Electrochemical Kinetics and Mechanisms of Iron Oxidation in CO$_2$-containing Aqueous Monoethanolamine

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Declaration of Originality

I, Folasade Labiyi, hereby certify that this thesis has been written by me, based on the original work conducted by me, under the guidance and advice of my academic supervisors in the Department of Chemical Engineering at Imperial College London. The information used or derived from other published or unpublished sources have been clearly sited and appropriately acknowledged in the list of references.

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Abstract

Concerns about the impact of anthropogenic CO₂ emissions on global climate change are necessitating the development of low-carbon technologies. Despite its energy requirements, carbon capture and sequestration (CCS) provides a promising approach to limiting carbon dioxide emissions, in addition to renewable energy and nuclear power. Due to the depth of technological experience and retrofitting capabilities associated with the process, post-combustion CO₂ capture based on absorption in alkanolamine solutions is presently the most feasible technology available for mitigating the soaring levels of atmospheric CO₂ and achieving the ambitious targets set by the Intergovernmental Panel for Climate Change (IPCC).

Whilst the process of CO₂ capture by alkanolamines involves a technologically mature process, it is still faced with numerous challenges, such as high energy requirements and operating costs, as well as operational difficulties. Monoethanolamine (MEA), the benchmark amine for the process, frequently becomes contaminated with degradation products and, when CO₂-loaded, is corrosive to the carbon steel process equipment. Hence, this thesis aimed to determine the oxidation and reduction reaction kinetics and mechanisms of iron in aqueous MEA-CO₂ systems as function of experimental variables, aiming to predict iron corrosion rates under process conditions.

The behaviour of iron in aqueous MEA solutions was characterized by voltammetry with a rotating disc electrode (RDE) and an electrochemical quartz crystal microbalance (EQCM), as functions of temperature (25-80°C), CO₂ loading (0-0.6 mol CO₂ (mol amine)⁻¹), pH (8.10-12.55), MEA concentration (5-60 wt%) and oxygen concentration. Electrode potential-pH and activity-pH diagrams of iron-water–CO₂ systems were used to assist with reaction assignments.
The passive electrochemical behaviour of Fe in MEA at pH ca. 12 switched to active dissolution on loading the MEA with CO₂, causing the pH to decrease to ca. 8. Analysis of the resulting kinetic data enabled corrosion rates to be predicted as functions of the experimental variables.

Based on the proposed corrosion mechanisms from the voltammetric results, a mechanistic model was developed for the uniform corrosion of iron in CO₂-loaded MEA systems, taking into account the CO₂ absorption equilibria reactions and the electrochemical reactions at the iron | solution interface. Equilibrium concentrations of the amine species (RNH₂, RNH₃⁺, RNHCOO⁻), carbon(IV) species (HCO₃⁻, CO₃²⁻) and hydrogen ions (H⁺) were calculated with a Kent-Eisenberg type model. The electrochemical reactions incorporated in the model were the anodic dissolution of iron and the cathodic reduction of H⁺, direct water reduction and the reduction of oxygen. The corrosion model was developed by simulating polarization curves based on the species concentrations and the transport limited current densities of the iron RDE defined by the Levich equation.

In order to measure dissolved iron concentrations under typical CO₂ absorption conditions, an electrochemical flow reactor was designed and fabricated from PTFE with an iron/steel anode, platinised titanium cathode and a cation-permeable Naion membrane. Inductively coupled plasma optical emission spectrophotometry (ICP-OES) was used to determine Fe(II) concentrations in the amine solution after potentiostatic electrolyses as a function of solution flow-rate, temperature, CO₂ loading, pH, MEA concentration, oxygen content, steel type and amine type, enabling partial current densities leading to iron dissolution to be deconvoluted from measured current densities.

Results from the voltammetric data from the RDE were used to propose a mechanism for the oxidation and reduction reactions occurring at the iron surface. During positive-going potential sweeps, the voltammograms were characterised by 3 anodic peaks corresponding to the anodic
dissolution of Fe to Fe\textsuperscript{II} at low potentials, leading to iron carbonate formation if its solubility product was exceeded, and a passive region from the formation of adsorbed products such as iron(III) (hydr-)oxide at higher potentials. The cathodic reactions at the iron surface included reductions of H\textsuperscript{+}, H\textsubscript{2}O and O\textsubscript{2}.

Based on the thermodynamic predictions, the anodic dissolution of iron was assigned to the formation of a soluble Fe\textsuperscript{II} species. Using a flow reactor operated in batch recycle mode, constant potential electrolyses at a potential -0.6 V, within the anodic dissolution potential range, resulted in a dissolution charge yield of less than unity, which varied depending on the experimental conditions, implying the formation of insoluble iron species such as Fe(OH)\textsubscript{2} or FeCO\textsubscript{3}. The mass transport behaviour of the flow reactor was characterised as a function of solution flow rate using the transport controlled reduction of hexacyanoferrate(III) ions at a platinised titanium electrode, resulting in a mass transport correlation for the reactor. A value of the diffusion coefficient for Fe\textsuperscript{II} from the literature enabled prediction of the conditions required for FeCO\textsubscript{3} and Fe(OH)\textsubscript{2} formation, based on measured fluxes and dissolved Fe\textsuperscript{II} concentrations in solution, from which the rate of FeCO\textsubscript{3} formation could also be estimated.

Kinetic analysis of the data from the RDE, EQCM, flow reactor and the corrosion model resulted in a complementary set of results. The corrosion behaviour of iron in aqueous MEA-CO\textsubscript{2} solutions was sensitive to changes in the operating parameters; iron dissolution rates were enhanced by increasing temperature, CO\textsubscript{2} loading, solution velocity and oxygen content. However, at high temperatures, high CO\textsubscript{2} loading and high Fe\textsuperscript{II} concentration and lower solution velocity provided favourable conditions under which a protective FeCO\textsubscript{3} layer could precipitate. Dissolution rates increased with concentration at lower concentrations of MEA (5-40 wt%) and decreased with increasing concentration at higher concentrations (40-60 wt%), due to viscosity effects. Significantly lower corrosion rates were measured in the other
commercially available solvents tested namely methyl-diethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP) and aminoethylpiperazine (AEP). Carbon steel exhibited similar dissolution rates to those of iron, whereas those for stainless steel were significantly lower.

From the comprehensive results on the oxidation and reduction kinetics of iron in benchmark MEA-CO$_2$ systems, the effect of MEA concentrations on predicted iron corrosion rates brings into question the effectiveness of the concentration of MEA used in amine scrubbing being limited to 30 wt%, specifically to limit corrosion related issues. The results also indicated that MEA was the most ‘aggressive’ in corrosion behaviour, as other amines such as MDEA, AMP and AEP provided more promising alternatives, based on both their predicted corrosion behaviour and their reported efficiencies in the absorption process.
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Contents

Declaration of Originality ........................................................................................................... I
Abstract ........................................................................................................................................ II
Acknowledgements ..................................................................................................................... V
Contents ......................................................................................................................................... VI
List of Figures ............................................................................................................................ XII
List of Tables ................................................................................................................................ XXIX
Nomenclature ............................................................................................................................ XXXIII

1. Chapter 1 Introduction ........................................................................................................... 1
   1.1. Motivation for carbon capture and sequestration ......................................................... 1
   1.2. Operational difficulties in CO$_2$ absorption process .................................................. 6
   1.3. Corrosion in Amine Scrubbing Plants ......................................................................... 7
   1.4. Existing Corrosion Control ......................................................................................... 8
   1.5. Limitation to Available Corrosion Data ................................................................... 9
   1.6. Project Aims .............................................................................................................. 10
   1.7. Project Scope and Objectives ..................................................................................... 10
      1.7.1. Project Tasks ........................................................................................................ 11
   1.8. Thesis outline: ........................................................................................................... 12
   1.9. References ............................................................................................................... 14

2. Chapter 2 Principles of Electrochemical Systems for Corrosion Studies ....................... 16
   2.1. Thermodynamics of Electrochemical reactions ......................................................... 18
      2.1.1. Nernst Equation ................................................................................................ 19
      2.1.2. Pourbaix Diagrams .......................................................................................... 20
2.2. Kinetics of Electrochemical Reactions ................................................................................................................................. 26
  2.2.1. Rate of reaction: Faraday’s Laws of Electrolysis .................................................................................................................. 26
  2.2.2. Rate limiting Mechanisms .................................................................................................................................................. 28
  2.2.3. Charge Transfer Controlled Reactions ............................................................................................................................. 28
  2.2.4. Mixed Potential Theory ...................................................................................................................................................... 33
2.3. Mass transport ........................................................................................................................................................................... 36
  2.3.1. Transport Processes in Electrochemical Systems .............................................................................................................. 36
  2.3.2. Electrochemical Reaction Coupled to Mass Transport ................................................................................................... 43
2.4. References .................................................................................................................................................................................. 46

3. Chapter 3 Literature Review .......................................................................................................................................................... 47
  3.1. The CO\textsubscript{2} Absorption Process ........................................................................................................................................ 48
  3.2. Solvents for CO\textsubscript{2} Absorption ........................................................................................................................................... 53
    3.2.1. CO\textsubscript{2} Absorption Reactions ............................................................................................................................................... 53
  3.3. CO\textsubscript{2} Induced Corrosion in Amine Plants ....................................................................................................................... 59
    3.3.1. Plant Experience ................................................................................................................................................................. 60
  3.4. Corrosion Mechanisms in Amine Plants .................................................................................................................................. 68
    3.4.1. Wet Acid Gas Corrosion ..................................................................................................................................................... 69
    3.4.2. Amine Solution Carbon Steel Corrosion ................................................................................................................................. 78
  3.5. Factors Affecting CO\textsubscript{2} Corrosion in Amine Plants ........................................................................................................ 80
    3.5.1. Temperature .......................................................................................................................................................................... 80
    3.5.2. CO\textsubscript{2} Loading ............................................................................................................................................................ 83
    3.5.3. Amine Type ............................................................................................................................................................................ 85
    3.5.4. Amine Concentration ............................................................................................................................................................ 88
    3.5.5. Effect of Oxygen .................................................................................................................................................................. 88
    3.5.6. Effect of Surface Films ......................................................................................................................................................... 89
    3.5.7. Amine Degradation Products ............................................................................................................................................... 91
3.6. Review of Corrosion Product Films ................................................................. 94
  3.6.1. Iron Carbide Films ..................................................................................... 95
3.7. Iron carbonate Film ....................................................................................... 97
  3.7.1. Mixed Iron Carbonate and Iron Carbide Film ............................................ 106
  3.7.2. Iron Carbonate and Iron Oxide Film ....................................................... 108
3.8. Corrosion Inhibitors for Amine Absorption Plants ......................................... 110
3.9. Equilibrium Models for Aqueous Amine CO₂ Systems .................................. 115
  3.9.1. Solution Chemistry .................................................................................. 115
  3.9.2. Thermodynamic Framework .................................................................. 116
3.10. Review of the mechanisms of iron dissolution and hydrogen evolution ......... 120
  3.10.1. Mechanism of the dissolution of iron ..................................................... 120
  3.10.2. The influence of halide ions on dissolution kinetics ............................... 129
  3.10.3. Mechanisms for Dissolution of Iron in Solutions in the Mid-pH range ...... 131
  3.10.4. Mechanisms of Iron Dissolution in Alkaline Solutions .......................... 132
3.11. The Mechanism of Hydrogen Evolution Reaction (HER) on Iron .................. 135
3.12. Experimental work in CO₂-containing solutions ......................................... 138
3.13. References .................................................................................................... 141

4. Chapter 4 Experimental Methods and Materials ............................................ 155
4.1. Materials ........................................................................................................ 157
  4.1.1. Chemicals ............................................................................................... 157
  4.1.2. Standard reagents .................................................................................. 157
  4.1.3. Electrode Materials ............................................................................... 158
  4.1.4. Cation Exchange Membrane .................................................................. 160
  4.1.5. Gases ...................................................................................................... 160
4.2. Electrode and Solution Preparation ................................................................ 160
  4.2.1. Electrodes .............................................................................................. 160
4.2.2. Aqueous Amine Solutions ................................................................. 161

4.3. Instrumentation for Electrochemical Measurements ........................................... 162

4.4. Experimental Methods for Micro-kinetic studies on Iron .................................... 162

4.4.1. Cyclic Voltammetry ............................................................................. 162

4.4.2. Kinetic Studies Using Rotating Disc Electrodes ............................................. 163

4.4.3. Tafel Slopes Extrapolation Method for Corrosion Rate Determination .......... 169

4.4.4. Electrochemical Quartz Crystal Microbalance ............................................. 171


4.5.1. Reactor design, configuration and materials .................................................. 178

4.5.2. Experiment Procedure ............................................................................... 180

4.6. References .................................................................................................. 184

5. Chapter 5 Electrochemical Study of Iron Electrodes in MEA-H₂O-CO₂ Systems 188

5.1. Fe in MEA+ H₂O (absence of CO₂) ............................................................. 188

5.2. Fe in MEA + H₂O + CO₂ ......................................................................... 194

5.3. Effect of electrochemical parameters ......................................................... 200

5.3.1. Effect of electrode rotation rate ............................................................... 200

5.3.2. Effect of positive potential limit ............................................................... 203

5.3.3. Effect of potential scan rate .................................................................... 206

5.4. Effect of Process Parameters ....................................................................... 210

5.4.1. Effect of temperature ............................................................................. 210

5.4.2. Effects of CO₂ loading and pH ............................................................... 214

5.4.3. Effect of MEA concentration ................................................................... 231

5.4.4. Effect of Oxygen .................................................................................... 237

5.5. Interpretation and Discussion ......................................................................... 239

5.6. Kinetic analysis ........................................................................................... 245
5.6.1. Effect of CO₂ loading................................................................. 246
5.6.2. Temperature effect........................................................................ 248
5.6.1. Effect of MEA Concentration.......................................................... 253
5.6.2. Effect of Mass Transport ................................................................. 260
5.6.2. Effect of Oxygen............................................................................... 262
5.7. Summary & Conclusions .................................................................. 266

6. Chapter 6 Mechanistic Model for the Prediction of Corrosion of Iron in MEA + H₂0 + CO₂ Solutions ................................................................. 270
6.1. Integrated Model for Fe corrosion in MEA+ H₂O+CO₂........................... 271
   6.1.1. Model scheme.................................................................................. 274
   6.1.2. Model Structure and Development.................................................... 276
   6.1.3. Thermodynamic Modelling of Aqueous MEA-CO₂ system..................... 280
   6.1.4. Electrochemical model for Iron in MEA-CO₂-H₂O............................... 282
6.2. Model Verification by Comparison with Experiments.............................. 290
6.3. Effect of CO₂ loading.......................................................................... 292
6.4. Effect of Temperature......................................................................... 295
6.5. Effect of MEA Concentration................................................................. 300
6.6. Discussion and Conclusions ................................................................. 305
6.7. References........................................................................................... 308

