyquist plots and the charge transfer resistance ($R_{ct}$) values for all amine systems in the presence of oxalic acid (Figure 4.29) confirms the corrosivity order obtained from the polarization results. The comparative Nyquist plots with and without oxalic acid are presented in Figure 4.30. In the presence of oxalic acid, the diameter of the semicircle decreased for all amine systems, indicating a decrease in charge transfer resistance in the corrosion process. Similar to the polarization results, the decrease in $R_{ct}$ value was higher with the MDEA and PZ systems than the other amines, showing the corrosive nature of these systems in presence of oxalic acid.
Figure 4.29: Effect of 10,000 ppm oxalate on (a) Nyquist plots and (b) charge transfer resistance of CS1018 in various amines
Figure 4.30: Impedance behaviour of CS1018 in various amines with and without 10,000 ppm oxalate (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA
4.2.2.3 Effect of sulfite

The results in Table 4.7 and Figure 4.31 show that the presence of 10,000 ppm sodium sulfite (Na$_2$SO$_3$) induces an increase in corrosion rate of CS1018 in MEA, DEA, PZ, and MDEA systems, whereas it decreases the corrosion rate in the AMP system. With the presence of Na$_2$SO$_3$, a major decrease in the cathodic current density was observed only in the AMP system (Figure 4.32), indicating a decreased corrosion rate. The corrosivity order can be ranked as MEA > DEA > PZ > MDEA > AMP. The presence of sodium sulfite also tended to induce pitting corrosion in most amine systems (MEA, DEA, PZ, and AMP), but not in the MDEA system. As seen from Figure 4.33(a-d), the cyclic polarization curves of MEA, AMP, DEA, and PZ exhibit a negative hysteresis loop, but the tendency of pitting is lower in these systems, as the repassivation potential is closer to the pitting potential. In general, the larger the area of the hysteresis loop, the greater the susceptibility to pitting corrosion. However, though the MEA system shows the largest hysteresis loop, the pitting tendency was minimal, which can be confirmed from the SEM images (Figure 4.34) of the specimen tested in the MEA system. It does not show any obvious pits, but a crater-like structure (as highlighted), can be observed from the image, which could be due to localized corrosion.

The decreased corrosion rate in the AMP system can be explained based on the stability of the adsorbed layer (the black-coloured layer) observed over the carbon steel surface in all amine systems. Similar to the thiosulfate experiment, the presence of sodium sulfite favoured the formation of a black-coloured adsorbed layer in all the amine systems. Figure 4.35(a) presents the photographic image of the CS1018 surface in the MEA system showing the black-coloured layer. For only the AMP system, the adsorbed
Figure 4.31: Effect of 10,000 ppm sodium sulfite on (a) polarization behaviour
and (b) corrosion rate of CS1018 in various amines.
Figure 4.32: Polarization behaviour of CS1018 in various amines with and without 10,000 ppm sulfite (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA
Figure 4.33: Localized corrosion behaviour of CS1018 in aqueous amine-CO₂ systems in presence of 10,000 ppm sulfite (a) MEA (b) AMP (c) DEA and (d) PZ
Figure 4.34: SEM image of corroded specimen in 5.0 kmol/m$^3$ MEA solution at CO$_2$ saturation & 80°C in presence of 10,000 ppm sulfite, showing crater like pits at different magnification (a) 1000 X and (b) 1500 X (Original in colour)

Figure 4.35: The photographic image of CS1018 in MEA-CO$_2$-H$_2$O system with 10,000 ppm sodium sulfite, showing the (a) presence of black coloured layer at the initial stages of experiment (b) presence of rusty surface on anodic polarization during the experiment (Original in colour)
layer was stable enough to offer corrosion protection and was found to be intact even after the experiment. For the other amine systems, the adsorbed layer was dissolved into the solution during anodic polarization, leaving the carbon steel surface rusty orange in colour (Figure 4.35-b). The surface complex formed in these systems might not be quite stable and might be easily desorbed from the surface. This would expose the fresh metal surface and accelerated the corrosion process. The presence of a stable adsorbed layer in the AMP system can be verified from the illustrated photographic image (Figure 4.36). It shows the image of the specimens tested in AMP and the DEA systems, removed after the active zone. A black-coloured layer can be observed on both specimens. However, the specimen in the AMP system shows a very intact adsorbed layer, whereas, for DEA, the layer was easily wiped off as a black paste by rubbing the specimen.

The SEM image and EDS plot of the corroded specimen (analyzed after cyclic polarization) in the AMP system is illustrated in Figure 4.37. A distinct crystal structure can be observed, which could be either iron carbonate (FeCO₃) or iron oxides (Fe₃O₄ or Fe₂O₃). The EDS plot with a major oxygen peak and a carbon peak confirms the possibility of passive layer formation. Also, a small peak for the elements Na and S in the EDS plot indicates the adsorption mechanism associated with the Na₂SO₃ addition, resulting in development of a surface complex with iron. The formation of the adsorbed layer with all amine systems can also be evidenced from the Nyquist plots with two depressed semicircles and a diffusion tail (Figure 4.38-a). The measured charge transfer resistances (R_{ct}) are presented in Figure 4.38(b). From the comparative Nyquist plots (Figure 4.39), the increase in the diameter of the capacitive loop in the presence of Na₂SO₃ can be observed only in the AMP system, indicating its increased R_{ct} value.
Figure 4.36: Photographic image of tested specimen in AMP-CO$_2$-H$_2$O and DEA-CO$_2$-H$_2$O system with 10,000 ppm Na$_2$SO$_3$ taken after the experiment, showing the presence of adsorbed black layer (Original in colour)

Figure 4.37: Surface analysis of corroded specimen in AMP-CO$_2$-H$_2$O system with 10,000 ppm Na$_2$SO$_3$ (a) SEM image and (b) EDS analysis (with elements wt %)

(Original in colour)
Figure 4.38: Effect of 10,000 ppm sulfite on (a) Nyquist plots and (b) charge transfer resistance of CS1018 in various amines.
Figure 4.39: Impedance behaviour of CS1018 in various amines with and without 10,000 ppm sulfite (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA
Similarly, a drop in double layer capacitance (C_{dl}) was observed only for the AMP system, and this can be verified from Table 2 and Table 5. This drop in C_{dl} again confirms the effective adsorption process that took place with the AMP solution, as the adsorbed film reduced the dielectric constant between the metal and electrolyte, decreasing the capacitance value.

### 4.3.2.4 Effect of Chloride

In presence of sodium chloride, a slight decrease in corrosion rate was observed with most amine systems (MEA, AMP, DEA, and PZ) other than MDEA. Carbon steel in the MDEA system underwent a slight increase in corrosion rate. The obtained polarization curves and corrosion rates are presented in Figure 4.40. From the comparative polarization curves (Figure 4.41), a slight increase in both anodic and cathodic current densities in the presence of NaCl was observed only with the MDEA system, indicating an increased corrosion rate. The corrosivity order remains same as that of blank amines (MEA > AMP > DEA > PZ > MDEA), and the experimental data obtained are presented in Table 4.7. Such a drop in corrosion rate for carbon steel in aqueous MEA solution in the presence of NaCl was also reported in Srinivasan (2006) and Soosaiprakasam (2007).

From the Nyquist plot (Figure 4.42-a), the diameter of the capacitive loops that indicated the charge transfer resistance (R_{ct}) decreased in the following order: MEA < AMP < DEA < PZ < MDEA, thereby confirming the corrosivity order (MEA > AMP > DEA > PZ > MDEA) obtained from the polarization results. The R_{ct} values are presented in Figure 4.42(b) and Table 4.7. From the comparative Nyquist plot (Figure 4.43), the
Figure 4.40: Effect of 10,000 ppm chloride on (a) polarization behaviour and (b) corrosion rate of CS1018 in various amines
Figure 4.41: Polarization behaviour of CS1018 in various amines with and without 10,000 ppm chloride (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA
Figure 4.42: Effect of 10,000 ppm chloride on (a) Nyquist plots and (b) charge transfer resistance of CS1018 in various amines
Figure 4.43: Impedance behaviour of CS1018 in various amines with and without 10,000 ppm chloride (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA
decrease in the diameter of the capacitive loop in the presence of NaCl was observed only with the MDEA system, indicating a decrease in $R_{ct}$ value.

The decrease in corrosion rate in the presence of chloride can be explained by considering the adsorptive properties of chloride ions on to the metal surface. Since chloride ions (Cl$^-$) in the solutions have a stronger tendency to adsorb on the metal surface, it creates an excess negative charge towards the solution. This favours physical adsorption of cations, for example, protonated amine ($RNH_3^+$), in the solution onto the iron surface. When protonated amine are adsorbed on the metal surface through chloride ions by electrostatic interaction, partial transfer of electrons from protonated amine (from a N atom with a lone pair of electrons) to the metal surface occurs and offers corrosion protection. This type of positive synergistic effect for an inhibitor molecule in presence of chloride ions has been reported in various studies (Lagrenee et al., 2002; Tang et al., 2006; Obot et al., 2009; Singh et al., 2012).

From Figure 4.44, pitting tendency was observed in the DEA and PZ systems. The pitting tendency in the PZ system was minimal, as its repassivation potential ($E_{rp}$) was close to the pitting potential ($E_b$). In contrast, in the DEA system, the difference between the $E_{rp}$ and $E_b$ was wide, inducing heavy pitting, and the pits were scattered throughout the specimen. The photographic and SEM images of the corroded specimen in the DEA-CO$_2$-H$_2$O-NaCl system, showing the scattered and deep pits, are given in Figure 4.45.
Figure 4.44: Localized corrosion behaviour of CS1018 in aqueous amine-CO$_2$ systems in presence of 10,000 ppm chloride (a) DEA and (b) PZ
Figure 4.45: Pitting corrosion of CS1018 specimen in aqueous DEA-CO₂ system in presence of 10,000 ppm NaCl (a) photographic image showing scattered pits during experiment (b) SEM image showing scattered pits (100 X magnification) and (c) SEM image showing pit depth (1000 X magnification) (Original in colour)
4.3 Comparative corrosiveness of blended amines

The corrosiveness of CS1018 was further investigated for five blended amines: MEA-PZ, MEA-AMP, MEA-MDEA, MDEA-PZ, and AMP-PZ mixtures with total concentrations of 5.0 kmol/m³ with 1:1 molar mixing ratios at two different temperatures (40 and 80°C) and under CO₂ saturated conditions. In general, amines with very fast absorption kinetics are required for CO₂ capture processes. Since PZ has the high reaction rate with CO₂ over the other amines, it was tested with three different amines: MDEA, AMP, and MEA. The effectiveness of these PZ blends has been discussed in various publications: MDEA-PZ blend (Appl et al., 1980; Xu et al., 1992; Bishnoi et al., 2002; Ali et al., 2004; Closmann et al., 2009), AMP-PZ blend (Sun et al., 2005, Samanta and Bandyopadhyay, 2009; Yang et al., 2010; Dash et al., 2011), and MEA-PZ blend (Dang and Rochelle, 2003; Dugas et al., 2009). MEA, being a widely used solvent, was tested with AMP and MDEA, as these solvents require lower energy for solvent regeneration when compared to MEA. The literature references for these blends are: MEA-MDEA blend (Mandal et al., 2001; Idem et al., 2006; Aroonwilas and Veawab, 2007; Setameteekul et al., 2008; Edali et al., 2009), and MEA-AMP blend (Mandal et al., 2001; Aroonwilas and Veawab., 2009; Choi et al., 2009; Sakwattanapong et al., 2009).

The polarization curves and the corrosion rates obtained at 40°C are illustrated in Figure 4.46. The corrosivity order at 40°C is MEA-PZ ≥ MEA-AMP ≥ MEA-MDEA > MDEA-PZ. The experimental data are presented in Table 4.8. The corrosion rates for the MEA blends are close to each other and range from 0.75 – 0.87 mmpy. For the MDEA-PZ blend, the corrosion rate is around 0.43 mmpy. The corrosion experiment for AMP-PZ blend at 40°C was not conducted, due to a solution precipitation problem experienced
Figure 4.46: Polarization behaviour of CS1018 in blended amine systems under 5.0 kmol/m³ (1:1 molar ratio) concentration at CO₂ saturation & 40°C (a) polarization behaviours and (b) corrosion rate
Table 4.8: Summary of pH, conductivity, and electrochemical parameters for CS1018 in blended amine systems

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental Condition</th>
<th>pH</th>
<th>σ (mS/cm)</th>
<th>βₐ (mV/decade)</th>
<th>βₜ (mV/decade)</th>
<th>Ecorr (mV)</th>
<th>Icorr (µA)</th>
<th>Corrosion rate (mmpy)</th>
<th>Rct (ohm cm²)</th>
<th>Cdl (µF/cm²)</th>
<th>Pitting Tendency</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA-PZ</td>
<td>5.0 kmol/m³ (1:1), 40°C, 0.80 mol/mol</td>
<td>7.86±0.07</td>
<td>20.16±0.05</td>
<td>175.40±5.30</td>
<td>78.87±2.50</td>
<td>-748.70±0.60</td>
<td>224.10±0.30</td>
<td>0.87±0.02</td>
<td>322.23</td>
<td>248.83</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³ (1:1), 80°C, 0.68 mol/mol</td>
<td>8.50±0.03</td>
<td>23.79±0.09</td>
<td>138.42±10.0</td>
<td>71.53±1.50</td>
<td>-762.82±1.00</td>
<td>804.70±4.00</td>
<td>3.12±0.01</td>
<td>106.72</td>
<td>311.09</td>
<td>Yes</td>
</tr>
<tr>
<td>MEA-AMP</td>
<td>5.0 kmol/m³ (1:1), 40°C, 0.70 mol/mol</td>
<td>8.01±0.01</td>
<td>22.89±0.60</td>
<td>160.66±8.00</td>
<td>73.71±5.00</td>
<td>-745.66±0.50</td>
<td>208.70±5.50</td>
<td>0.81±0.01</td>
<td>328.88</td>
<td>243.79</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³ (1:1), 80°C, 0.52 mol/mol</td>
<td>8.81±0.04</td>
<td>27.05±1.00</td>
<td>144.04±1.50</td>
<td>71.60±3.50</td>
<td>-761.24±1.00</td>
<td>774.30±0.50</td>
<td>3.01±0.02</td>
<td>108.15</td>
<td>307.01</td>
<td>No</td>
</tr>
<tr>
<td>MEA-MDEA</td>
<td>5.0 kmol/m³ (1:1), 40°C, 0.61 mol/mol</td>
<td>8.07±0.04</td>
<td>21.08±0.50</td>
<td>117.54±3.00</td>
<td>93.20±2.00</td>
<td>-759.19±0.88</td>
<td>193.95±0.30</td>
<td>0.75±0.02</td>
<td>330.09</td>
<td>242.90</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³ (1:1), 80°C, 0.37 mol/mol</td>
<td>8.53±0.08</td>
<td>18.72±0.65</td>
<td>124.26±1.50</td>
<td>63.12±1.00</td>
<td>-763.96±0.55</td>
<td>735.60±0.80</td>
<td>2.86±0.01</td>
<td>125.03</td>
<td>265.03</td>
<td>Yes</td>
</tr>
<tr>
<td>MDEA-PZ</td>
<td>5.0 kmol/m³ (1:1), 40°C, 0.81 mol/mol</td>
<td>8.12±0.04</td>
<td>8.68±0.08</td>
<td>95.25±10.00</td>
<td>53.54±4.00</td>
<td>-755.90±0.40</td>
<td>111.25±2.20</td>
<td>0.43±0.01</td>
<td>451.19</td>
<td>238.46</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>5.0 kmol/m³ (1:1), 80°C, 0.54 mol/mol</td>
<td>8.65±0.10</td>
<td>8.57±0.05</td>
<td>116.44±6.00</td>
<td>78.71±1.82</td>
<td>-770.68±0.30</td>
<td>543.70±3.00</td>
<td>2.11±0.01</td>
<td>168.55</td>
<td>354.64</td>
<td>No</td>
</tr>
<tr>
<td>AMP-PZ</td>
<td>5.0 kmol/m³ (1:1), 80°C, 0.69 mol/mol</td>
<td>8.84 ± 0.06</td>
<td>10.95 ± 0.02</td>
<td>157.77±2.00</td>
<td>72.28±1.05</td>
<td>-768.12±1.00</td>
<td>514.90±1.00</td>
<td>1.99±0.02</td>
<td>174.19</td>
<td>343.14</td>
<td>No</td>
</tr>
</tbody>
</table>