7. Chapter 7 Analysis of Time-dependent Corrosion of Iron in MEA- H₂O- CO₂ Systems..................................................................................................... 310
7.1. Electrochemical Behaviour of Iron in Large Scale Electrode ....................... 312
7.2. Effect of Electrode Potential.................................................................. 314
7.3. Effect of Solution Velocity.................................................................... 319
   7.3.1. Reactor Characterisation with Mass Transport Correlations................. 319
   7.3.2. Reactor Characterisation by the Reduction of Hexacyanoferrate(III)........ 321
   7.3.3. Effect of solution flow rate on iron corrosion in MEA+ CO₂ solutions..... 325
7.4. Temperature Effect - Full CO₂ saturation ................................................................. 330
7.5. Effect of CO₂ loading ............................................................................................ 337
7.6. Effect of Oxygen Content ....................................................................................... 346
7.7. Effect of MEA concentration .................................................................................. 350
7.8. Effect of Metal Type ............................................................................................... 361
7.9. Effect of Amine Type ............................................................................................. 367
7.10. Longer Term Corrosion Measurements ................................................................ 376
7.11. References ........................................................................................................... 376

8. Chapter 8 Conclusions and Future Work ................................................................. 382
8.1. Summary of this project ......................................................................................... 383
8.2. Rotating Disc Electrode and Electrochemical Quartz Crystal Results ............... 383
8.3. Mechanistic Modelling ......................................................................................... 387
8.4. Electrochemical Flow reactor ............................................................................... 388
8.5. Future Work Proposals ......................................................................................... 391

9. Chapter 9 Appendices ............................................................................................... 393
I. CO₂ Solubility Data .................................................................................................... 394
II. Cyclic Voltammetry Data ........................................................................................ 396
III. Effect of MEA Concentration ................................................................................. 397
IV. The influence of ionic composition on the electrochemical behaviour of iron in sodium carbonate-hydrogen carbonate solutions at pH 8.01 ..................................... 401
V. Kinetic Data obtained from Polarization curves ....................................................... 402
VI. Thermodynamic Data ............................................................................................. 406
List of Figures

Figure 1-1: Post-combustion, pre-combustion and oxy-fuel combustion CO\textsubscript{2} capture systems (Figueroa et al., 2008). ................................................................. 5

Figure 2-1: Pourbaix diagram of water; 298 K, 0.1 MPa. ............................................. 22

Figure 2-2: Potential-pH diagram for Fe-H\textsubscript{2}O systems with dissolved iron activity of 10\textsuperscript{-4}, 298 K and 0.1 MPa (Kelsall 2011). ................................................................. 26

Figure 2-3: Schematic representation of the relationship between current and potential for a simple electrochemical reaction under kinetic control. ................................................. 29

Figure 2-4: Plot of Butler-Volmer Equation for charge transfer limited reaction. ............. 31

Figure 2-5: Schematic of Tafel plot ........................................................................... 32

Figure 2-6: Anodic and cathodic half-cell reactions present simultaneously on a corroding iron surface in acidic media ................................................................. 34

Figure 2-7: Relationship of measured polarization curve to the Evans diagram for corroding metal in acidic media .......... 35

Figure 2-8: Schematic of an electrochemical system showing the transport processes and one dimensional distribution of electrical potential .................................................................. 38

Figure 2-9: Regions of Cathodic Current density-Overpotential Relationship ............... 44

Figure 3-1: Amine CO\textsubscript{2} capture system flow diagram ..................................... 49

Figure 3-2: Reaction Scheme of Alkanolamines with CO\textsubscript{2} .................................. 54

Figure 3-3: Flow diagram of a typical amine plant showing principal areas of corrosion and suggested materials of construction (Kohl & Nielsen, 1997). ............................................. 68

Figure 3-4: Effects of temperature and CO\textsubscript{2} partial pressures on carbon steel corrosion rates (de Waard and Lotz, 1993) ................................................................. 82

Figure 3-5: Nomograph for corrosion rates of carbon steel in aqueous CO\textsubscript{2} environments (de Waard and Lotz, 1993). ................................................................. 82
Figure 3-6: Calculated growth rate of iron carbonate as a function of temperature and supersaturation (Jonson and Tomson, 1991).

Figure 3-7: FeCO$_3$ embedded in a Fe$_3$C Film; 80°C, 10-100 supersaturation ratio (Dugstad, 1998).

Figure 3-8: FeCO$_3$ embedded in a Fe$_3$C film; 60°C, 10-100 supersaturation ratio (Dugstad, 1998).

Figure 3-9: FeCO$_3$ embedded in a Fe$_3$C film; 60°C, 1-3 supersaturation ratio (Dugstad, 1998).

Figure 3-10: The composition of protective and non-protective iron carbide and iron carbonate films (Crolet et al., 1996).

Figure 3-11: Potential-pH diagram for Fe-CO$_2$-H$_2$O System, showing the lines for dissolved iron activity of 10$^{-4}$ and (0.1 MPa CO$_2$, 298 K) (Kelsall 2013).

Figure 3-12: Potential-PH diagram for the V-H$_2$O system at 298K. Activity of dissolved species = 0.01 (Kelsall et al., 1992).

Figure 3-13: General reaction scheme for iron dissolution (Drazic, 1989).

Figure 4-1: Schematic of the side and end view of the RDE and the flow pattern induced by rotation of an RDE system.

Figure 4-2: Rotating disc electrode system.

Figure 4-3: Tafel plot for the determination of corrosion current density and hence rate.

Figure 4-4: Acoustic waves propagating through a quartz crystal, electrodes and deposit.

Figure 4-5: Schematic diagram of membrane-divided electrochemical flow reactor.

Figure 4-6: Schematic diagram of the experimental set-up of the electrochemical flow reactor.

Figure 4-7: (a) The assembled electrochemical flow reactor in action (b) The anolyte compartment (c) The catholyte compartment (d) A Fe plate (anode)

Figure 5-1: Cyclic voltammogram of a stationary iron RDE in 30 wt% MEA, at 10 mV s$^{-1}$ (T = 25°C, pH 12.55).

Figure 5-2: Influence of electrode rotation rate on voltammogram of iron RDE in 30 wt% MEA, at 10 mV s$^{-1}$ (T = 25 °C, pH 12.55).
Figure 5-3: Influence of rotation rate on the voltammogram obtained on an iron RDE in 30 wt% MEA, at 10 mV s\(^{-1}\) (T = 40 °C, pH 12.27) .......................................................... 192

Figure 5-4: Influence of electrode rotation rate on voltammograms of iron RDE in 30 wt% MEA, at 10 mV s\(^{-1}\) (T = 60°C, pH 12.10) ........................................................................... 192

Figure 5-5: Stable (black) and meta-stable (red) potential-pH diagrams for Fe-H\(_2\)O system for dissolved iron activity of \(10^{-6}\), 298 K and 0.1 MPa (Kelsall 2011); red lines correspond to meta-stable behaviour of iron hydroxides rather than the more stable oxides.......................... 193

Figure 5-6: Liquid-phase composition of 30wt% MEA solution loaded with CO\(_2\) at 25°C. Compositions were calculated with the Kent-Eisenberg Model (Kent and Eisenberg, 1976). .......................................................................................................................... 195

Figure 5-7: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA + H\(_2\)O + CO\(_2\); 10 mV s\(^{-1}\) (T = 25 °C, pH 8.01). ........................................................................................................... 196

Figure 5-8: Cyclic voltammogram of a stationary iron RDE in 30 wt% MEA + H\(_2\)O + CO\(_2\), at 10 mV s\(^{-1}\) (T = 25 °C, pH 8.01) with reactions assigned. .......................................................... 196

Figure 5-9: Potential-pH diagram for Fe-CO\(_2\)-H\(_2\)O System, showing the lines for dissolved iron activity of \(10^{-4}\) and (0.1 MPa CO\(_2\), 298 K). ............................................................. 199

Figure 5-10: Effect of rotation rate on cyclic voltammograms of an iron RDE in 30wt% MEA + H\(_2\)O + CO\(_2\), at 10 mV s\(^{-1}\) (T = 25°C, pH 8.01). ............................................................................... 201

Figure 5-11: Effect of rotation rate on \(j_p\) for Fe RDE in 30wt% MEA + H\(_2\)O + CO\(_2\), at 10 mV s\(^{-1}\) (T = 25 °C, pH 8.01) in the a) positive-going and b) negative-going potential scan. ....... 203

Figure 5-12: Cyclic voltammograms for Fe | 30wt% MEA + H\(_2\)O + CO\(_2\), at 10 mV s\(^{-1}\) (T = 25 °C, pH 8.01) with positive potential limits: (a) -0.40 V, (b) -0.20 V, (C) +0.20 V (d) +0.60 V (e) +1.0 V.......................................................... 205

Figure 5-13: Effect of potential scan rate on voltammograms for a Fe RDE in 30wt% MEA + H\(_2\)O + CO\(_2\) (T = 25°C, pH 8.01, f = 1500 rpm,) (a) 100 \(\leq v \leq\) 10 mV s\(^{-1}\) (b) 10 \(\leq v \leq\) 1 mV s\(^{-1}\). ........................................................................................................... 208

Figure 5-14: Effect of potential scan rate on current density for peak I of stationary Fe electrode in 30wt% MEA + H\(_2\)O + CO\(_2\) (T = 25 °C, pH 8.01). ................................................................. 208
Figure 5-15: Effects of rotation and potential scan rates on current density of peak(II), \( j_{\text{PII}} \), on Fe in 30wt\% MEA + H\(_2\)O + CO\(_2\), at scan rates 100 \( \leq v \leq 10 \text{ mV s}^{-1} \) .......................................................... 209

Figure 5-16: Effects of rotation and potential scan rates on peak (II) current density \( j_{\text{PII}} \) of Fe in 30wt\% MEA + H\(_2\)O + CO\(_2\), at various scan rates 10 \( \leq v \leq 1 \text{ mV s}^{-1} \) .......................................................... 209

Figure 5-17: Effect of aqueous solution temperature on cyclic voltammograms for iron RDE in 30 wt\% MEA + H\(_2\)O + CO\(_2\) at pH ~8.01; 10 mV s\(^{-1}\), \( f = 1500 \text{ rpm} \) .......................................................... 210

Figure 5-18: Effect of rotation rate and temperature (18 \( ^{\circ}\text{C} \leq T \leq 80 \text{ \circ{C}} \)) on \( j_{\text{PII}} \) for Fe RDE in 30 wt\% MEA + H\(_2\)O + CO\(_2\) at 10 mV s\(^{-1}\) (pH 8.01) .......................................................... 212

Figure 5-19: Arrhenius plot for \( j_{\text{PII}} \) 30 wt\% MEA + H\(_2\)O + CO\(_2\), at 10 mV s\(^{-1}\) (pH 8.01) for varying aqueous solution temperatures (18 \( ^{\circ}\text{C} \leq T \leq 80 \text{ \circ{C}} \)) and rotation speeds (60 rpm \( \leq f \leq 1500 \text{ rpm} \)) .......................................................... 213

Figure 5-20: Cyclic voltammogram and corresponding massogram for Au quartz crystal in 300 g dm\(^{-3}\) aqueous FeSO\(_4\) at pH 3.2; at 10 mV s\(^{-1}\), \( T = 25 \text{ \circ{C}} \) .......................................................... 215

Figure 5-21: Potentiostatic deposition of Fe on Au quartz crystal in 300 g dm\(^{-3}\) FeSO\(_4\) at pH 3.2, -1.0 V (AgCl|Ag) and \( T = 25 \text{ \circ{C}} \) .......................................................... 216

Figure 5-22: Cyclic voltammogram obtained on the deposited Fe quartz crystal in 30 wt\% MEA + H\(_2\)O, at 100 mV s\(^{-1}\) (\( T = 25 \text{ \circ{C}} \), pH 12.55) with equilibrium reaction potentials assigned. 217

Figure 5-23: Mass change corresponding to voltammogram () of electrodeposited Fe quartz crystal in 30 wt\% MEA + H\(_2\)O, at 100 mV s\(^{-1}\) (\( T = 25 \text{ \circ{C}} \), pH 12.55) with reactions assigned. .......................................................... 218

Figure 5-24: Cyclic voltammogram of electrodeposited Fe quartz crystal in 30 wt\% MEA + H\(_2\)O + CO\(_2\) at pH 8.01, 100 mV s\(^{-1}\), \( T = 25 \text{ \circ{C}} \); equilibrium reaction potentials assigned. 219

Figure 5-25: Mass change corresponding to voltammogram (Figure 5-23) of electrodeposited Fe quartz crystal in 30 wt\% MEA + H\(_2\)O + CO\(_2\), at 100 mV s\(^{-1}\) (T=25 \text{ \circ{C}}, pH 8.01) .......................................................... 220

Figure 5-26: Effect of rotation rate on cyclic voltammograms of iron RDE in 30 wt\% MEA at pH 12.55 and \( T = 25 \text{ \circ{C}} \); 10 mV s\(^{-1}\), with equilibrium potentials of reactions assigned. ..... 221

Figure 5-27: Cyclic voltammogram of stationary iron RDE in 30 wt\% MEA+ CO\(_2\) at pH 11.00 and \( T = 25 \text{ \circ{C}} \); 10 mV s\(^{-1}\), with equilibrium potentials of reactions assigned. .......................... 221
Figure 5-28: Cyclic voltammogram of stationary iron RDE in 30wt% MEA+ CO₂ at pH 10.01 and T = 25 °C; 10 mV s⁻¹, with equilibrium potentials of reactions assigned..............................................222

Figure 5-29: Cyclic voltammogram of stationary iron RDE in 30wt% MEA+ CO₂ at pH 9.54 and T = 25 °C; 10 mV s⁻¹, with equilibrium potentials of reactions assigned..............................................222

Figure 5-30: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA+ CO₂ at pH 9.06 and T = 25 °C; 10 mV s⁻¹, with equilibrium potentials of reactions assigned..........................223

Figure 5-31: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA+ CO₂ at pH 8.78 and T = 25 °C; 10 mVs⁻¹, with equilibrium potentials of reactions assigned..........................223