σ = conductivity; βₐ = anodic Tafel slope; βₜ = cathodic Tafel slope; Ecorr = corrosion potential; Icorr = corrosion current; Rct = charge transfer resistance; Cdl = double layer capacitance.
at CO₂ saturation conditions. From the polarization curves (Figure 4.46a), projection in the passive region was observed only with the MEA-AMP blend. This is characteristic of the AMP precursor, as a similar projection can be observed with the AMP polarization curve (Figure 4.16). No localized corrosion behaviour was observed at 40°C.

The impedance behaviour of the blended system at 40°C also confirms the above corrosivity trend. The Nyquist plots and the charge transfer resistance (R_{ct}) values are illustrated in Figure 4.47. Two capacitive loops (time constants) can be observed from the Nyquist plots, one each at the high and low frequencies. The high frequency loop is due to the charge transfer process, and the low frequency loop can be associated with free amine adsorption.

At 80°C, the corrosivity order was the same as that at 40°C, with AMP-PZ blend being the least corrosive. The polarization curves and the corrosion rates are illustrated in Figure 4.48. The blend that contained MEA was more corrosive than any other blends, for which the corrosion rates were close to each other. For instance, at 80°C, the MEA-PZ system yielded a corrosion rate of 3.12 mmpy, for the MEA-AMP system, the corrosion rate was 3.01 mmpy, and for MEA-MDEA, it was 2.86 mmpy. With MEA being the most corrosive solvent, this trend shows the impact of the precursor MEA on other solvents. Similar to the results at 40°C, heavy disruption in the passive zone was observed only with the AMP blends (MEA-AMP and AMP-PZ) as evident from Figure 4.48(a). At 80°C, pitting tendency was identified with the MEA-PZ and MEA-MDEA blends (Figure 4.49). The impedance measurements at 80°C yielded a similar corrosivity order as polarization results, and the results are presented in Figure 4.50. Similar to the impedance results at 40°C, the Nyquist plot at 80°C shows two capacitive loops.
Figure 4.47: Impedance behaviour of CS1018 in blended amine systems under 5.0 kmol/m$^3$ (1:1 molar ratio) concentration at CO$_2$ saturation & 40°C (a) Nyquist plots and (b) charge transfer resistance
Figure 4.48: Polarization behaviour of CS1018 in blended amine systems under 5.0 kmol/m³ (1:1 molar ratio) concentration at CO₂ saturation & 80°C (a) polarization behaviours and (b) corrosion rate
Figure 4.49: Localized corrosion behaviour of CS1018 in blended amine systems under 5.0 kmol/m³ (1:1 molar ratio) concentration at CO₂ saturation & 80°C (a) MEA-PZ and (b) MEA-MDEA blends.
Figure 4.50: Impedance behaviour of CS1018 in blended amine systems under 5.0 kmol/m$^3$ (1:1 molar ratio) concentration at CO$_2$ saturation & 80°C (a) Nyquist plots and (b) charge transfer resistance
The comparative polarization curves, corrosion rates, and charge transfer resistances of CS1018 in five blended amine systems with their parent amines obtained at 80°C are illustrated in Figures 4.51- 4.52. The corrosiveness in blended systems appears to be a combination of the corrosiveness in precursor systems. The MEA-PZ blend remains the highest corrosive blend, irrespective of PZ being one of its precursors. This highlights the corrosive nature of the MEA precursor. However, the MEA-PZ blend experiences a lower corrosion rate (3.12 mmpy) than the MEA precursor (4.17 mmpy). With the MEA-PZ blend, both MEA and PZ have the major impacts on the corrosion behaviour of the blend. From Figure 4.51(a), it can be observed that the cathodic curve of the MEA-PZ blend traces the PZ curve, whereas the anodic curve of the blend traces the MEA curve. This confirms that the anodic dissolution mechanism of the MEA-PZ blend is similar to that of MEA.

For the MEA-AMP blend, the corrosion rate is less than that of both precursors, as illustrated in Figure 4.52. It can also be confirmed from Figure 4.51(b) that both the cathodic and anodic current densities of the MEA-AMP blend are lower than both the precursors. This indicates that the MEA-AMP blend has a lower concentration of the corroding species than its respective precursors, and, therefore, it experiences a lower corrosion rate than the precursors.

In the case of the MEA-MDEA blend, the CS1018 experienced a high corrosion rate (2.86 mmpy), though the blend contains the least corrosive amine MDEA (0.89 mmpy) as one of its precursors. This trend can be explained by referring to the comparative polarization curves. From Figure 4.51(c), the MEA precursor appears to have the major impact on the corrosiveness of the blend. Both the anodic and cathodic
Figure 4.51: Polarization behaviour of CS1018 in blended amine systems and their precursors under CO₂ saturation and at 80°C (a) MEA-PZ (b) MEA-AMP (c) MEA-MDEA (d) MDEA-PZ and (e) AMP-PZ
Figure 4.52: Corrosion comparison between the precursors and the blended amine

(a) corrosion rate and (b) charge transfer resistance
curves of the MEA-MDEA blend are close to the MEA curves, and their Tafel slopes are almost the same (Table 4.2 and 4.8). Thus, the corrosion mechanism of the MEA-MDEA blend is similar to that of the MEA precursor. This, again, highlights the impact of the precursor MEA on the corrosiveness of the blend.

In the case of the MDEA-PZ blend, the corrosion rate of CS1018 in the blend was higher than both the precursors (Figure 4.52). From Figure 4.51(d), the anodic current density of the MDEA-PZ blend is higher than both the parent amines, indicating the higher anodic dissolution rate of the blend. The possible reason for this corrosion behaviour could be due to the high CO₂ loading of the MDEA-PZ blend (0.54 mol CO₂/mol amine) compared to the precursor MDEA (0.14 mol CO₂/mol amine). This could have resulted in more bicarbonate ion (HCO₃⁻) concentration with the MDEA-PZ blend. The increased HCO₃⁻ concentration could possibly accelerate the anodic dissolution rate of the blend, as indicated by the increased anodic current density.

The AMP-PZ blend remains the least corrosive system, irrespective of its high CO₂ content (0.69 mol CO₂/mol amine) and the corrosive nature of the AMP precursor. From Figure 4.51(e), the cathodic current density of the AMP-PZ blend is less than both the precursors. This suggests that the AMP-PZ blend has a lower concentration of oxidizing agents than its respective precursors, resulting in a reduced corrosion rate. Moreover, the PZ precursor appears to have the major impact on the corrosion behaviour of the blend, as the anodic curve of the blend appears similar to that of the PZ curve. This behaviour keeps the corrosion rate of the blend close to PZ precursor and lower than the AMP precursor.
4.4  Corrosion correlation

The properties of amine solutions, i.e., pH, conductivity, and CO₂ loading of the solution, were analyzed to determine their relationship with corrosion rate, which is useful for corrosion monitoring. The analysis was carried out using all of the experimental corrosion data from Sections 4.2.1, 4.2.2, and 4.3. As in Figure 4.53(a), the relationship between pH and corrosion rates cannot be correlated. This means the pH of the solution cannot be used as an indicator during plant operation to monitor the corrosiveness of the solution. This also means that H⁺ is not the primary corroding agent (oxidizer) in amine systems.

Unlike pH, conductivity of the solution for each temperature exhibits a linear relationship with the corrosion rate. As illustrated in Figure 4.53(b), the corrosion rate increases with conductivity. Thus, the conductivity can be used as a corrosion indicator for corrosion monitoring and prediction purposes.

For the CO₂ loading of a solution, a linear relationship between corrosion rate and CO₂ loading in the unit of mol CO₂/mol amine can be observed (Figure 4.53-c) when the PZ data are not included. However, no correlation can be observed when the PZ data are included in the plot (Figure 4.53-d). This is because the corrosion data of the PZ systems are scattered from the general trend, as the corrosion rates in PZ systems are lower irrespective of its high value of CO₂ loading. When CO₂ loading in the unit of mol CO₂/mol alkalinity is considered, the linear relationship between CO₂ loading and all the corrosion data, including the PZ system data, can be established (Figure 4.53-e). Since PZ has two amine groups, its total alkalinity should be taken as 2.0. For a blend containing PZ (e.g., MEA-PZ), the CO₂ loading is defined as in Equation 4.5.
Figure 4.53: Correlation plot for corrosion rate of CS1018 with properties of amine solution in all tested amine systems including single and blended amines (a) pH (b) Conductivity (c) CO₂ loading (mol CO₂/mol amine) without PZ data (d) CO₂ loading (mol CO₂/mol amine) with PZ data and (e) CO₂ loading (mol CO₂/mol alkalinity) with all corrosion data
\[ CO_{2\text{loading}} = \frac{n_{CO_2}}{n_{MEA} + 2n_{PZ}} \]  \hspace{1cm} (4.5)

where \( n_{CO_2} \), \( n_{MEA} \), and \( n_{PZ} \) denote the number of moles of CO\(_2\), MEA, and PZ, respectively.

### 4.5 Corrosion resistance of stainless steel

Corrosion resistance of austenitic stainless steels (SS304 and SS316) were tested with 5.0 kmol/m\(^3\) aqueous MEA solution at CO\(_2\) saturation and 80°C, and their corrosion performances were compared with those of carbon steel. MEA was chosen for the evaluation, as it was found to be the most corrosive amine to carbon steel compared to other tested amines. The polarization curves obtained for three different specimen materials (CS1018, SS304, and SS316) in aqueous MEA solutions at similar test conditions are illustrated in Figure 4.54(a). The corrosion rates were 4.17 mmpy for CS1018; 0.036 mmpy for SS304, and 0.027 mmpy for SS316. The corrosion rates of SS304 and SS316 were below the minimum industrial standard for corrosion rate, which is 0.07 mmpy (Khatak and Raj, 2002). Thus, considering the corrosion performance, stainless steel can be a better plant construction material compared to carbon steel.

The superior corrosion resistant character of stainless steels can be explained by considering their polarization curves (4.54-a). Both SS304 and SS316 do not undergo any active dissolution process. Instead, the anodic curve enters the passive zone immediately after the corrosion potential, whereas CS1018 is in an active dissolution process. The primary passivation potential (\( E_{pp} \)) for stainless steel is close to the corrosion potential (\( E_{corr} \)), since alloys like stainless steel can easily form passive film (chromium oxide) that
Figure 4.54: Corrosion behaviour of CS1018, SS304 and SS316 in 5.0 kmol/m$^3$ MEA solution at CO$_2$ saturation & 80°C. (a) polarization behaviour (b) Nyquist plot
offers corrosion protection. The critical current density ($i_{\text{crit}}$) required for passivation with stainless steel is much lower than that for carbon steel. It is also evident from the curves that the passive layer formed with stainless steel is not stable, as it undergoes two breakdown potentials. No localized corrosion behaviour was observed with the stainless steels.

The passivation with stainless steel close to $E_{\text{corr}}$ can also be verified from the Nyquist plot (Figure 4.54-b) measured at the point of open circuit potential. Two time constants can be observed, indicating two processes controlling the corrosion mechanism. The high frequency capacitive semicircle is associated with the charge transfer process at the electrode/electrolyte interface, and the low frequency capacitive loop can be attributed to the passive film formation on the stainless steel surface.

Other amines were also tested using SS304 in order to check its corrosion resistance property with all amine systems. Due to its cheaper cost of material, SS304 was selected over SS316 as the test material for the rest of the amines. The experiments were carried out at similar operating conditions ($CO_2$ saturation and 80°C). The obtained polarization curves are illustrated in Figure 4.55(a). From Table 4.9, the corrosion rate of SS304 in all amine systems was in the range of 0.006 – 0.036 mmpy, well below the standard minimum acceptable corrosion rate (0.07 mmpy). Similar to the MEA system, SS304 in all amine systems readily underwent passivation. No localized corrosion behaviour was observed. From the Nyquist plots (Figure 4.55-b), the existence of a passive system close to the corrosion potential in all the amine systems can be verified by the presence of two time constants.
Figure 4.55: Corrosion behaviour of SS304 in various amines at CO₂ saturation & 80°C (5.0 kmol/m³ of MEA, DEA, MDEA & PZ; and 4.0 kmol/m³ of AMP)

(a) polarization curves and (b) Nyquist plot
Table 4.9: Summary of pH, conductivity, and electrochemical parameters for SS304 and SS316 in different amine systems