Figure 5-32: Cyclic voltammogram of stationary iron RDE in 30wt% MEA+ CO₂ at pH 8.43 and T = 25 °C; 10 mV s⁻¹, with equilibrium potentials of reactions assigned..........................224

Figure 5-33: Cyclic Voltammogram obtained on a stationary iron RDE in 30 wt% MEA+ CO₂ at pH 8.17 and T = 25 °C; 10 mV s⁻¹, with equilibrium potentials of reactions assigned. ....224

Figure 5-34: Cyclic Voltammogram obtained on a stationary iron RDE in 30wt% MEA+ CO₂ at pH 8.01 and T = 25 °C; 10 mV s⁻¹, with equilibrium potentials of reactions assigned. ....225

Figure 5-35: Effect of pH on voltammograms of a stationary iron RDE in 30wt% MEA+ CO₂ at T = 25 °C; 10 mV s⁻¹, f = 1500 rpm..............................................................225

Figure 5-36: Effects of rotation rate and pH on peak current density $j_{PII}$ of Fe in 30 wt% MEA + H₂O + CO₂; potential scan rate: 10 mV s⁻¹...............................................................226

Figure 5-37: Effect of aqueous solution pH on peak (II) electrode potential $E_{PII}$. ...............226

Figure 5-38: Effects of CO₂: – Comparisons between cyclic voltammogram for iron RDE in 30 wt% MEA+ CO₂ and 30 wt% MEA+ 1 M H₂SO₄; 10 mV s⁻¹ (T = 25 °C, f = 0- 1500 rpm). ..................................................................................................................229

Figure 5-39: Cyclic voltammogram of electrodeposited Fe quartz crystal in 30 wt% MEA + H₂SO₄ at pH 8.01 and T = 25°C; 100 mV s⁻¹, with equilibrium potentials of reactions assigned. ..............................................................................................................230

Figure 5-40: Mass change corresponding to voltammograms (Figure 5-39) of electrodeposited Fe quartz crystal in 30 wt% MEA + H₂O + CO₂ at pH 8.01 and T = 25 C; 100 mV s⁻¹......230

Figure 5-41: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at f = 1500 rpm in MEA+ CO₂ at pH=8.01 and T = 25 °C; 10 mV s⁻¹.................232
Figure 5-42: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at \( f = 1500 \text{ rpm} \) in MEA+ CO\(_2\) at pH-8.01 and \( T = 25 \text{ °C} \); 10 mV s\(^{-1}\)...........233

Figure 5-43: Effects on \( j_{\text{PiI}} \) of rotation rate, temperature (25-80 °C) and aqueous MEA concentration (10-60 wt%) for Fe RDE in MEA + H\(_2\)O + CO\(_2\) at pH-8.01; 10 mV s\(^{-1}\)...........234

Figure 5-44: Cyclic voltammograms and corresponding mass change of electrodeposited Fe quartz crystal in (5-30 wt%) MEA + H\(_2\)O + CO\(_2\) at pH\( \approx 8.01 \) and \( T = 25 \text{ °C} \); 100 mV s\(^{-1}\)...........235

Figure 5-45: Cyclic voltammogram of electrodeposited Fe on quartz crystal in (5-30) wt% MEA + H\(_2\)O at pH = 8.01 and \( T = 25 \text{ °C} \); 100 mV s\(^{-1}\)...........236

Figure 5-46: Mass changes corresponding to voltammograms (Figure 5-45) of electrodeposited Fe quartz crystal in (5-30 wt%) MEA + H\(_2\)O + CO\(_2\) at pH 8.01; 100 mV s\(^{-1}\)...........236

Figure 5-47: Effect of oxygen concentration and temperature on cyclic voltammograms of iron RDE rotating at \( f = 1500 \text{ rpm} \) in 30 wt% MEA+ CO\(_2\) at pH (7.24-8.01) ; 10 mV s\(^{-1}\)...........238

Figure 5-48: Activity-pH diagram of Fe-H\(_2\)O-CO\(_2\) at 0.1 MPa CO\(_2\); 298 K (Kelsall, 2015).241

Figure 5-49: Effect of pH on polarisation behaviour of an iron RDE in 30 wt% MEA+ CO\(_2\), at 10 mV s\(^{-1}\); \( T = 25 \text{ °C} \), f = 1500 rpm.................................................................247

Figure 5-50: Effect of pH on oxidation / corrosion rates of an iron RDE in 30 wt% MEA+ CO\(_2\), at 10 mV s\(^{-1}\) (\( T = 25 \text{ °C} \), f = 1500 rpm). .................................................................248

Figure 5-51: Effect of CO\(_2\) loading on hydrogen ion concentration based on the Kent-Eisenberg model for 30 wt% MEA solution and 25 °C. .................................................................248

Figure 5-52: Effect of solution temperature on polarisation curves of iron RDE in 30 wt% MEA + H\(_2\)O + CO\(_2\) at pH 7.24 - 8.01; 10 mV s\(^{-1}\), f = 1500 rpm.................................................................250

Figure 5-53: Effect of solution temperature on the corrosion rate obtained on iron RDE in 5-60 wt% MEA + H\(_2\)O + CO\(_2\) at pH 7.24 - 8.01; 10 mV s\(^{-1}\), f = 1500 rpm.................................................................250

Figure 5-54: Effect of temperature on hydrogen ion concentration \([H^+]\) based on the Kent-Eisenberg model for 30 wt% MEA solution and 25°C.................................................................251

Figure 5-55: Effect of solution temperature on polarisation curves of iron RDE in 5-60wt% MEA + H\(_2\)O + CO\(_2\) at pH 7.24-8.01; 10 mV s\(^{-1}\), f = 1500 rpm.................................................................252

Figure 5-56: Effect of MEA concentration on the polarisation curves obtained on iron RDE in MEA + H\(_2\)O + CO\(_2\) at pH 8.01 and \( T = 25 \text{ °C} \); 10 mVs\(^{-1}\), f = 1500 rpm.................................................................255
Figure 5-57: Effect of MEA concentration on polarisation curves of iron RDE in MEA + H₂O + CO₂ at pH 7.83 and T = 40 °C; 10 mV s⁻¹, f = 1500 rpm. ..............................................256

Figure 5-58: Effect of MEA concentration on polarisation curves of iron RDE in MEA + H₂O + CO₂, at 10 mV s⁻¹; pH 7.49, f = 1500 rpm, T = 60 °C. ..............................................256

Figure 5-59: Effect of MEA concentration on polarisation curves of iron RDE in MEA + H₂O + CO₂ at pH 7.24 and T = 80 °C; 10 mV s⁻¹, f = 1500 rpm................................................257

Figure 5-60: Effect of MEA concentration on the corrosion rate obtained on iron RDE in MEA + H₂O + CO₂ at pH 7.24 – 8.01 and T = 25-80 °C; 10 mV s⁻¹, f = 0-1500 rpm. ......................258

Figure 5-61: Effect of MEA concentration on the species concentrations of the aqueous bulk solution at chosen CO₂ loading of 0.6 CO₂ loading / mol CO₂ (mol amine)⁻¹, T = 25 °C, calculated by the Kent-Eisenberg Model (Kent and Eisenberg, 1976) ................................................259

Figure 5-62: Effect of rotation rate on polarisation curves of iron RDE in 30 wt% MEA + H₂O + CO₂, at 10 mV s⁻¹; pH 8.01, f = 0-1500 rpm, T = 25 °C................................................261

Figure 5-63: Effect of rotation rate on corrosion rates of iron RDE in 5-30 wt% MEA + H₂O + CO₂ at pH 8.01; 10 mV s⁻¹, f = 0-1500 rpm, T = 25 °C................................................261

Figure 5-64: Effect of oxygen on the polarisation curves obtained on iron RDE in 30wt% MEA + H₂O + CO₂ at pH 7.24-8.01 and T = 25-80 °C; 10 mV s⁻¹, f = 1500 rpm. ......................265

Figure 6-1: Schematic representation of the corrosion process in aqueous MEA-CO₂ solutions, including the chemical reactions occurring at the iron surface ..................275

Figure 6-2: Flow diagram showing the model structure ..........................................................279

Figure 6-3: Comparison between predicted and measured voltammetric sweep for iron RDE in 30 wt% MEA+ CO₂, at pH=8.1 and T = 25 °C; 10 mV s⁻¹, f = 1500 rpm. Black dotted lines represent the Tafel extrapolation of the anodic and cathodic linear sections to find the intersection at E₉ and i₉.................................................................290

Figure 6-4: Comparison between predicted and measured voltammetric sweep for iron RDE in 30 wt% MEA+ CO₂, at pH=8.1 and T = 25 °C; 10 mV s⁻¹, f = 960 rpm, 540 rpm and 240 rpm. .................................................................................................................291

Figure 6-5: Comparisons of experimental and model-predicted corrosion rates as a function of rotation rate for iron RDE in 30 wt% MEA+ CO₂, at pH=8.1 and T = 25 °C; 10 mV s⁻¹ ....292
Figure 6-6: Predicted effect of CO$_2$ loading on liquid phase compositions of 30 wt% aqueous MEA solution at 25 °C, as predicted by the Kent-Eisenberg Model (Kent and Eisenberg, 1976).

Figure 6-7: Comparison between predicted and measured voltammetric sweep for iron RDE in 30 wt% MEA+ CO$_2$, at T = 25 °C; 10 mV s$^{-1}$, f = 1500 rpm as a function of CO$_2$ loading($\alpha$).

Figure 6-8: Comparisons of experimental and model-predicted corrosion rates for iron RDE in 30 wt% MEA+ CO$_2$, at T = 25 °C; 10 mV s$^{-1}$, f = 1500 rpm as a function of CO$_2$ loading($\alpha$).

Figure 6-9: Comparison of model-predicted and experimental current density – electrode potential data for iron RDE in 30 wt% MEA+ CO$_2$ at pH=8.1 and T = 25 °C; 10 mV s$^{-1}$, f = 1500 rpm. Direct reduction of HCO$_3^-$ included.

Figure 6-10: Figure 6-11: Comparison between predicted and measured voltammetric sweep for iron RDE in 30 wt% MEA+ CO$_2$, at pH=8.1 10 mV s$^{-1}$, f = 1500 rpm as a function of temperature.

Figure 6-11: Comparison of experimental and model-predicted Fe corrosion rates in 30 wt% MEA solution at different temperatures.

Figure 6-12: Effect of temperature and CO$_2$ loading on hydrogen ion concentration [H$^+$] predicted by Kent-Eisenberg model for 30 wt% aqueous MEA solution.

Figure 6-13: Comparison of experimental and model-predicted corrosion rates at different MEA concentrations, T = 25°C, CO$_2$ loading = 0.5 mol CO$_2$ (mol amine)$^{-1}$.

Figure 6-14: Dynamic viscosity of 30 wt% MEA at 25 °C and CO$_2$ loading ($\alpha$ =0.5), as a function of mass fraction (Amundsen et al., 2009).

Figure 7-1: Cyclic voltammograms of an iron electrode in 30 wt% MEA + H$_2$O + CO$_2$ at 10 mV s$^{-1}$ (T = 25°C, pH 8.03) with a linear velocity of 0.5 mm s$^{-1}$.

Figure 7-2: Effect of potential on chronoamperograms obtained on iron electrode at -0.80 V ≤ E ≤ -0.20 V in contact with 30 wt% MEA + H$_2$O + CO$_2$ (T = 25°C, pH 8.03) with a linear velocity of 0.5 mm s$^{-1}$. 
Figure 7-3: Effect of potential on the charge density-time data for iron electrode at \(-0.80\, \text{V} \leq \text{E} \leq -0.20\, \text{V}\) in 30 wt% MEA + H₂O + CO₂ (\(T = 25^\circ\text{C}, \text{pH 8.03}\)) with a linear velocity of \(0.5\, \text{mm s}^{-1}\). .......................................................... 316

Figure 7-4: Effect of potential on Fe²⁺ concentration-time data for iron electrode at \(-0.80\, \text{V} \leq \text{E} \leq -0.20\, \text{V}\) in contact with 30 wt% MEA + H₂O + CO₂ (\(T = 25^\circ\text{C}, \text{pH 8.03}\)) with a linear velocity of \(0.5\, \text{mm s}^{-1}\). .......................................................... 317

Figure 7-5: Images of iron electrode in 30 wt% MEA + H₂O + CO₂ at \(\text{pH 8.03}\) and \(T = 25^\circ\text{C}\), with a solution velocity of \(0.5\, \text{mm s}^{-1}\) (Re = 1.69) after constant electrolyses at \(-0.70\, \text{V}, -0.60\, \text{V}, -0.50\, \text{V} \& -0.40\, \text{V}\). .......................................................... 318

Figure 7-6: Dependences of Sherwood number on Reynold number and distance from inlet of the flow reactor based on the reactor geometry, solution flowrate \(0.01 - 0.1\, \text{m s}^{-1}\) and MEA solution viscosity \((3.22 \times 10^{-6}\, \text{m}^2\, \text{s}^{-1})\). .......................................................... 320

Figure 7-7: Cyclic voltammograms of an iron electrode in contact with \(50\, \text{mol m}^{-3}\) of \(\text{K}_3\text{Fe(CN)}_6 / 100\, \text{mol m}^{-3}\) of \(\text{K}_4\text{Fe(CN)}_6\) and \(1000\, \text{mol m}^{-3}\) of \(\text{Na}_2\text{CO}_3\) at \(\text{pH 11.3}\) with a flow rate of \(0.1\, \text{mm s}^{-1}\). .......................................................... 322

Figure 7-8: Mass transfer coefficient versus linear velocity for \(\text{Fe(CN)}_6^{3-}\) measured during hexacyanoferrate(III) reduction and the corresponding values calculated for Fe²⁺ with comparisons to the calculations based on mass transport correlations. .......................................................... 324

Figure 7-9: Effect of solution velocity on the diffusion layer thickness for Fe²⁺ measured by the reduction of hexacyanoferrate(III) with comparisons to the calculations based on mass transport correlations. .......................................................... 324

Figure 7-10: Effect of solution velocity on chronoamperometric data for iron electrode in 30 wt% MEA + H₂O + CO₂ at \(\text{pH 8.03}\) and \(T = 25^\circ\text{C}, -0.60\, \text{V (AgCl|Ag)}\). .......................................................... 325

Figure 7-11: Idealised Nernst diffusion layer and concentration profile for Fe²⁺ ions required for FeCO₃ and Fe(OH)₂ precipitation. .......................................................... 326