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental Condition</th>
<th>pH</th>
<th>σ (mS/cm)</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (µA)</th>
<th>Corrosion rate (mmpy)</th>
<th>$R_{ct}$ (ohm cm$^2$)</th>
<th>$C_{dl}$ (µF/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>SS316 in 5.0 kmol/m$^3$, 0.53 mol/mol &amp; 80°C</td>
<td>8.45±0.02</td>
<td>48.50±0.30</td>
<td>70.50±5.70</td>
<td>37.24±3.30</td>
<td>-657.20±1.20</td>
<td>7.05±0.33</td>
<td>0.027</td>
<td>292.31</td>
<td>113.59</td>
</tr>
<tr>
<td></td>
<td>SS304 in 5.0 kmol/m$^3$, 0.53 mol/mol &amp; 80°C</td>
<td>8.45±0.01</td>
<td>48.50±0.35</td>
<td>79.33±7.10</td>
<td>32.6±8.00</td>
<td>-671.82±2.80</td>
<td>9.19±0.55</td>
<td>0.036</td>
<td>236.16</td>
<td>78.10</td>
</tr>
<tr>
<td></td>
<td>SS304 in 5.0 kmol/m$^3$, 0.53 mol/mol, 80°C &amp; 10,000 ppm NaCl</td>
<td>8.36±0.01</td>
<td>58.55±0.10</td>
<td>45.92±14.55</td>
<td>31.84±1.43</td>
<td>-669.64±2.20</td>
<td>4.41±0.19</td>
<td>0.017</td>
<td>843.79</td>
<td>100.01</td>
</tr>
<tr>
<td>DEA</td>
<td>SS304 in 5.0 kmol/m$^3$, 0.40 mol/mol, &amp; 80°C</td>
<td>8.41±0.02</td>
<td>14.79±0.06</td>
<td>42.01±12.60</td>
<td>38.74±0.26</td>
<td>-681.60±2.40</td>
<td>4.09±0.05</td>
<td>0.016</td>
<td>475.65</td>
<td>110.15</td>
</tr>
<tr>
<td></td>
<td>SS304 in 5.0 kmol/m$^3$, 0.40 mol/mol, 80°C &amp; 10,000 ppm NaCl</td>
<td>8.45±0.02</td>
<td>18.47±0.02</td>
<td>54.46±1.80</td>
<td>35.59±7.10</td>
<td>-680.69±2.00</td>
<td>4.18±0.05</td>
<td>0.017</td>
<td>474.74</td>
<td>110.37</td>
</tr>
<tr>
<td>MDEA</td>
<td>SS304 in 5.0 kmol/m$^3$, 0.14 mol/mol, &amp; 80°C</td>
<td>8.85±0.01</td>
<td>4.52±0.01</td>
<td>36.23±3.20</td>
<td>29.55±7.12</td>
<td>-696.03±8.50</td>
<td>1.67±0.03</td>
<td>0.006</td>
<td>1155.45</td>
<td>117.59</td>
</tr>
<tr>
<td></td>
<td>SS304 in 5.0 kmol/m$^3$, 0.14 mol/mol, 80°C &amp; 10,000 ppm NaCl</td>
<td>8.89±0.02</td>
<td>8.85±0.04</td>
<td>43.40±1.70</td>
<td>21.56±1.70</td>
<td>-712.74±1.10</td>
<td>2.69±0.20</td>
<td>0.009</td>
<td>965.19</td>
<td>87.43</td>
</tr>
<tr>
<td>AMP</td>
<td>SS304 in 4.0 kmol/m$^3$, 0.51 mol/mol, &amp; 80°C</td>
<td>8.99±0.02</td>
<td>25.01±0.07</td>
<td>54.89±9.80</td>
<td>28.26±4.1</td>
<td>-712.97±5.90</td>
<td>4.82±0.02</td>
<td>0.019</td>
<td>444.24</td>
<td>117.95</td>
</tr>
<tr>
<td></td>
<td>SS304 in 4.0 kmol/m$^3$, 0.51 mol/mol, 80°C &amp; 10,000 ppm NaCl</td>
<td>8.94±0.02</td>
<td>32.60±0.05</td>
<td>60.14±5.83</td>
<td>27.64±0.25</td>
<td>-729.38±3.70</td>
<td>9.08±0.22</td>
<td>0.035</td>
<td>414.04</td>
<td>78.58</td>
</tr>
<tr>
<td>PZ</td>
<td>SS304 in 5.0 kmol/m$^3$, 0.82 mol/mol, &amp; 80°C</td>
<td>8.47±0.02</td>
<td>14.07±0.04</td>
<td>46.29±1.20</td>
<td>29.56±0.14</td>
<td>-678.44±5.40</td>
<td>3.12±0.14</td>
<td>0.012</td>
<td>552.06</td>
<td>94.91</td>
</tr>
<tr>
<td></td>
<td>SS304 in 5.0 kmol/m$^3$, 0.82 mol/mol, 80°C &amp; 10,000 ppm NaCl</td>
<td>8.40±0.01</td>
<td>19.10±0.05</td>
<td>56.52±14.80</td>
<td>43.76±1.60</td>
<td>-680.22±7.70</td>
<td>4.12±0.20</td>
<td>0.016</td>
<td>430.65</td>
<td>196.77</td>
</tr>
</tbody>
</table>

$\sigma =$ conductivity; $\beta_a =$ anodic Tafel slope; $\beta_c =$ cathodic Tafel slope; $E_{corr} =$ corrosion potential; $I_{corr} =$ corrosion current; $R_{ct} =$ charge transfer resistance; $C_{dl} =$ double layer capacitance.
Examination of the corrosion behaviour of SS304 with all amines in the presence of 10,000 ppm sodium chloride (NaCl) was also carried out at similar test conditions to the other experiments to test the possibility of pitting corrosion in the presence of process contaminants. The obtained polarization curves are illustrated in Figure 4.56(a), and the measured corrosion rates are presented in Table 4.9. The experimental results suggest that the presence of chloride ions does not have a major influence on the corrosion behaviour of SS304 in an amine-CO$_2$-H$_2$O system. Similar to the blank solution, the polarization curves did not show any active dissolution process, and the specimen exhibited similar passivation behaviour. No pitting corrosion was observed with any of the amine systems. Nyquist plots (Figure 4.56-b) in the presence of NaCl show similar impedance behaviour as that of the blank system.

The comparative polarization curves with and without chloride ions are illustrated in Figure 4.57. The presence of chloride reduces the corrosion rate of SS304 in aqueous MEA solution. From Figure 4.57(a), the presence of NaCl shifts the corrosion potential towards the noble direction and reduces the anodic current density, thereby reducing the corrosion rate. Similar behaviour was also observed for CS1018 in the MEA solution in the presence of NaCl, as discussed in Section 4.3.2.4. In the case of DEA, the polarization curves (Figure 4.57-c) looks alike with very little difference. Thus, the chloride ion has no apparent impact on the corrosion behaviour of SS304 in DEA solution. For the rest of the amines, a minimal increase in the corrosion rate was observed, as presented in Table 4.9. From the polarization curves for AMP, PZ, and MDEA (Figure 4.57), the presence of NaCl resulted in slight increases in anodic current densities, making the solutions slightly more corrosive with these amines.
Figure 4.56: Corrosion behaviour of SS304 in various amines at CO$_2$ saturation & 80°C in presence of 10,000 ppm NaCl (5.0 kmol/m$^3$ of MEA, DEA, MDEA & PZ; and 4.0 kmol/m$^3$ of AMP) (a) polarization curves and (b) Nyquist plot.
**Figure 4.57:** Polarization behaviour of SS304 in various amines with and without 10,000 ppm NaCl (a) MEA (b) AMP (c) DEA (d) PZ and (e) MDEA
4.6 Weight loss experiments

In the previous sections, the corrosion data collected through electrochemical experiments were presented. The corrosivity orders for both single and blended amines were established. However, these electrochemical experiments were based on short-term test durations. In this section, weight loss experiments based on long-term test durations were carried out for single amine systems (MEA, DEA, MDEA, AMP, and PZ) for up to 28 days. CS1018 and SS304 materials were exposed to amine solutions saturated with CO₂ at 80°C. The test concentration of the amine solution was fixed as in the electrochemical experiments, i.e., 5.0 kmol/m³ for MEA, DEA, PZ, and MDEA and 4.0 kmol/m³ for AMP. The weight loss results obtained were used to check the corrosivity trend established from the electrochemical experiments.

Experiments were conducted for 28 days, and the specimens were taken out from the solution at intervals of 7, 14, 21, and 28 days. The corrosion data of CS1018 obtained for all the amines at the specified intervals was presented in Figure 4.58. For amines like DEA, MDEA, AMP, and PZ, the corrosion rates of CS1018 reached maximum levels after 7 days, after which the corrosion rates continued to decrease gradually until the test completion. For MEA, the corrosion rate increased even after 7 days and began to decrease only after 21 days. The corrosivity order at the end of the 28 days was MEA > DEA > PZ > AMP ≈ MDEA. The corrosivity trend established from the weight loss test varies with the electrochemical experiments, as a shift in position of AMP can be observed. For stainless steel (SS304), only MEA was tested since the corrosion rates of SS304 in all amine systems obtained from the electrochemical experiments were low and below the minimum acceptable level of corrosion rate. The weight loss corrosion data for
Figure 4.58: Comparison of weight loss corrosion rate of CS1018 in all amines at CO₂ saturation and 80°C (MEA, DEA, AMP, MDEA - 5.0 kmol/m³ and AMP - 4.0 kmol/m³)
SS304 in the MEA system were compared with the data of CS1018. The results showed no appreciable weight loss with the SS304 specimen, even after 28 days.

The initial increase in corrosion rate followed by a reduced corrosion rate (Figure 4.58) in all amine systems can be explained by considering the passive film forming process. Initially, the metal specimens were clean and film free, exposing the fresh surface with more anodic and cathodic sites to the aqueous amine solution, which favours the corrosion process. Higher anodic dissolution and cathodic reduction rate at the initial stages enhances the corrosion rate and increases the amount of corrosion products. As further corrosion leads to the formation of a passive layer, corrosion protection is developed, resulting in a reduction in corrosion rate. The photographic images of fresh specimens and tested specimens from each amine system (after 28 days), which were covered with corrosion products, are given in Figure 4.59. The level of initial increase in corrosion rate and its later decrease was different for each amine system. Such variations in the trends are directly related to the protectiveness of the passive film and the availability of corrosive species in the solution.

4.6.1 Surface analysis

The SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive X-ray Spectroscopy) analysis of a fresh CS1018 specimen are illustrated in Figure 4.60. From the EDS analysis, elements such as Fe, Mn, and C, which form the basic skeleton of the CS1018 material, were detected from the fresh surface by percent weight (wt%). To determine the nature of the corrosion products formed over the CS1018 specimens in each amine system, XRD (X-ray diffraction) and SEM-EDS analysis was conducted
Figure 4.59: Photographic images of (a) fresh specimen, and tested specimens withdrawn after 28 days (b) MEA (c) DEA (d) PZ (e) AMP and (f) MDEA (Original in colour)
**Figure 4.60**: Fresh CS1018 specimen (a) SEM image (Magnification – 500 X) and (b) EDS analysis with Wt% of the element (Original in colour)
using the tested specimens when they were withdrawn after 28 days. The XRD spectra and SEM-EDS analysis obtained for CS1018 in all amine systems are presented below: MEA-CO$_2$-H$_2$O (Figure 4.61), DEA-CO$_2$-H$_2$O (Figure 4.62), PZ-CO$_2$-H$_2$O (Figure 4.63), AMP-CO$_2$-H$_2$O (Figure 4.64), and MDEA-CO$_2$-H$_2$O (Figure 4.65).

(a) **CS1018 in MEA-CO$_2$-H$_2$O system**

From the XRD spectra (Figure 4.61-a), most of the obtained peaks are broader indicating, either the corrosion products constitute smaller crystallite size or the corrosion products are amorphous in nature. The peak broadening made the peak analysis harder, but the 2-theta (reflection angle) values for most of the peaks nearly coincided with magnetite (Fe$_3$O$_4$) (ICDD No.08-0087). Thus, the corrosion products formed in the MEA system can be indexed to iron oxides, both in crystalline and amorphous form. The formation of such poorly crystallized iron oxides (amorphous rust) over a steel surface has been reported in the literature (Waseda and Suzuki, 2006). The major peak associated with iron (Fe) (ICDD No. 06-0696) can be observed from the XRD spectra, indicating that the passive layer formed is thin and less protective. The less protective nature of the passive film could also be the possible reason for the continuous increase in corrosion rate from 0.40 mmpy (after 7 days) to 0.58 mmpy (after 21 days). Moreover, the availability of all the major corroding agents in MEA solution also plays a vital role in raising the system corrosiveness. None of the peaks match with the iron carbonate (FeCO$_3$) crystals, suggesting that the MEA system does not favour formation of a FeCO$_3$ passive layer over a carbon steel surface under the given test conditions.

The SEM images (Figure 4.61-b) of the corroded specimen do not show any
Figure 4.61: Surface analysis of the CS1018 specimen tested in 5.0 kmol/m$^3$ MEA solution at CO$_2$ saturation and 80°C, removed after 28 days (a) XRD spectra (b) SEM image (Magnification - 1000X) and (c) EDS analysis (Original in colour)
Figure 4.62: Surface analysis of the CS1018 specimen tested in 5.0 kmol/m$^3$ DEA solution at CO$_2$ saturation and 80°C, removed after 28 days (a) XRD spectra (b) SEM image (Magnification - 1000X) and (c) EDS analysis (Original in colour)
Figure 4.6: Surface analysis of the CS1018 specimen tested in 5.0 kmol/m$^3$ PZ solution at CO$_2$ saturation and 80°C, removed after 28 days (a) XRD spectra  (b) SEM image (Magnification - 1000X) and (c) EDS analysis (Original in colour)
Figure 4.64: Surface analysis of the CS1018 specimen tested in 4.0 kmol/m$^3$ AMP solution at CO$_2$ saturation and 80°C, removed after 28 days (a) XRD spectra (b) SEM image (Magnification - 1000X) and (c) EDS analysis (Original in colour)
Figure 4.65: Surface analysis of the CS1018 specimen tested in 5.0 kmol/m$^3$ MDEA solution at CO$_2$ saturation and 80°C, removed after 28 days (a) XRD spectra (b) SEM image (Magnification - 1000X) and (c) EDS analysis (Original in colour)
distinct crystal structures but, rather, a disintegrated rough surface with non-uniform porous deposits can be observed. From the EDS analysis (Figure 4.61-c), a small peak for the element O can be found, confirming the formation of iron oxides as corrosion products. The weight percent of the element Fe is 96.60, which is close to the value obtained for fresh surface (Fe - 97.24%). This, again, confirms the thin nature of the passive layer formed in the MEA system. Since EDS analysis has a depth limit of approximately 1.0 micron, the obtained results suggest that the passive layer formed is very thin and highly porous, bringing out the elemental wt% of freshly exposed surface.