Figure 7-12: Effect of solution velocity on charge density-time data for iron electrode in 30 wt% MEA + H₂O + CO₂ at \(\text{pH 8.03}\) and \(T = 25^\circ\text{C}, -0.60\, \text{V (AgCl|Ag)}\). .......................................................... 328

Figure 7-13: Effect of solution velocity on time dependence of mass of Fe²⁺ dissolved from iron electrode in 30 wt% MEA + H₂O + CO₂ at \(\text{pH 8.03}\) and \(T = 25^\circ\text{C}, -0.60\, \text{V (AgCl|Ag)}\). .......................................................... 329
Figure 7-14: Effect of temperature on current density – time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H_2O + CO_2 (T = 25-80 °C, pH 8.03) with a velocity of 0.5 mm s^{-1} .................................................................331

Figure 7-15: Effect of temperature on the charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H_2O + CO_2 (T = 25–80 °C, pH 8.03) with a solution velocity of 0.5 mm s^{-1}. ........................................................................................................332

Figure 7-16: Temperature effect on Fe^{II} concentration-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H_2O + CO_2 (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s^{-1}. .................................................................334

Figure 7-17: Effect of temperature on the FeCO_3 precipitation rate at iron electrode in contact with 30 wt% MEA + H_2O + CO_2 (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s^{-1} after constant potential electrolyses at -0.60 V (AgCl|Ag)........................................335

Figure 7-18: Images of iron electrode in contact with 30 wt% MEA + H_2O + CO_2 (T = 25–80 °C, pH 8.03) with a solution velocity of 0.5 mm s^{-1} after constant electrolyses at -0.60 V (AgCl|Ag). .................................................................................................335

Figure 7-19: Chronoamperometric data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H_2O (T = 25-80 °C, pH 12.31, α = 0) with a solution velocity of 0.5 mm s^{-1}..................................................339

Figure 7-20: Charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in contact with 30 wt% MEA + H_2O (T = 25-80 °C, pH 12.31, α = 0) with a solution velocity of 0.5 mm s^{-1}. ........................................................................................................339

Figure 7-21: Corrosion-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H_2O (T = 25-80 °C, pH 12.31, α = 0) with a solution velocity of 0.5 mm s^{-1} ..................................................339

Figure 7-22: Chronoamperometric data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H_2O (T = 25-80 °C, pH 10.70, α = 0.2) with a solution velocity of 0.5 mm s^{-1} ......................340

Figure 7-23: Charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H_2O (T = 25-80 °C, pH 10.70, α = 0.2) with a solution velocity of 0.5 mm s^{-1} ......................340

Figure 7-24: Fe^{II} concentration-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H_2O (T = 25-80 °C, pH 10.70, α = 0.2) with a solution velocity of 0.5 mm s^{-1} ......340
Figure 7-25: Chronoamperogram for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, pH 9.90, α = 0) with a solution velocity of 0.5 mm s⁻¹. ........................................341

Figure 7-26: Charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, pH 9.90, α = 0.4) with a solution velocity of 0.5 mm s⁻¹. ..................341

Figure 7-27: Fe²⁺ concentration-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, pH 9.90, α = 0.4) with a solution velocity of 0.5 mm s⁻¹. ..........341

Figure 7-28: Effect of CO₂ loading on the Fe²⁺ concentration-time data for iron electrode at -0.60 V (AgCl|Ag) in contact with 30 wt% MEA + H₂O (pH 8.03-12.3, α = 0-0.6) with a solution velocity of 0.5 mm s⁻¹ for a) 25 °C b) 40 °C c) 60 °C d) 80 °C. ........................................342

Figure 7-29: Effect of CO₂ loading on current density - time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (pH 8.03-12.3, α = 0-0.6) with a solution velocity of 0.5 mm s⁻¹ for a) 25 °C b) 40 °C c) 60 °C d) 80 °C. ........................................343

Figure 7-30: Effect of CO₂ loading on charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (pH 8.03-12.3, α = 0-0.6) with a solution velocity of 0.5 mm s⁻¹ for a) 25 °C b) 40 °C c) 60 °C d) 80 °C. ........................................344

Figure 7-31: Effect of CO₂ loading and temperature on total dissolved [Fe²⁺] from iron electrode in 30 wt% MEA + H₂O (T = 25-80 °C, α = 0-0.6) at -0.60 V (AgCl|Ag) with a solution velocity of 0.5 mm s⁻¹. ........................................................................345

Figure 7-32: Effect of CO₂ loading and temperature on total charge density for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, α = 0-0.6) with a solution velocity of 0.5 mm s⁻¹. ........................................................................345

Figure 7-33: Effect of CO₂ loading on the FeCO₃ precipitation rate at the iron electrode in 30 wt% MEA + H₂O + CO₂ (T = 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹ after constant potential electrolyses at -0.60 V (AgCl|Ag). .................................................................346

Figure 7-34: Effect of oxygen on current density – time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 40°C, pH 8.03, α = 0.6) with a solution velocity of 0.5 mm s⁻¹. ........................................................................347

Figure 7-35: Hydrogen abstraction mechanism for the oxidative degradation of MEA (Petryaev et al., 1984) ........................................................................................................348
Figure 7-36: Effect of CO$_2$ loading on charge-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H$_2$O (T= 40 °C, pH 8.03, α = 0.6) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-37: Effect of CO$_2$ loading on Fe$^{II}$ concentration - time data for iron electrode at -0.60 V in 30 wt% MEA + H$_2$O (T = 40 °C, pH 8.03, α = 0.6) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-38: Effect of temperature on current density – time data for iron electrode at -0.60 V (AgCl|Ag) in 5 wt% MEA + H$_2$O + CO$_2$ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-39: Effect of temperature on charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 5 wt% MEA + H$_2$O + CO$_2$ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-40: Temperature effect on Fe$^{II}$ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 5 wt% MEA + H$_2$O + CO$_2$ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-41: Effect of temperature on current density - time for iron electrode at -0.60 V (AgCl|Ag) in 10 wt% MEA + H$_2$O + CO$_2$ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-42: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 10 wt% MEA + H$_2$O + CO$_2$ (T = 25-80°C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-43: Temperature effect on Fe$^{II}$ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 10 wt% MEA + H$_2$O + CO$_2$ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-44: Effect of temperature on current density-time data for iron electrode at -0.6 V (AgCl|Ag) in 20 wt% MEA + H$_2$O + CO$_2$ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-45: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 20 wt% MEA + H$_2$O + CO$_2$ (T = 25 - 80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 
Figure 7-46: Temperature effect on Fe$^{II}$ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 20 wt% MEA + H$_2$O + CO$_2$ (T = 25 - 80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................354

Figure 7-47: Effect of temperature on current density-time data for iron electrode at -0.6 V (AgCl|Ag) in 40 wt% MEA + H$_2$O + CO$_2$ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................355

Figure 7-48: Effect of temperature on charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 40 wt% MEA + H$_2$O + CO$_2$ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................355

Figure 7-49: Temperature effect on the Fe$^{II}$ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 40 wt% MEA + H$_2$O + CO$_2$ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................355

Figure 7-50: Effect of temperature on current density - time data for iron electrode at -0.6 V (AgCl|Ag) in 50 wt% MEA + H$_2$O + CO$_2$ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................356

Figure 7-51: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 50 wt% MEA + H$_2$O + CO$_2$ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................356

Figure 7-52: Temperature effect on Fe$^{II}$ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 50 wt% MEA + H$_2$O + CO$_2$ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................356

Figure 7-53: Effect of [MEA] on Fe$^{II}$ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 5-50wt% MEA + H$_2$O + CO$_2$ (pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................357

Figure 7-54: Effect of [MEA] on current density - time data for iron electrode at -0.6 V (AgCl|Ag) in 5 - 50 wt% MEA + H$_2$O + CO$_2$ (pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................358

Figure 7-55: Effect of [MEA] on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 5 - 50wt% MEA + H$_2$O + CO$_2$ (pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. .................................................................................................................................359
Figure 7-56: Potential-pH diagram for Fe-Cr-Ni-H₂O system at 298 K, 0.1 MPa and dissolved activities = 10⁻⁴

Figure 7-57: Effect of temperature on current density – time data for carbon steel S355 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹

Figure 7-58: Effect of temperature on charge density – time data for carbon steel S355 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹

Figure 7-59: Temperature effect on the dissolved Fe²⁺ concentration-time data for carbon steel S355 electrode at -0.6 V (AgCl|Ag) in 30wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹

Figure 7-60: Effect of temperature on current density – time data for carbon steel EN8 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹

Figure 7-61: Effect of temperature on charge density – time data for carbon steel EN8 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹

Figure 7-62: Temperature effect on Fe²⁺ concentration-time data for carbon steel EN8 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹

Figure 7-63: Effect of temperature on current density - time data for stainless steel electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹

Figure 7-64: Effect of temperature on charge density – time data for stainless steel electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹

Figure 7-65: Temperature effect on dissolved Fe²⁺ concentration - time data for stainless steel electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹
Figure 7-66: Effect of steel composition on the corrosion-time curve obtained on iron electrode at -0.6 V (AgCl|Ag) in contact with 30 wt% MEA + H₂O + CO₂ (pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................366

Figure 7-67: Effect of temperature on current density – time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% MDEA + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................370

Figure 7-68: Effect of temperature on charge density - time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% MDEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................370

Figure 7-69: Temperature effect on Fe^{II} concentration - time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% MDEA + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................371

Figure 7-70: Effect of temperature on current density-time data of iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AEP + H₂O + CO₂ (T = 25 - 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................371

Figure 7-71: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AEP + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................371

Figure 7-72: Temperature effect on Fe^{II} concentration - time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AEP + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................372

Figure 7-73: Effect of temperature on current density – time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AMP + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................372

Figure 7-74: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AMP + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................372

Figure 7-75: Temperature effect on Fe^{II} concentration - time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AMP + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹. ........................................................................................................................................372
Figure 7-76: Effect of amine type on current density – time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% [Amine] (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-77: Effect of amine type on Fe²⁺ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% [Amine] (T = 25 - 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-78: Effect of amine type on charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in contact with 30 wt% [Amine] (T = 25 - 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-79: Time dependence of open circuit potentials of iron and steel electrodes at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-80: Time-dependence of iron(II) concentrations dissolved from iron and steel S355 electrodes at -0.6 V (AgCl|Ag) in contact with 30 wt% MEA + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-81: Images of the flow reactor system for the longer term studies at open circuit potential for a) 7 days b) 14 days c) 28 days.

Figure 7-82: Images of the iron and carbon steel S355 electrodes after immersion in 30 wt% MEA + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹ at open circuit potential for 28 days.

Figure 9-1: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at f = 1500 rpm in MEA+ CO₂ at pH~8.01 and T = 25 °C; 10 mV s⁻¹.

Figure 9-2: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at f = 1500 rpm in MEA+ CO₂ at pH~8.01 and T = 25 °C; 10 mV s⁻¹.

Figure 9-3: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at f = 1500 rpm in MEA+ CO₂ at pH~8.01 and T = 40 °C; 10 mV s⁻¹.

Figure 9-4: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at f = 1500 rpm in MEA+ CO₂ at pH~8.01 and T = 40 °C; 10 mV s⁻¹.

Figure 9-5: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at f = 1500 rpm in MEA+ CO₂ at pH~8.01 and T = 60 °C; 10 mV s⁻¹.
Figure 9-6: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at \( f = 1500 \text{ rpm} \) in MEA+ CO\(_2\) at pH\(\approx\)8.01 and \( T = 60 \, ^\circ\text{C} \); 10 mV s\(^{-1}\)............399

Figure 9-7: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at \( f = 1500 \text{ rpm} \) in MEA+ CO\(_2\) at pH\(\approx\)8.01 and \( T = 80 \, ^\circ\text{C} \); 10 mV s\(^{-1}\)...............400

Figure 9-8: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at \( f = 1500 \text{ rpm} \) in MEA+ CO\(_2\) at pH\(\approx\)8.01 and \( T = 80 \, ^\circ\text{C} \); 10 mV s\(^{-1}\)...............400

Figure 9-9: Effect of NaHCO\(_3\) + Na\(_2\)CO\(_3\) concentration on cyclic voltammograms of an iron RDE rotating at \( f = 1500 \text{ rpm} \) in MEA+ CO\(_2\) at pH\(\approx\)8.01 and \( T = 80 \, ^\circ\text{C} \); 10 mV s\(^{-1}\)...............401

Figure 9-10: Effect of NaHCO\(_3\) concentration on current density for peak II of stationary Fe electrode in NaHCO\(_3\) + Na\(_2\)CO\(_3\) solutions (\( T = 25 \, ^\circ\text{C} \), pH 8.01). ..............................................401
List of tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>List of Symbols</td>
<td>XXXIII</td>
</tr>
<tr>
<td>2</td>
<td>List of Abbreviations</td>
<td>XXXIV</td>
</tr>
<tr>
<td>3</td>
<td>List of subscripts and superscripts</td>
<td>XXXIV</td>
</tr>
<tr>
<td>2-1</td>
<td>Modes of mass transport (Walsh, 1993)</td>
<td>37</td>
</tr>
<tr>
<td>3-1</td>
<td>Chemical Structures of the amines commonly used in CO$_2$ capture</td>
<td>56</td>
</tr>
<tr>
<td>3-2</td>
<td>Summary of Amine Scrubbing Plant Experience on Corrosion</td>
<td>66</td>
</tr>
<tr>
<td>3-3</td>
<td>Summary of Amine Scrubbing Plant Experience on Corrosion (Continued)</td>
<td>67</td>
</tr>
<tr>
<td>3-4</td>
<td>Growth kinetics of FeCO$_3$, 2σ = 95% confidence level</td>
<td>101</td>
</tr>
<tr>
<td>3-5</td>
<td>Standard State Formation Properties of FeCO$_3$ at 298.15 K and 0.1 MPa</td>
<td>104</td>
</tr>
<tr>
<td>3-6</td>
<td>Types of corrosion films formed from 30-150°C in steel-CO$_2$-H$_2$O systems</td>
<td>110</td>
</tr>
<tr>
<td>3-7</td>
<td>Equilibrium constants used in the Kent-Eisenberg model (Kent and Eisenberg, 1976)</td>
<td>119</td>
</tr>
<tr>
<td>3-8</td>
<td>Compilation of diagnostic criteria for Fe dissolution and deposition reactions obtained under different experimental conditions (Drazic, 1989)</td>
<td>122</td>
</tr>
<tr>
<td>4-1</td>
<td>Common reagents</td>
<td>157</td>
</tr>
<tr>
<td>4-2</td>
<td>Standard reagents</td>
<td>158</td>
</tr>
<tr>
<td>4-3</td>
<td>Electrode Materials</td>
<td>159</td>
</tr>
<tr>
<td>4-4</td>
<td>Cation exchange membrane</td>
<td>160</td>
</tr>
<tr>
<td>5-1</td>
<td>Effects of rotation and potential scan rates on anodic charge / C m$^{-2}$ passed with Fe RDE in 30 wt% MEA + H$_2$O + CO$_2$ (T = 25°C, pH 8.01)</td>
<td>207</td>
</tr>
<tr>
<td>5-2</td>
<td>Effect of temperature on the peak (II) electrode potential after taking into account the shift in electrode potential of AgCl/Ag with respect to standard hydrogen electrode (SHE)</td>
<td>211</td>
</tr>
</tbody>
</table>
Table 5-3: Activation energy associated with j_{pll} for Fe RDE in 30 wt% MEA + H_2O + CO_2, at 10 mV s^{-1} (pH 8.01) for varying aqueous solution temperatures (18 °C ≤ T ≤ 80 °C) and rotation speeds (60 rpm ≤ f ≤ 1500 rpm) ................................................................. 213