(b) **CS1018 in DEA-CO\(_2\)-H\(_2\)O system**

In the case of DEA, the carbon steel experienced a high initial corrosion rate of around 0.80 mmpy for 7 days of immersion. On visual observation, a discontinuous layer with loose corrosion products was noticed on the specimen. This suggests that either the passivation was not complete or the passive layer formed was not stable enough to offer corrosion protection, resulting in the high initial corrosion rate. By comparison, the specimen removed after 14 days had intact corrosion products (on visual observation), reducing the corrosion rate from 0.80 mmpy (after 7 days) to 0.59 mmpy (after 14 days). The photographic image of the specimen with corrosion products (passive layer) is shown in Figure 4.59(c). From the XRD analysis (Figure 4.62-a), the major corrosion product was found to be iron carbonate. Most of the strong and sharp diffraction peaks in the patterns can be readily indexed to FeCO\(_3\), with 2-theta (reflection angle) values in agreement with the standard values (ICDD No. 29-0696). The presence of Fe\(_3\)O\(_4\) in the passive layer was also confirmed from the XRD peak (ICDD No. 08-0087).
From the SEM image (Figure 4.62-b), crystallite deposits of varying sizes can be observed. The dense FeCO$_3$ film was more uniformly distributed on the surface, which protected the metal from corrosion attack. Magnetite (Fe$_3$O$_4$) deposits were, in general, found underneath the FeCO$_3$ layer (Revie, 2011). From EDS surface analysis (Figure 4.62-c), the presence of a peak for the element O with 22.70 wt% can be observed. In comparison with the fresh surface, the wt% of the element C increased from 1.41 to 10.35, and the wt% of Fe decreased from 97.24 to 65.05. These values substantiate the presence of FeCO$_3$ and Fe$_3$O$_4$ passive layer. Localized corrosion attack (Figure 4.66) was observed with the specimen (after chemical cleaning). This is in accordance with the findings from the electrochemical polarization curve, which showed pitting tendency with the DEA system.

(c) **CS1018 in PZ-CO$_2$-H$_2$O system**

Unlike the DEA system, the tested specimen in the PZ system, when withdrawn after 7 days, had an intact passive layer on visual observation. The XRD spectra obtained for the PZ system (Figure 4.63-a) matched exactly the spectra obtained for the DEA system but with varying peak intensity. Thus, the major corrosion product was found to be FeCO$_3$ with a small amount of Fe$_3$O$_4$. The SEM image (Figure 4.63-b) shows a much larger crystallite size than that obtained for the DEA system. Such comparatively large crystals were visually observed as tiny white dots over the carbon steel specimen, as shown in Figure 4.59(d). The presence of these corrosion products can also be verified from the EDS analysis showing a major oxygen peak (Figure 4.63-c). Figure 4.67 presents the microscopic images of the specimens withdrawn from the PZ system after 7
Figure 4.66: SEM image of CS1018 (after chemical cleaning) tested in DEA system showing localized corrosion behaviour (a) 250 X (b) 500 X (Original in colour)

Figure 4.67: Microscopic image (Magnification – 50 X) of corrosion products over CS1018 surface immersed in 5.0 kmol/m³ PZ at CO₂ saturation and 80°C (a) after 7 days (b) after 14 days (Original in colour)
and 14 days. The definite increase in crystallite size between the two specimens (7 and 14 days) can be observed. This can be related to the increase in surface coverage of the specimen with the passive layer, resulting in a reduced corrosion rate.

(d) **CS1018 in AMP-CO\textsubscript{2}-H\textsubscript{2}O system**

With the AMP system, a distinct passive layer was visually observed for all the specimens withdrawn from the solution. The colour of the passive layer formed in the AMP system was different from the rest of the amine systems (Figure 4.59). For the AMP system, XRD spectra (Figure 4.64-a) similar to the DEA and PZ systems were obtained, indicating the formation of FeCO\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} deposits as corrosion products. Unlike with DEA and PZ, the SEM image (Figure 4.64-b) obtained for the AMP system shows small crystallite deposits. The EDS analysis (Figure 4.64-c) with high oxygen and carbon weight% confirms the presence of FeCO\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} deposits. The passive layer formed was not very intact, as it was peeled off very easily (Figure 4.68). However, the system experienced lower corrosion rate, which was determined by the type and availability of the corrosive species. The corrosion rate of CS1018 in the AMP system measured after 7, 14, 21 and, 28 days was very similar to that of the MDEA system, as illustrated in Figure 4.57. Moreover, the corrosion rate in the AMP system (0.08 mmpy) after 28 days was less than both the PZ (0.16 mmpy) and DEA (0.27 mmpy) systems. These results contradict the electrochemically established corrosion trends.

(e) **CS1018 in MDEA-CO\textsubscript{2}-H\textsubscript{2}O system**

With the MDEA system, all the withdrawn specimens had intact passive films on
Figure 4.68: Photographic image of corroded specimen (before chemical cleaning) in AMP system taken after 28 days (a) undisturbed passive layer and (b) specimen with peeled off passive layer (Original in colour)
visual observation, as shown in Figure 4.59(f). The XRD spectra (Figure 4.65-a) obtained for the MDEA system were similar to those of the DEA, PZ, and AMP systems, indicating the presence of FeCO$_3$ and Fe$_3$O$_4$ deposits over the carbon steel surface. The SEM image (Figure 4.65-b) shows the presence of uniform crystallite deposits of varying sizes, and EDS analysis (Figure 4.65-c) indicated the presence of iron carbonate and iron oxide corrosion products.

(f) **SS304 in MEA-CO$_2$-H$_2$O system**

In comparison with CS1018, the SS304 specimen in the MEA system appeared fresh and polished on visual observation, even after 28 days of immersion (Figure 4.69). The SS304 material had not undergone any corrosion attack and remained stable even after 28 days. As discussed in Section 4.5, the formation of a chromium oxide layer with stainless steel offered greater corrosion protection right from the early stages of testing. The SEM and EDS analyses of the fresh and tested SS304 specimens are shown in Figures 4.70 – 4.71. From the SEM image, scattered dark patches can be observed on the tested specimen. These might be due to the preferential etching of some of the elements from the grain boundaries, resulting in alloy depleted regions.

4.6.2 **Amine degradation during experiments**

All amines are prone to both oxidative and thermal degradation, but the rates of degradation differ for each amine. Though all the test solutions were saturated with CO$_2$, the solution might contain trace amounts of oxygen, which can induce oxidative degradation. Moreover, the intrusion of oxygen into the system was inevitable during the
Figure 4.69: Photographic image of SS304 (left) and CS1018 (right) specimens tested with MEA system (a) Before immersion and (b) After 28 days (Original in colour)
**Figure 4.70:** Fresh SS304 specimen (a) SEM image (Magnification – 500 X) and (b) EDS analysis (Original in colour)

**Figure 4.71:** Surface analysis of SS304 surface immersed in 5.0 kmol/m³ MEA at CO₂ saturation and 80°C, after 28 days (a) SEM image (Magnification - 500X) and (b) EDS analysis (Original in colour)
solution sampling and the specimen removal process. The weight loss solution was not analyzed for the presence of degradation products. However, the degradation of amines was observed from the colour change of the weight loss solutions during the experiments.

The colour changes observed with each amine system are illustrated in Figures 4.72-4.76. In general, the presence of metal cations such as iron (II), copper (II), chromium (III), and nickel (II) (Fe$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, and Ni$^{2+}$) will catalyze the amine oxidation reactions (Blachly and Ravner, 1966; Chi and Rochelle, 2002). The above metal catalyzed oxidation mechanism was confirmed during the weight loss experiments with the MEA system using CS1018 and SS304 specimens. Since carbon steel is highly corrosive compared to stainless steel, the concentration of ferrous ion (Fe$^{2+}$) in the weight loss solution should be higher with carbon steel experiment. This should have enhanced the amine oxidation reaction with CS1018 experiment. This metal ion catalyzed degradation process was confirmed with the rapid colour change of amine solution observed with the carbon steel experiment, whereas with stainless steel experiment, the colour change was very minimal even after 28 days (Figure 4.72).