Table 5-4: Effect of solution temperature on the pH for 30 wt% MEA at full CO_2 saturation. ............................................................................................................................................. 251

Table 6-1: Chemical and electrochemical reactions represented in the mechanistic corrosion model .......................................................................................................................... 276

Table 6-2: Equilibrium expressions for chemical reactions ............................................. 281

Table 6-3: Temperature dependent equilibrium constants for chemical reactions 1-5........ 282

Table 6-4: Diffusion Coefficients for species in water at 25°C ......................................... 284

Table 6-5: Liquid properties as a function of temperature (Haynes and Lide, 2011)............. 284

Table 6-6: Density ρ / kg m^{-3} for MEA +H_2O from (T= 25- 80°C) as a function of MEA mass fraction w (Amundsen et al., 2009) ................................................................. 285

Table 6-7: Density ρ / kg m^{-3} for 30 wt% MEA +H_2O from (T= 25- 80°C) as a function of temperature and CO_2 loading (α =0.1 - 0.5) (Amundsen et al., 2009) ................................................................. 285

Table 6-8: Dynamic viscosity µ / mPa s^{-1} for MEA +H_2O from (T= 25- 80°C) as a function of MEA mass fraction w (Amundsen et al., 2009) ................................................................. 285

Table 6-9: Dynamic viscosity µ / mPa s^{-1} for 30 wt% MEA +H_2O from (T= 25- 80°C) as a function of temperature and CO_2 loading (α =0.1 - 0.5) (Amundsen et al., 2009) ................................................................. 286

Table 6-10: Kinetic parameters of the electrochemical reactions ..................................... 289

Table 6-11: Predicted species concentration / kmol m^{-3} for 30 wt% MEA-H_2O-CO_2 systems at 25°C .................................................................................................................. 298

Table 6-12: Predicted species concentration / kmol m^{-3} for 30 wt% MEA-H_2O-CO_2 systems at 40°C .................................................................................................................. 298

Table 6-13: Predicted species concentration / kmol m^{-3} for 30 wt% MEA-H_2O-CO_2 systems at 60°C .................................................................................................................. 299

Table 6-14: Predicted species concentration / kmol m^{-3} for 30 wt% MEA-H_2O-CO_2 systems at 80°C .................................................................................................................. 299
Table 6-15: Predicted species concentration / M for 20 wt% MEA-H2O-CO2 systems at 25°C
.................................................................................................................................................. 302

Table 6-16: Predicted species concentration / M for 40 wt% MEA-H2O-CO2 systems at 25°C
.................................................................................................................................................. 302

Table 6-17: Predicted species concentration / M for 50 wt% MEA-H2O-CO2 systems at 25°C
.................................................................................................................................................. 303

Table 7-1: Effect of solution velocity on the conditions required for FeCO3 and Fe(OH)2 precipitation by determining the [FeII] at the iron electrode surface, equilibrium [CO32-] from the Kent Eisenberg model and the results from iron electrode in 30 wt% MEA + H2O + CO2 (T = 25 °C, pH 8.03) at -0.60 V (AgCl|Ag). ................................................................. 329

Table 7-2: Effect of temperature on the conditions required for FeCO3 precipitation by determining the [FeII] at the iron electrode surface, equilibrium [CO32-] from the Kent Eisenberg model and the results from iron electrode in contact with 30 wt% MEA + H2O + CO2 (T = 25 °C, pH 8.03) at -0.60 V. ........................................................................................................................................ 336

Table 7-3: Effect of temperature on the solubility product, Ksp (calculated from thermodynamic data in (Benezeth et al., 2009))........................................................................................................... 336

Table 9-1: Solubility data in a solution of MEA (30 mass %) and water (70 mass %) at T = 25°C from (Jou et al., 1995)................................................................................................. 394

Table 9-2: Solubility data in a solution of MEA (30 mass %) and water (70 mass %) at T = 40°C from (Jou et al., 1995) and (Tong et al., 2012)........................................................................... 394

Table 9-3: Solubility data in a solution of MEA (30 mass %) and water (70 mass %) at T = 60°C from (Jou et al., 1995)................................................................................................. 395

Table 9-4: Solubility data in a solution of MEA (30 mass %) and water (70 mass %) at T = 80°C from (Jou et al., 1995)................................................................................................. 395

Table 9-5: Effects on jPII of rotation rate, temperature (25-80 °C) and aqueous MEA concentration (10-60 wt%) for Fe RDE in MEA + H2O + CO2 at pH=8.01; 10 mV s⁻¹......396

Table 9-6: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at f = 1500 rpm in 10 wt% MEA+ CO2 at pH~8.01; 10 mV s⁻¹................................. 402

Table 9-7: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at f = 1500 rpm in 20 wt% MEA+ CO2 at pH~8.01; 10 mV s⁻¹................................. 402
Table 9-8: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at \( f = 1500 \) rpm in 30 wt\% MEA + CO\(_2\) at pH-8.01; 10 mV s\(^{-1}\) ...........................................403

Table 9-9: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at \( f = 1500 \) rpm in 40 wt\% MEA + CO\(_2\) at pH-8.01; 10 mV s\(^{-1}\) ...........................................404

Table 9-10: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at \( f = 1500 \) rpm in 50 wt\% MEA + CO\(_2\) at pH-8.01; 10 mV s\(^{-1}\) .........................405

Table 9-11: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at \( f = 1500 \) rpm in 60 wt\% MEA + CO\(_2\) at pH-8.01; 10 mV s\(^{-1}\) .........................405

Table 9-12: Thermodynamic properties of species in Fe-CO\(_2\)-H\(_2\)O systems at 298K (Bard et al., 1985). ..................................................................................................................................................406

Table 9-13: Specific Heat Capacity Coefficients(HSC Software Database, 2016) ...........407
# Nomenclature

Figure 1: List of Symbols

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Activity of species ( i )</td>
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<td>( A )</td>
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</tr>
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β  Tafel coefficient  \( V^{-1} \)
\( β \)  Tafel slope  \( \text{mV}^{-1} \text{dec}^{-1} \)
\( \delta_n \)  Nernst diffusion layer thickness  \( \text{m} \)
κ  Conductivity  \( \text{S} \text{m}^{-1} \)
μ  Dynamic viscosity  \( \text{Pa s} \)
η  Overpotential  \( V \)
ϕ  Interfacial potential drop  \( V \)
ρ  Density  \( \text{kg m}^{-3} \)
ν  Kinematic viscosity  \( \text{m}^2 \text{s}^{-1} \)
ν_e  Electron stoichiometry
Φ_e  The charge yield

Figure 2: List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
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<tr>
<td>RDS</td>
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</tr>
<tr>
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<td>RDE</td>
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</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>AEP</td>
<td>Aminoethylpiperazone (AEP)</td>
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<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>MDEA</td>
<td>N-Methyl-diethanolamine</td>
</tr>
</tbody>
</table>

Figure 3: List of Subscripts and Superscripts

<table>
<thead>
<tr>
<th>Subscript/ Superscript</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Anodic</td>
</tr>
<tr>
<td>c</td>
<td>Cathodic</td>
</tr>
<tr>
<td>Ads</td>
<td>Adsorbed state</td>
</tr>
<tr>
<td>Sol</td>
<td>Solute state</td>
</tr>
<tr>
<td>b</td>
<td>Bulk value</td>
</tr>
<tr>
<td>s</td>
<td>Surface value</td>
</tr>
<tr>
<td>x= 0</td>
<td>Value at the electrode surface</td>
</tr>
</tbody>
</table>
1. Chapter 1

Introduction

1.1. Motivation for carbon capture and sequestration

The debate over the possibly devastating phenomenon of climate change, the classification of CO₂ as the primary greenhouse gas (GHG) and a major trigger for rising global average temperatures is considered to have reached a consensus (IPCC, 2001). The increase in global average temperature since the mid-20th century has been attributed to the observed increase in anthropogenic greenhouse gases, in particular rising CO₂ concentrations (IPCC, 2007). The consequences of such changes could be dire and lead to the collapse of ecosystems, adverse weather conditions and the extinction of 15 to 40 percent of all species (Figueroa et al., 2008).

Fossil fuels currently supply 85% of the world’s energy needs due to their low cost, availability, and most importantly the existing reliable technology for electrical power production (Strazisar et al., 2003); however, the combustion of carbonaceous fuels leads to the production of CO₂. In fact, it is estimated that 83% of GHG emissions are produced from
the combustion of fossil fuels, with CO$_2$ having the most negative impact (66%). The consumption of fossil fuels in the U.S for example, is expected to increase by 27% over the next 20 years, thereby increasing the CO$_2$ emissions from the current 6 Gt a$^{-1}$ to 8 Gt a$^{-1}$ by 2030 (Figueroa et al., 2008). In particular, coal-fired power stations emit twice as much CO$_2$ per kW h in comparison to natural gas plants. However, coal will remain the primary source of energy until at least 2030, due to its abundance and wide geological distribution (IEA, 2008), especially in rapidly growing economies such as China and India.

However, it has been considered that the emissions of CO$_2$ should be vastly reduced and the Intergovernmental Panel on Climate Change (IPCC) has recommended a 50 to 85 percent reduction of global GHG emissions from 2000 to 2050 (IPCC, 2001). In the Energy Technology Perspectives publication by the International Energy Agency (IEA), (IEA, 2008), a baseline scenario and a BLUE map scenario for the world’s energy system from 2012 to 2050 were created. The baseline scenario which makes an assumption of no new energy or climate change policies beyond the existing policies results in a doubling of CO$_2$ emissions in 2050 compared to 2007. On the other hand, in the BLUE map scenario when effective policies and technology advancements were predicted and taken into consideration, the anthropogenic emissions of CO$_2$ in 2050 could be cut to half of the 2007 levels. Achieving these optimistic goals would limit the global temperature increase to between 2$^\circ$C and 3$^\circ$C above pre-industrial levels by 2100 (IPCC 2001; Michaels and Balling, 2009).

Taking these facts into consideration, it has become a matter of extreme urgency to develop technologies to tackle the issue of carbon emissions and decarbonise the global energy system. Effecting a more than 50% reduction in the 2050 CO$_2$ emissions from the baseline scenario of 57 Gt to the BLUE Map scenario requires substantial efforts to be made globally across almost every energy related sector.
Carbon Capture and Sequestration (CCS) is one of the many technologies being developed currently to achieve these ambitious emission reduction targets and is expected to contribute 19% of the total predicted emission cuts, 10% resulting from CCS in power generation and 9% from CCS in industry and transformation (IPCC, 2001). CCS involves capturing CO₂ from large point source such as power stations, compressing and transporting by pipeline or tankers to an injection site and sequestrating for long-term storage in underground geological formations. It is currently the most probable approach for combating CO₂ emissions, while still allowing the continued use of fossil fuels. CCS could reduce CO₂ emissions from power stations and industrial processes by more than 85% (Michaels and Balling, 2009; IPCC, 2001). Without the implementation of CCS, the overall costs to reduce CO₂ emissions could increase by up to 70% (IEA, 2008). However, the BLUE Map scenario is particularly ambitious and requires over 3000 projects with a predicted expenditure of US$ 2.5 - 3 trillion by 2050 (IEA, 2008).

The capture of CO₂ could be beneficial not only to the environment but economically, as it could potentially be used for by-product end use in the industrial and energy production sectors. While totally avoiding the emission of carbon has been considered via the use of renewable energy technologies, it will be extremely difficult to achieve the targeted atmospheric CO₂ of below 450ppm without employing CCS technologies (IEA, 2008).

On an individual basis, each of the stages of CCS namely capture, compression, transport and storage are technically viable; however, there have been several challenges associated with the integration and scale-up of these technologies. According to the Global CCS Institute in its 2015 update report, there are at present 15 large scale integrated CCS projects operating globally, 7 that are under currently under construction and a further 22 at various stages of development planning (Global CCS Institute, 2015). The total CO₂ capture capacity of the 22 projects in operation or under construction is more than 40 Mt a⁻¹. According to the report 2
of the large scale CCS projects, The Quest Project, Alberta, Canada and The Uthmaniyah CO₂-EOR Demonstration Project, Saudi Arabia became operational in 2015 and 2 more are expected to begin operation in 2016. The almost doubling in large scale CCS projects since the start of 2010 is a strong indication in the determination of governments and energy-related industries to make significant advancements in CCS technology at a commercial scale.

CO₂ capture can be classified broadly into three main technologies: post-combustion, pre-combustion capture and oxy-fuel combustion as shown schematically Figure 1-1. Post combustion capture entails the CO₂ being separated from the flue gas produced by combustion in power plants. Power plants currently in existence use air for combustion and produce a flue gas which has a CO₂ concentration of less than 15% (Michaels and Balling, 2009; IPCC, 2001). Pre-combustion capture involves the separation of CO₂ from fuel prior to combustion. The fuel is first gasified to produce H₂ and CO₂ before the H₂ is separated and combusted. This involves higher concentrations of CO₂ than the post combustion method facilitating the separation. Oxy-fuel combustion, which is in demonstration phase, involves the combustion of the fuel in pure oxygen instead of air, causing the flue gas to contain mostly CO₂ and steam which can be separated easily.

In the case of diluted and low CO₂ pressure streams such as flue gases from power plants, the current technology of choice for CO₂ capture is the post-combustion capture method, based on the use of amine solvents to absorb CO₂ reversibly. This method of separating CO₂ from flue gas streams was first developed in the 1970s, not to tackle the greenhouse effect but for the potential economic benefits such as enhanced oil recovery and improving the quality of natural gas. It is already well established in the natural gas ‘sweetening’ (i.e. H₂S removal), ammonia production and hydrogen manufacture industries. An additional benefit of this method is that it can be retrofitted to existing power plants. In fact, it is currently the only
proven technology that is suited to the huge investment that has been made in fossil fuel infrastructure.

Figure 1-1: Post-combustion, pre-combustion and oxy-fuel combustion CO₂ capture systems (Figueroa et al., 2008).

This method of CO₂ capture is installed downstream of the power plant, so if the capture system encounters any issues, the power plant can continue to operate uninterruptedly. Employing amine-based carbon capture techniques will not decrease CO₂ emissions only by 85 to 90 percent, but also remove considerable amounts of other pollutants such as NOₓ and SO₂ due to prior treatment of the flue gas (Michaels and Balling, 2009; IPCC, 2001). This method involves a reversible reaction between the amine and CO₂ which, under ideal conditions, would allow for the recycling of the amine once the CO₂ has been released.
1.2. Operational difficulties in CO₂ absorption process

Although the concept of CO₂ capture by amine scrubbing involves proven technology, which has been used in industry for over 50 years, the process is still plagued with technology risks and technical barriers. There are numerous challenges hindering the deployment and successful operation of CCS technology, notably the high energy requirements (parasitic needs) and costs, which must be overcome before it can become commercially viable on a large scale. Currently, the cost of utilizing this process has been estimated to run as high as 66-75 % of the total power plant operating cost (McKinsey & Company, 2008). Furthermore, the process faces several operational difficulties such as degradation of the amines, pre-precipitation, corrosion of process equipment, solvent loss, fouling, increased viscosity of amine and foaming.

The amine solutions regularly become contaminated with degradation products, heat stable salts, heavy hydrocarbons and particulates (Abdi and Meisen, 2000). These degradation products are a result of irreversible side reactions with CO₂ and other flue gas components. As the amine process usually involves cycles of absorption and desorption which permit the recycling of the absorbent, the closed loop nature of this process leads to an accumulation of the degradation products which can yield a significant decrease in the absorption capacity of the amines. These large volumes of spent solution have to be disposed of by incineration or deep well injection. For instance, on a plant which uses monoethanolamine (MEA), it has been estimated that 2.2 kg of MEA must be replaced per tonne of CO₂ captured (Strazisar et al., 2003). However, this practice is undesirable due to the degradation products being toxic and represent several environmental and health risks, while it also amounts to a loss of valuable amine, as spent solutions contain about 85 % of virgin amine (Abdi and Meisen, 2000).
Amongst the numerous difficulties facing the use of alkaonolamines for CO\textsubscript{2} absorption, corrosion is the most serious operating problem, so it requires and has received the most attention. Several inconclusive theories have been proposed to explain the corrosion mechanisms, patents have emerged to alleviate the issue and a few papers have been published on the subject.

### 1.3. Corrosion in Amine Scrubbing Plants

Based on substantial information from a large number of amine treating plants, corrosion has been found to occur in several sections of the plant, such as the bottom of the absorber, the heat exchanger, the entire stripper and the overhead condenser. Corrosion of the carbon steel equipment occurs in both the form of uniform corrosion and localised attack such as pitting, galvanic, stress cracking and inter-granular corrosion (Veawab et al., 1999). While uniform corrosion results in a more significant loss of the carbon steel, it is less likely to result in catastrophic process failures, due to the relative ease in detection and monitoring. On the contrary, localised corrosion consumes less material but results in more calamitous failures as it can easily go undetected. Chronic corrosion can lead to significant economic losses as it results in unplanned downtime, production losses, reduced life of the equipment and even injury or death (Veawab et al., 1999); Hawkes & Mago, (1971) estimated that the economic consequence of unplanned downtime of a typical plant can cost up to $30,000 per day in terms of production losses. In addition to losses due to unplanned downtime, there is also the added expenditure of restoring the corroded units and treatments used to mitigate corrosion, the costs of which can run up to millions of pounds yearly (Veawab et al., 1999). Leaking units, tanks and pipelines result in significant loss of products, which are not only associated with a high cost, but could also be hazardous to the surrounding environment. An accumulation of corrosion products in units such as the heat exchanger tubing and pipelines could decrease efficiencies and reduce pumping capacity (Jones, 1996). The most devastating
consequence of corrosion is the threat to the safety of plant personnel. According to Craig and McLaughlin (1996), seventeen workers on a refinery plant in Lemont, Illinois were killed in an explosion in an MEA absorber caused by a leakage of flammable gasses from a non-stress-relieved weld repair to the vessel.

In addition to the economic penalties discussed above, corrosion can also affect the economy of the plant in a more indirect manner by limiting the operating conditions of the process. It is a generally accepted practice that low concentrations of amines have to be used to keep corrosion rates to acceptable levels and operating beyond a typical concentration (10-20 wt% monoethanolamine) can cause a significant increase in the system’s corrosiveness (Kohl & Riesenfeld, 1985; DuPart et al., 1993; Veawab et al., 1999). This decreases the effectiveness of the solvent, bringing about the need for bigger equipment, faster circulation rates and larger energy requirements (Strazisar et al., 2003, Strazisar et al., 2002). The extra energy requirement would in turn increase the parasitic load of the plant, leading to higher fuel consumption, costs and ironically CO₂ emissions. Employing this method almost completely negates the benefits of sequestration (Strazisar et al., 2002). However, operating the process beyond these conditions may also increase the system’s corrosiveness; hence, the capacity of existing plants may not be easily increased.

1.4. Existing Corrosion Control

There are several approaches which have been considered strongly for corrosion control on amine scrubbing plants: i) appropriate equipment design and operating conditions, ii) use of more corrosion-resistant alloys of steel instead of carbon steel, iii) the frequent and intermittent removal of solid contaminants from the amine solutions, and iv) use of corrosion inhibitors (Kohl & Riesenfeld, 1985; Veawab et al., 1999). While the use of corrosion inhibitors has been recommended and even patented as the most economical and easy to
implement technique for corrosion control, it has not been employed successfully in amine units (Kohl & Riesenfeld, 1985). This could be due to the most effective corrosion inhibitors currently available containing toxic inorganic substances such as vanadium compounds, which make for difficult disposal and pose serious environmental concerns.

1.5. Limitation to Available Corrosion Data

While it is apparent that CO₂ capture based on the use of amines can be improved by reducing or completely eliminating the excessive corrosion issues associated with the process, it has been difficult to establish the mechanisms under which it occurs and in turn impossible to recommend a long-lasting solution. This is in part, due to the limitations in the current knowledge of the corrosion phenomena. There is a limited amount of research data on corrosion in amine plants available in literature. Corrosion rates were measured using weight loss or rudimentary electrochemical techniques to establish the effect of operating conditions such as amine concentration, CO₂ loading and temperature on corrosion rate; those rates vary significantly depending on the source and the testing environments under which they were determined. The available data are sparse and in some cases are uncorrelated because they were measured by different sources under either laboratory or field conditions using as aforementioned different corrosion measuring techniques. As such, the information available in open literature has been useful only for describing the corrosion behaviour qualitatively and establishing some common trends between the operating parameters and corrosion rates. Most of the data collected so far have also been reported with an incomplete list of crucial operating conditions, making it difficult to derive a complete understanding of the role of process parameters on the corrosion phenomenon. Therefore, to be able to establish further understanding of the corrosion behaviour, it was essential for a comprehensive set of data to be generated under well-controlled conditions, similar to those found in amine absorption plants.
A number of corrosion mechanisms have been proposed to explain the corrosion in amine plants (DuPart et al., 1993, Tomoe et al., 1996) and it has been hypothesized that the oxidising agents driving the corrosion reactions are the same as those commonly present in CO$_2$-water systems, i.e. hydrogen ion (H$^+$) and bicarbonate ion (HCO$_3^-$). However, it has yet to be established whether this is indeed the case in amine-$\text{H}_2\text{O}$-CO$_2$ systems, as such the exact mechanisms of corrosion in such systems are little understood and remain undefined.

### 1.6. Project Aims

An ideal amine plant would be able to achieve a high degree of CO$_2$ capture at a minimal financial and environmental cost. These concerns about efficiency, parasitic needs and the economics of running amine scrubbing plants have made decreasing solvent degradation and corrosion rates a matter of high priority. As the knowledge of corrosion in amine-$\text{H}_2\text{O}$-CO$_2$ systems is currently sparse and inconclusive, hitherto corrosion prevention and mitigation has been difficult to achieve. A thorough understanding of the mechanisms of the corrosion of carbon steel in the solvent would constitute significant progress towards achieving this goal. Thus, this thesis aimed to extend and bridge the gaps in the current knowledge by determining the oxidation and reduction kinetics and mechanisms of iron in aqueous MEA-CO$_2$-$\text{H}_2\text{O}$ systems as functions of experimental variables, with the view to predicting iron corrosion rates under typical CO$_2$ absorption process conditions.

### 1.7. Project Scope and Objectives

This project focused on iron as the principal component of carbon steel used as construction material in the amine scrubbing technology, concentrating on the electrochemical behaviour and characterisation, both experimentally and via thermodynamic and electrochemical modelling. The project had three objectives:
1. Quantification of the electrochemical kinetics and mechanisms of iron oxidation and hence corrosion rates, in aqueous MEA-CO$_2$-H$_2$O systems, as a function of experimental variables.

2. A mechanistic model for iron oxidation kinetics in aqueous MEA-H$_2$O-CO$_2$.

3. A description of the dependence of iron(II) dissolution rates on experimental variables, using a specially-designed electrochemical flow reactor with subsequent analysis of dissolved iron(II) concentrations, enabling deconvolution of total oxidation current densities in the small scale electrochemical experiments, into rates of reactions leading to adsorbed and dissolved products.

1.7.1. Project Tasks

The following tasks were defined in order to achieve the aims and objectives of this project:

1. Characterisation of the electrochemical behaviour of iron in MEA-CO$_2$-H$_2$O by cyclic voltammetry with the use of a rotating disk electrode (RDE) and electrochemical quartz crystal microbalance (EQCM), thus permitting the following:
   a) Determination of the reaction mechanisms for iron oxidation in amine systems in the absence and presence of CO$_2$.
   b) Investigation of the effects of process parameters, MEA concentration, temperature, CO$_2$ loading, pH, mass transport rates and dissolved oxygen concentration on the electrochemical behaviour of iron.
   c) Kinetic analysis and identification of quantitative trends in corrosion rates as functions of the experimental parameters.

2. Identification of primary solution species in CO$_2$ loaded MEA systems, permitting analysis of the chemical speciation and equilibrium concentrations of the amine
species (RNH₂, RNH₃⁺, RNHCOO⁻) and carbon (IV) species (HCO₃⁻, CO₃²⁻) and hydrogen ions (H⁺) via a Kent-Eisenberg type model.

3. Determination of unknown electrochemical parameters (e.g. exchange current densities, Tafel slopes) and their dependence on operating conditions from reliable data published in the literature.

4. Development of a predictive micro-kinetic model for the uniform corrosion of Fe in MEA-H₂O-CO₂ systems based on the proposed corrosion mechanisms from the voltammetric results taking into account the CO₂ absorption equilibria reactions and the kinetic equations that describe the electrochemical reactions at the iron surface.

5. Design, construction and characterisation of a large scale electrochemical flow reactor fabricated from PTFE with an iron/steel anode, platinised titanium cathode and a cation-permeable Nafion membrane.

6. Operation of the flow reactor in order to:
   (a) Measure dissolved iron (II) concentrations under typical CO₂ absorption conditions.
   (b) Determine the charge yield for dissolution, so enabling discrimination between current densities leading to dissolution from those resulting in adsorbed products.

1.8. Thesis outline:

This thesis is organised into 8 main sections. The general introduction and background theory on electrochemical systems with a focus on corrosion is detailed in Chapter 2. Chapter 3 presents a comprehensive literature survey covering the carbon capture technology and the types of amines employed in the carbon capture process. The literature review also evaluates previous experimental work on corrosion in CO₂-loaded amine systems and advancements in iron and steel corrosion in CO₂-H₂O systems within other technical fields, such as the oil and
gas industry. In Chapter 4, the experimental apparatus and procedures for the various electrochemical and analytical techniques used are described. Chapters 5 to 7 detail the results from the experimental and electrochemical model based on the objectives outlined above. Chapter 5 details the electrochemical reaction mechanisms and kinetics analysis of Fe in MEA solutions based on cyclic voltammetry experiments conducted with the RDE and EQCM. Based on the proposed corrosion mechanisms, a mechanistic model for the uniform corrosion of iron in CO₂-loaded MEA systems was developed and detailed in Chapter 6, taking into account the solution speciation and the electrochemical reactions at the iron interface. Chapter 7 is dedicated to the experimental results and discussion from the flow-through reactor from which, dissolved iron concentrations were measured after constant potential electrolysers. Finally, conclusions are summarised and recommendations for future work are suggested in Chapter 8.
1.9. References


2. Chapter 2

Principles of Electrochemical Systems for Corrosion Studies

Studies of metallic corrosion can be traced back at least to the end of the 18th century during the industrial revolution, when references to corrosion phenomena in literature first occurred. The emergence of modern corrosion science occurred in the twentieth century when (Evans, 1937) proposed a local cell model and (Wagner and Traud, 1938) introduced the mixed potential corrosion model. These two models have served as the basis for the electrochemical theory of corrosion, which describes corrosion as coupled electrochemical reactions consisting of anodic metal oxidation and cathodic oxidant reduction(s) leading to the metal’s disintegration into its constituent ions.

This chapter addresses the fundamental principles of electrochemistry which provides background theory on the experimental techniques employed and the analysis of the results reported in subsequent chapters. This includes the fundamental definitions within electrochemical systems, thermodynamics and kinetics of electrochemical reactions and transport processes.
Electrochemistry is the study of chemical reactions that occur via the transfer of charge across
the interface of an electrode, which is a metallic or semiconducting solid and an electrolyte
which is a liquid or solid ionic conductor (Walsh, 1993). Two types of charge transfer reactions
occur at the interface: ion transfer reactions from electrode to the electrolyte, or vice versa;
electron transfer reactions between ions or molecules in the electrolyte and an electrode surface.