Unlike the MEA system, the colour change was not as rapid in the DEA system. A slight change in colour was observed only after 4 days. The final colour of the DEA solution (Figure 4.73) after 28 days was less intense compared to the MEA system. With the PZ system, the colour change was as rapid as that of the MEA system (Figure 4.74). Since, AMP is a more stable amine than MEA (as discussed in Chapter 1), a minimum colour change was observed for the AMP solution at the end of the experiments (Figure 4.75). The visual appearance of the MDEA weight loss solution after 28 days (Figure 4.76), showed colour change similar to that of DEA system.
Figure 4.72: Weight loss solution of MEA system tested with SS304 (left corrosion cell) and CS1018 (right corrosion cell) (a) Day 1 and (b) Day 28

(Original in colour)
Figure 4.73: Weight loss solution of DEA system (a) Day 1 (b) Day 28

(Original in colour)

Figure 4.74: Weight loss solution of PZ system (a) Day 1 (b) Day 28

(Original in colour)
**Figure 4.75:** Weight loss solution of AMP system (a) Day 1 (b) Day 28

(Original in colour)

**Figure 4.76:** Weight loss solution of MDEA system (a) Day 1 (b) Day 28

(Original in colour)
5. CONCLUSIONS AND FUTURE WORK

5.1 Conclusion

In this work, we have significantly extended the knowledge of corrosion in the CO₂ absorption process using aqueous solutions of five different amine absorption solvents. An engineering corrosion database has been created for the amine-based CO₂ capture process. Comparative corrosion analysis was carried out with both single amine and blended amine systems in order to establish a corrosivity order among the studied amine systems. It is the first research work that has tested the corrosivity of concentrated PZ as an absorption solvent for the CO₂ capture process. The corrosion analysis of single amines was successfully performed by considering the quantity of corroding agents in each amine system and by utilizing corrosion inhibitor principles including Quantitative Structure Activity Relationship (QSAR) method and Hard and Soft Acid and Base (HSAB) theory. The performances of corrosion resistant alloys (CRA) in the aqueous amine-CO₂ environment were also tested in this work. More specific conclusions, drawn from the experimental and theoretical analyses, are listed below:

- Corrosiveness of carbon steel in amine systems is greatly influenced by solution temperature and CO₂ loading. The temperature dependency of corrosion rate follows Arrhenius behaviour.

- The corrosivity order of carbon steel in single amine systems saturated with CO₂ at 80°C decreases in the following order: MEA > AMP > DEA > PZ > MDEA. Localized corrosion behaviour was observed with the DEA and PZ systems.
• The passive layer formed over carbon steel in the DEA-CO₂-H₂O system was more compact and less porous, and the compactness of the passive film for all tested amine systems decreases in the following order: DEA > MDEA > PZ > MEA > AMP.

• The presence of thiosulfate significantly decreased the corrosion rate of carbon steel in the MEA system.

• The presence of oxalate increased the corrosion rate of carbon steel in all amine systems. The corrosion rate in the MDEA and PZ systems increased drastically compared to MEA, AMP, and DEA. The corrosivity order decreases in the following order: MEA > AMP > PZ > DEA > MDEA. Pitting tendency was observed with the PZ system.

• The presence of sodium sulfite in amine solution resulted in minimal increase in corrosion rate of carbon steel in most amine systems other than AMP. The corrosivity order decreases in the following order: MEA > DEA > PZ > MDEA > AMP. Other than MDEA, minimal pitting tendency was observed with all other amines.

• With sodium chloride, a slight increase in corrosion rate of carbon steel was observed only in the MDEA system, and the corrosion rate decreased for the rest of the amines. The corrosivity order remained same as that of a blank amine systems (MEA > AMP > DEA > PZ > MDEA). The presence of chloride ions induced heavy pitting with the DEA system and minimum pitting with the PZ system.

• Corrosivity order of CS1018 in blended amine systems was predicted as MEA-PZ ≥ MEA-AMP ≥ MEA-MDEA > MDEA-PZ > AMP-PZ. Localized corrosion behaviour was observed with MEA-PZ and MEA-MDEA blends.
• A direct correlation was established between the conductivity of the solution and the corrosion rate of carbon steel in both single and blended amine systems. Thus, conductivity can be used as a corrosion indicator for corrosion monitoring purposes. The pH of the solution was not correlated with the corrosion rate. The linear relationship between the corrosion rate and CO₂ loading of the solution in the unit of mol CO₂/mol alkalinity was established.

• The corrosion resistance of stainless steel (SS304) in all amine systems was very high, and the corrosion rate was well below the industrially acceptable minimum corrosion level (0.07 mmpy). The presence of chloride ions did not induce any form of localized corrosion with stainless steel.

• From the weight loss experiments, the corrosivity order of CS1018 in single amine systems after 28 days duration was MEA > DEA > PZ > AMP ≈ MDEA. From the surface analysis, the corrosion products formed over the carbon steel surface were found to be iron carbonate (FeCO₃) and iron oxide (Fe₃O₄). No appreciable weight loss was observed with the SS304 specimen in the aqueous MEA-CO₂ system.

5.2 Recommendations for future work

This present work serves as a guideline for the selection of suitable absorption solvents in either single or blended amine systems in terms of minimum corrosion difficulties. This work can be further strengthened by focusing on the following points in future work:

• Most of our experiments were conducted at 80°C. Since CO₂ capture plants operate up to 120°C, experiments need to be conducted at higher temperatures (80 - 120°C).
This would address potential corrosion problem in the entire amine unit and help in service life prediction of construction material exposed to such high temperatures. These experiments can be conducted with the help of a high temperature autoclave.

- Lots of other parametric studies such as the effect of oxygen inclusion, amine concentration, and solution velocity can be considered in building up the corrosion database. All the electrochemical experiments and the weight loss experiments were conducted under static conditions. Flow loop experiments can be planned in the future in order to simulate actual plant conditions.

- Speciation studies for each amine system under the test conditions can present a wider picture on the possible corroding agents in the aqueous amine-CO$_2$ environment.

- Not many process contaminants were examined in this present work. As each amine reacts differently to the process contaminants, experiments need to be conducted with many other heat stable salts and contaminants.

- Since blended absorption solvents are considered to be a promising alternative for the CO$_2$ capture process, more experiments need to be conducted with blended amines.

- A more realistic approach can be planned by conducting experiments using the solution samples collected from industries.
REFERENCES


Appl, M., Wagner, U., Henrici, H. J., Kuessner, K., Volkamer, K., Fuerst, E., (1980), Removal of CO\textsubscript{2} and/or H\textsubscript{2}S and/or COS from gases containing these constituents, Canadian Patent No. 1,090,098.


Herzog, H., Vukmirovic, N., (1999), CO\textsubscript{2} sequestration: opportunities and challenges. 

Presented at the Seventh Clean Coal Technology Conference; Knoxville, Tennessee.


Howard, M., Sargent, A., (2001), Texas gas plant faces ongoing battle with oxygen contamination, Oil Gas J.,


IPCC (1990), Policymaker’s Summary of the Scientific Assessment of Climate Change, Report to IPCC from Working Group; Meteorological Office, Branknell, UK.


Setameeteekul, A., Aroonwilas, A., Veawab, A., (2008), Statistical factorial design analysis for parametric interaction and empirical correlations of CO₂ absorption