The general form of electrochemical reactions is expressed in equation (2.1) where the redox
couple O and R denote the oxidised and reduced species, respectively.

\[
O + ne^- \xrightarrowspace_\text{cathodic reduction}\xrightarrow{\text{anodic oxidation}} R
\]  \hspace{1cm} (2.1)

When a metal is immersed into a solution, electrochemical reactions may occur at the surface
of the metal causing the metal to corrode. Two or more reactions simultaneously occur: the
oxidation of the metal (anodic reaction) and the reduction of the oxidizing agent (cathodic
reaction). Oxidation involves the loss of electrons, while reduction occurs when electrons are
 gained.

A typical example of corrosion may be a piece of metal which becomes wet leading to the
occurrence of corrosion. Ions are exchanged through the surface water layer (electrolyte)
between the anode and cathode while electronic exchange will take place through the bulk
metal. Corrosion often involves oxidation of metal atoms to form ionic species with higher
oxidation states and the liberation of electrons.

For a generic metal M:

\[
M \xrightarrowspace M^{n+} + ne^-
\]  \hspace{1cm} (2.2)

In the case of iron:

\[
Fe \rightarrow Fe^{2+} + 2e^-
\]  \hspace{1cm} (2.3)

These are called half-cell reactions because the electrons liberated by the oxidation reaction
must be consumed by a reduction reaction occurring on the same electrode. A common
reduction reaction is the hydrogen evolution reaction:
2H^+ + 2e^- → H_2 \hspace{1cm} (2.4)

This would give an overall reaction of

Fe + 2H^+ → Fe^{2+} + H_2 \hspace{1cm} (2.5)

Anodes and cathodes can be spatially separated at fixed locations associated with heterogeneities on the electrode surface. Alternatively, the locations of the anodic and cathodic reactions can fluctuate randomly across the sample surface. The former case results in a localised form of corrosion, such as pitting, crevice corrosion, inter-granular corrosion, or galvanic corrosion and the latter case results in nominally uniform corrosion.

2.1. Thermodynamics of Electrochemical reactions

Thermodynamic calculations can be used to predict the tendency for a metal to corrode in a particular environment. The driving force for a spontaneous reaction is a negative value of Gibbs free energy change (\(\Delta G < 0\)) at a fixed temperature and pressure. For non-spontaneous reaction such as an electrolytic cell, the Gibbs free energy change is positive, so an input of energy is required for the reaction to proceed. The Gibbs energy change for a reaction is defined by equation (2.6). Where \(\Delta H\) is the enthalpy change, \(T\) is the temperature and \(\Delta S\), the entropy change associated with the cell reaction.

\[
\Delta G = \Delta H - T\Delta S
\]  \hspace{1cm} (2.6)

The Gibbs energy for any species, \(G\) is related to the standard Gibbs energy, \(G^0\) (the free energy for the species in its standard state) by equation (2.7), where \(R\) is the gas constant, and \(a\) denotes the activity of the species.

\[
G = G^0 + RT\ln a
\]  \hspace{1cm} (2.7)

For a given reaction, the Gibbs energy change is given by the difference between the summation of values for the products and reactants:

\[
\Delta G = \sum \Delta G_{\text{products}} - \sum \Delta G_{\text{reactants}}
\]  \hspace{1cm} (2.8)
The Gibbs energy change for an electrochemical cell reaction is directly related to the reversible potential, $E_{O/R}$ via equation (2.9). In this expression $F$ is Faraday constant, the product of Avogadro’s constant $N_a$ and the charge on a single electron $Q_e$ ($F = N_a Q_e$, 96 485 C mol$^{-1}$).

$$\Delta G = -nFE_{O/R} \quad (2.9)$$

Half-cell potentials are established with reference to the standard hydrogen electrode (SHE) with the electrode potential of hydrogen arbitrarily assigned a value of zero volts. The SHE (Pt, H$_2$/H$^+$) represents the electro-active species in the electrolyte in their standard states: H$_2$ gas at 0.1 MPa pressure, 298.15 K and the activity of H$^+$ protons is 1. Essentially, the electrode whose standard electrode potential is being measured is configured as the cathode and the anode is the reference electrode.

### 2.1.1. Nernst Equation

The standard state requires all reactants and products to be at unit activity. The Nernst equation was established to calculate the effect of deviation from standard state on the reversible potential. Equation (2.10) represents the free energy change for a generalised reaction in which the reactants and products are not in their standard states.

$$\Delta G = \Delta G^\circ + RT \ln \left\{ \frac{\prod \alpha_{prod}^m}{\prod \alpha_{react}^n} \right\} \quad (2.10)$$

If the reaction is a reduction reaction (the reactants and products are the oxidised and reduced forms of the species respectively) substituting $\Delta G = -nFE_{O/R}$ and $\Delta G^\circ = -nFE_{O/R}^\circ$ into equation (2.10) results in:

$$E_{O/R} = E_{O/R}^\circ + \frac{RT}{nF} \ln \left\{ \frac{\prod \alpha_{ox}^m}{\prod \alpha_{red}^n} \right\} \quad (2.11)$$

Equation (2.11) is called the Nernst Equation and it describes the equilibrium potential of an electrochemical half reaction in which the oxidised or reduced species are not necessarily in their standard states.
2.1.2. Pourbaix Diagrams

As mentioned previously, an electrode reaction is in a state of dynamic equilibrium at its equilibrium potential at which no net reaction current flows. The anodic reaction (metal corrosion) can only occur at potentials more positive than the equilibrium potential and the cathodic reaction (oxidant reduction) proceeds at potentials more negative than its equilibrium potential. Thermodynamically it is known that the corrosion of metals in solutions is not only dependent on the electrode potential but also on the pH of the solution. Thus, when several reactions are possible, as is the case with Fe oxidation, the electrochemical behaviour in aqueous systems can be illustrated by Pourbaix diagrams in the form of phase stability plots which are created by relating the reversible potential to pH and total dissolved cation activity. These visual representations of the equilibrium conditions in the potential/pH space were pioneered by Professor Marcel Pourbaix (Bard, 2003). They are based purely on the thermodynamics and indicate the stability of predominant species under given conditions but give no indication of the rates of reactions from one phase to another.

2.1.2.1. Pourbaix Diagrams for water

In corrosion mechanisms, the most important cathodic reactions involve water. There are two primary cathodic reactions, each of which takes a different form in acids or bases. The first is the hydrogen evolution reaction (HER), in which hydrogen gas is evolved.

In acids:

\[
2H^+ + 2e^- \leftrightarrow H_2(g) \tag{2.12}
\]

\[
E_{(H^+/H_2)} = E^\circ_{(H^+/H_2)} + \left(\frac{0.059}{2}\right)\log[H^+]^2 \tag{2.13}
\]

\[
= -0.059pH
\]

In bases:
\[ 2H_2O + 2e^- \leftrightarrow H_2(g) + 2OH^- \]  \hspace{1cm} (2.14)

The Nernst equation for the base form of the HER equation given is also given by \( E_{(H_2O/H_2)} = -0.059pH \).

When dissolved oxygen gas is present in the aqueous solution the following oxygen reduction reactions are also possible:

In acids:

\[ O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \]  \hspace{1cm} (2.15)

\[ E_{(O_2/H_2O)} = E^0_{(O_2/H_2O)} - \left(\frac{0.059}{4}\right) \log[H^+]^{-4} \]  \hspace{1cm} (2.16)

\[ = 1.229 - 0.059pH \]

In bases:

\[ O_2 + 4H_2O + 4e^- \leftrightarrow 4OH^- \]  \hspace{1cm} (2.17)

The Nernst equation in equation (2.16) also applies for the oxygen reduction reaction in bases.

The Nernst equation for the HER \( E_{(H^+/H_2)} = -0.059pH \) is represented on the Pourbaix diagram for water shown above (Figure 2-1) with an intersection at (0, 0) and a slope of \(-0.059\) pH\(^{-1}\) at 298 K. The hydrogen evolution reaction is in equilibrium along this line. At potentials above this line in E/pH space, water (H\(^+\)) is the stable phase and any dissolved H\(_2\) gas that might be present in solution is oxidised. Below this line, H\(_2\) gas is the stable phase, and water (or H\(^+\)) is reduced.

The Nernst equation for the oxygen reduction reactions is also plotted in Figure 2-2 with a line parallel to the HER line, which intersects at 1.23V. Above the oxygen line, O\(_2\) is the stable phase and water (OH\(^-\)) is oxidised. Below the oxygen line, water is stable and O\(_2\) is reduced.
The two plots combined give the region of water stability with water being stable in between both lines. It is oxidised to O₂ above the oxygen line and reduced to H₂ below the hydrogen line.

It can be seen from the Nernst equations that as the activity of the oxidizer H⁺ increases, pH decreases and \( E_{(H^+/H_2)} \) increases. This is the case for all oxidizers according to the Nernst equation.

![Pourbaix diagram of water](image)

Figure 2-1: Pourbaix diagram of water; 298 K, 0.1 MPa.

### 2.1.2.2. Pourbaix Diagram for Iron

Pourbaix diagrams for metals in aqueous solutions are created in order to visualise the regions of stability for the metal and its various corrosion products. To generate a Pourbaix diagram, the possible reaction products in an aqueous solution must be known. Commonly, a metal will oxidize to form a soluble cation, a soluble anion and a metal oxide or hydroxide.

In the case of iron, it will dissolve to form ferrous cations via reaction:

\[
Fe \rightarrow Fe^{2+} + 2e^-
\]  

(2.18)

With the Nernst Equation
At 298 K:

\[ E_{(Fe^{2+}/Fe)} = E_{(Fe^{2+}/Fe)}^0 + \left( \frac{0.059}{2} \right) \log [Fe^{2+}] \]  

\[ = -0.44 + 0.0295 \log [Fe^{2+}] \]  

This line is dependent only on the dissolved Fe^{II} activity and is independent of the pH. It is characterized by horizontal lines in the E/pH space depending on the value of [Fe^{II}]. Horizontal lines on Pourbaix diagrams represent reactions which are purely electrochemical. Above this line the oxidation reaction will proceed and Fe^{2+} is the stable phase while Fe is stable below it.

Iron can react with water to form ferrous hydroxide:

\[ Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^- \]  

\[ E_{(Fe(OH)_2/Fe)} = E_{(Fe(OH)_2/Fe)}^0 + \left( \frac{0.059}{2} \right) \log[H^+]^2 \]  

\[ = -0.047 - 0.059pH \]  

This is represented by a line parallel to the HER and oxygen reduction lines with a slope of -0.059 pH\(^{-1}\) and intersection of -0.047 V. Sloping lines on Pourbaix diagrams indicate a reaction which involves both electrons and protons.

Ferrous iron reacts to form ferrous hydroxide:

\[ Fe^{2+} + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^+ \]  

The equilibrium constant for this reaction describes the combinations of Fe^{2+} concentration and pH for which this reaction is in equilibrium

\[ K = \frac{[H^+]^2}{[Fe^{2+}]} = 10^{-13.29} \]  

\[ pH = 6.645 - 0.5 \log[Fe^{2+}] \]  

This relationship is independent of potential and is displayed in the Pourbaix diagram as a vertical line at a given pH that depends on [Fe^{2+}] and separates the Fe^{2+} and Fe(OH)\(_2\) phases. Vertical lines on Pourbaix diagrams represent purely chemical reactions which involve protons but not electrons.
Fe can react to form an oxy-anion such as HFeO$_2^-$ according to:

$$Fe + 2H_2O \rightarrow HFeO_2^- + 3H^+ + 2e^-$$  \hspace{1cm} (2.24)

$$E_{(HFeO_2^-/Fe)} = E^0_{(HFeO_2^-/Fe)} + \frac{0.0592}{2} \log ([H^+]^3[HFeO_2^-])$$  \hspace{1cm} (2.25)

$$= E^0_{(HFeO_2^-/Fe)} + \frac{0.0592}{2} \log[HFeO_2^-] - \left(\frac{3}{2}\right)(0.059)pH$$

$$= 0.493 + 0.295 \log [HFeO_2^-] - 0.0886 \text{ pH}$$

Ferrous hydroxide (Fe(OH)$_2$) dissolves chemically to form HFeO$_2^-$:

$$Fe(OH)_2 \leftrightarrow HFeO_2^- + H^+$$  \hspace{1cm} (2.26)

$$K = [H^+][HFeO_2^-] = 10^{-18.3}$$  \hspace{1cm} (2.27)

$$pH = 18.3 + \log[HFeO_2^-]$$

Other possible reactions and their accompanying Nernst (or equilibrium) equations are listed below.

$$Fe^{2+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ + e^-$$  \hspace{1cm} (2.28)

$$E_{(Fe(OH)_3/Fe^{2+})} = 1.057 - 0.1773pH - 0.0591\log[Fe^{2+}]$$  \hspace{1cm} (2.29)

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$$  \hspace{1cm} (2.30)

$$pH = 1.613 - \frac{1}{3}\log[Fe^{3+}]$$  \hspace{1cm} (2.31)

$$Fe(OH)_2 + H_2O = Fe(OH)_3 + H^+ + e^-$$  \hspace{1cm} (2.32)

$$E^{rev} = 0.271 - 0.0591pH$$  \hspace{1cm} (2.33)

The full Pourbaix diagram for Fe-H$_2$O systems showing the equilibrium lines for dissolved iron activity of $10^{-4}$ is displayed in Figure 2-2. Examples of points that can be taken from the potential-pH diagram are as follows:
Any point on the diagram will give the most thermodynamically stable (abundant) form of Fe at that potential and pH. For example at $E = +0.80$ V and pH 6, Iron (III) oxide, Fe$_2$O$_3$ is predominant and at $E = +0.20$ V and pH 2, ferrous ions, Fe$^{II}$ are most stable.

In general, there are three phase fields in $E$-$pH$ diagrams: immune, active and passive. Elemental Fe is most stable at low potentials, in the region of immunity. In this region corrosion is thermodynamically unfavourable. The tendency will be for any Fe ions in solutions to plate out. The active phase field in which dissolved ions such as Fe$^{II}$ and Fe$^{III}$ are predominant and regions where the tendency would be for corrosion to occur. Solid oxides and hydroxides are most stable in the regions of passivity, the condition of corrosion resistance occurring when certain metals form thin, oxidized protective films on the metal surface.

The diagram also visualises the oxidising and reducing abilities of the stable forms of Fe. Oxidising agents are at the top of the diagram while reducing agents are at the bottom. For example HFeO$_4^-$ and FeO$_4^{2-}$ are the most oxidising form of iron while the elemental Fe is the strongest reducing agent.

Pourbaix diagrams for metal-water systems always include the $E$-$pH$ lines for the cathodic reactions in water (HER and oxygen reduction). The position of these lines relative to the stable phases indicate the availability of the cathodic reactions for corrosion.
2.2. Kinetics of Electrochemical Reactions

While the information about the tendency for corrosion to occur can be obtained from thermodynamic calculations, this does not necessarily mean that it will actually occur nor does it give any information about corrosion rates, which are determined by reaction kinetics. An understanding of the fundamental laws of corrosion kinetics is essential in developing a more thorough understanding of the electrochemical system being studied.

2.2.1. Rate of reaction: Faraday’s Laws of Electrolysis

As electrochemical reactions result in the production or consumption of electrons, the rate of electron flow to or from a reacting surface gives a measure of the reaction rate. The overall rate of the electrochemical reaction may be expressed by Faraday’s laws of electrolysis. The amount
of reactant or product material undergoing electrochemical change \( m \) (mols) is proportional to the amount of electrical energy, \( Q \), involved:

\[
m = \frac{Q}{nF}
\]  
(2.34)

The charge, \( Q \) is defined as the integral of cell current with respect to time, \( t \).

\[
Q = \int I \, dt
\]  
(2.35)

If the current is constant:

\[
Q = It
\]  
(2.36)

Equation (2.34) becomes:

\[
m = \frac{It}{nF}
\]  
(2.37)

Differentiating with respect to time gives the expression for the rate of reaction (mols\(^{-1}\)):

\[
\frac{dm}{dt} = \frac{I}{nF}
\]  
(2.38)

\( \partial m/\partial t \) represents the loss of reactant (O) which is equal and opposite to the rate of formation of the product (R).

If the expression is divided by the area (A), it can be expressed in terms of the current density \( j \), \( j = I/A \)

\[
r = \frac{1}{A} \frac{dm}{dt} = \frac{j}{nF}
\]  
(2.39)

The units on both sides of the equation are in mol m\(^{-2}\) s\(^{-1}\).

It is also possible to expresses the amount of material transformed per unit reactor volume, \( V_R \) per unit time with the units mol m\(^{-3}\) s\(^{-1}\)

\[
r = \frac{I}{V_R} \frac{dm}{dt} = \frac{j}{nFV_R}
\]  
(2.40)
2.2.2. Rate limiting Mechanisms

From equations (2.39) and (2.40) it can be seen that the rate of reaction is proportional to the current density. However prior to the charge transfer reaction, the reactant must be transported from the bulk solution to the electrode interface, and the reaction products, once formed will diffuse away from the electrode. A particular reaction may be controlled by the kinetics of the electron transfer or by the rate at which material is brought to (or from) the electrode through mass transport. The overall reaction rate will be limited by the slowest step. Purely electron transfer controlled reactions will be discussed before taking into account mass transport considerations.

2.2.3. Charge Transfer Controlled Reactions

2.2.3.1. Exchange Current density

Consider again reaction (2.1), the forward reaction representing the cathodic reduction of O to form R, and the reverse reaction is the anodic oxidation of R to O. Electrochemical equilibrium is a dynamic process in which electrons are continuously being passed back and forth at the metal-solution interface. The exchange current density \( j_o \) for an electrochemical half cell reaction occurs at equilibrium, when the rate of the forward and reverse reactions are equal.

\[
    r_f = r_r = \frac{j_o}{nF}
\]

(2.41)

The exchange current density \( j_o \), a fundamental parameter of electrode kinetics can be determined using the following equation:

\[
    j_o = nFk^o a_H^w.
\]

(2.42)

Where \( k^o \) is a specific rate constant, \( a \) is the activity of the associated component and \( w \) is the reaction order. However, in practice it is difficult to calculate the exchange current density directly from equation (2.42) above due to the unavailability of the specific rate constan \( (k^o) \)
value for half-cell reactions, as such the exchange current density \( j_o \) can only be determined experimentally.

### 2.2.3.2. Electrochemical Polarization

The darkened dot on Figure 2-3 (a) below representing equilibrium \( (E_{O/R}, j_o) \) signifies a finite exchange current density. At this point, both the forward and reverse current densities are equal and the net current density is zero. Electrochemical polarization is a phenomenon that changes the equilibrium state of an electrochemical reaction and causes the potential to differ from the equilibrium potential \( E_{O/R} \). Polarization, \( \eta = E - E_{O/R} \), is defined as the change in potential from the reversible potential of a given half-cell electrode reaction (Bard, 2003).

![Figure 2-3: Schematic representation of the relationship between current and potential for a simple electrochemical reaction under kinetic control.](image)

This deviation from \( E_{O/R} \) in Figure 2-3 (b) causes the half cell reaction to proceed preferentially in one direction over the other resulting in a net current. For anodic polarization the potential is changed positively to a value higher than the equilibrium potential due to the removal of electrons from the metal surface. The reverse is the case for cathodic polarization, electrons are
supplied to the surface and a build-up in the metal causes the surface potential to become negative to $E_{O/R}$.

In electrochemistry, potential and current are interdependent. It is common practice to control one and measure the effect on the other

2.2.3.3. **Butler-Volmer Equation**

The overpotential that results from a change in potential is called activation overpotential if the concentrations of the reactants and products at the electrode surface are the same as in the bulk solution and the rate of charge transfer in the electrochemical reaction is governed only by an electron transfer step of the half-cell reaction at the metal-solution interface. This occurs when the rate of mass transport is fast compared to the rate of charge transfer. For such a system, the rate of reaction is limited by activation overpotential or charge transfer rate. Equation (2.43) is called the Butler-Volmer equation which relates the rate of reaction (current density) and the driving force for the reaction (overpotential).

$$j = j_0 \left[ \exp \left\{ \frac{\alpha_A F}{RT} \eta \right\} - \exp \left\{ - \frac{\alpha_C F}{RT} \eta \right\} \right]$$

(2.43)

Where $\alpha_A$ and $\alpha_C$ represent the transfer coefficients for the anodic and cathodic reactions respectively. They indicate the fraction of the applied overpotential, $\eta$ used to provide a driving force for the reaction.

$$\eta = E - E_{O/R}$$

(2.44)

The first term of the Butler-Volmer Equation represents the anodic partial current density $j_a$ and is taken as positive while the second term, $j_c$, the cathodic partial current density is taken as negative. The net current (the sum of the two terms) is positive when the electrode is polarised anodically and negative when the electrode is polarized cathodically.
The Butler-Volmer equation illustrated in Figure 2-4, represents the kinetics for charge-transfer controlled electrochemical reactions. When plotted on a current density versus electrode potential axes, the curve crosses the x-axis at the reversible potential.

\[ j = j_0 \left[ \exp \left( \frac{\alpha_{a}F}{RT} \eta \right) - \exp \left( - \frac{\alpha_{c}F}{RT} \eta \right) \right] \]

\[ j_0 = j_0 \exp \left( \frac{\alpha_{a}F}{RT} \eta \right) \]

\[ -j_c = j_c \exp \left( - \frac{\alpha_{c}F}{RT} \eta \right) \]

\[ E_{O/R} \]

\[ \eta \] / V

Figure 2-4: Plot of Butler-Volmer Equation for charge transfer limited reaction.

2.2.3.4. **Tafel Equation**

For particularly large values of anodic polarization from the equilibrium potential (\( \eta_a \geq 10 \text{ mV} \)), the first term on the of Butler-Volmer equation (anodic part) dominates over the cathodic contribution. Therefore, at large anodic overpotentials, the Butler-Volmer equation simplifies to the Tafel equation (2.47):

\[ j = j_a = j_0 \exp \left( \frac{\alpha_{a}F}{RT} \eta \right) \]  \hspace{1cm} (2.45)

\[ \log (j_a) = \log (j_0) + \left( \frac{\alpha_{a}F}{2.303 RT} \eta \right) \]  \hspace{1cm} (2.46)
\[
\eta = \beta_a \log \left( \frac{j}{j_o} \right)
\]

(2.47)

Where:

\[
\beta_a = \frac{2.303RT}{\sigma_{AF}}
\]

(2.48)

Cathodic polarization results in a similar equation:

\[
\eta_c = -\beta_c \log \left( \frac{j}{j_o} \right)
\]

(2.49)

As corrosion reactions typically occur at relatively high overpotentials, the Tafel equation is applicable in describing the corrosion kinetics under negligible mass transfer considerations.

Figure 2-5: Schematic of Tafel plot

An Evans diagram (a semi-logarithmic plot of \( \log |j| \) versus \( E \)) is displayed in Figure 2-5. As polarisation proceeds in either the cathodic or anodic direction, the current density \( (j) \) deviates linearly from the equilibrium current density \( (j_o) \). The linear deviation of the potential current density with activation polarisation can be described by the Tafel equations. These slopes
referred to as Tafel constants ($\beta$), give the magnitude of polarization per decade of current density and may be used to determine the transfer coefficient $\alpha$. The value of Tafel constants usually ranges from a value of 0.03 to 0.20 V depending on the conditions such as pH and temperature the activity of the interacting species (Jones 1992). Once the values of the electrochemical parameters are known for a particular system, the charge-transfer controlled current densities can be predicted as a function of the electrode overpotential. Values such as $j_o$ and $\beta$ can sometimes be obtained from open literature, otherwise they have to be determined experimentally.

### 2.2.4. Mixed Potential Theory

The Mixed Potential principle of charge conservation states that the sum of all the anodic oxidation currents must be equal to the sum of all the oxidant reduction currents, i.e. the total rate of oxidation must be equal to the total rate of reduction. When a metal is corroding in an aqueous solution both the anodic and cathodic half-cell reactions occur simultaneously on the surface. Each of these half-cell reactions will have its own half-cell electrode potential and exchange current density. As the half cell reactions (anodic and cathodic) polarize on the same surface, the half-cell electrode potentials change respectively, according to the Tafel equations until they become equal at $E_{corr}$, the corrosion potential at which:

$$\sum I_a + \sum I_c = 0$$  \hspace{1cm} (2. 50)

The corrosion potential is also referred to as the open-circuit potential or rest potential. This is a mixed potential as the value is determined by both the rate of the anodic and cathodic reactions and it lies somewhere in between the equilibrium potentials of the anodic metal dissolution and the cathodic oxidant reduction. The net measured current for a corroding metal in an aqueous solution typically take a similar form to the Evans diagram (Figure 2-6) below. For an electrochemical reaction in which HER is the main cathodic reaction, the Evans diagram shows the Tafel lines for the anodic and cathodic parts of the hydrogen evolution reaction along with
the Tafel lines for the dissolution and plating of the metal with a reversible potential below that of the HER. $E_{M^{+}/M}$ and $E_{H^{+}/H_2}$ are the reversible potentials while $j_{o,M^{+}/M}$ and $j_{o,H^{+}/H_2}$ are the current exchange densities for the metal dissolution and HER respectively.

![Tafel lines diagram](image)

Figure 2-6: Anodic and cathodic half-cell reactions present simultaneously on a corroding iron surface in acidic media.

As the two reactions then polarize on the conducting surface to $E_{corr}$, the half-cell electrode potentials change according to the following relationship.

$$
\eta_{M^{+}/M} = \beta_{M^{+}/M} \log \left( \frac{j_{M^{+}/M}}{j_{o,M^{+}/M}} \right) \\
\eta_{H^{+}/H_2} = -\beta_{H^{+}/H_2} \log \left( \frac{j_{H^{+}/H_2}}{j_{o,H^{+}/H_2}} \right)
$$

At the potential $E_{corr}$, the rates of the anodic and cathodic reactions are equal, which is the rate of corrosion.

$$
j_{M^{+}/M} = j_{H^{+}/H_2} = j_{corr}
$$
Arranging equations (2.51) & (2.52) into (2.53) gives an equation for calculating $j_{corr}$:

$$j_{corr} = j_{0,M^+/M} \cdot 10^{\left(\frac{\eta_{M^+/M}}{F_{M^+/M}}\right)} = j_{0,H^+/H_2} \cdot 10^{\left(\frac{\eta_{H^+/H_2}}{F_{H^+/H_2}}\right)}$$  \hspace{1cm} (2.54)

Where $\eta_{M^+/M} = E_{corr} - E_{M^+/M}$ and $\eta_{H^+/H_2} = E_{corr} - E_{H^+/H_2}$.

The net current goes to zero at the corrosion potential and extrapolation to the corrosion potential of the Tafel regions (the linear regions of the semi-logarithmic plot) gives the corrosion rate. The corrosion potential is predicted by the point at which the extrapolated anodic line for the metal dissolution intersects that of the cathodic line for the HER. At this potential, the oxidation and reduction current densities are equal. The rate of the anodic dissolution at the corrosion potential is the corrosion rate (corrosion current density). This corrosion potential always takes a value between the reversible potential for the two half reactions. The electrode is not in equilibrium at the corrosion potential since net changes are occurring: metal is oxidised and water is reduced.

Figure 2-7: Relationship of measured polarization curve to the Evans diagram for corroding metal in acidic media.
The concept of corrosion potential is further illustrated in Figure 2-7. The potential at which the rate of metal dissolution is equal to the HER rate is the potential corresponding to the corrosion current density / corrosion rate.

While the corrosion potential clearly depends on both the anodic and cathodic reactions, the rate of corrosion may be controlled by either one of these reactions. In most cases of metallic corrosion in acidic media, HER controls the rate of corrosion while oxygen reduction controls the rate in neutral media (Bard, 2003).

2.3. Mass transport

The term ‘mass transport’ in electrochemical systems refers to the mode by which reactant and product species are supplied to and from the solution | electrode interface. For kinetically controlled reactions, the rate determining step is the rate of the electrochemical reaction at the electrode surface rather than the rate of diffusion of species to the surface. Thus, the kinetics explained in Section 2.3 only applies in cases where the surface concentrations of all the species are equal to the bulk solution concentrations. At larger overpotentials and high current densities, mass transport effects have to be taken into consideration as the rate of transport to (or from) the surface can also affect or control the overall reaction rate. In such cases, the reaction at the electrode surface occurs faster than the reactants can diffuse from the bulk to the solution | electrode interface. Therefore, the reactant species are depleted at the reaction surface resulting in a mass transport limited current discussed in more detail in the following section.

2.3.1. Transport Processes in Electrochemical Systems

As discussed above, the rate of an electrochemical reaction is dependent on the applied potential difference, the kinetics and the transport rate of reactant species to and from the electrode surface. Ionic motion in the electrolyte will respond to differences in density, concentration gradients and electric fields as well as bulk motion of the fluid. In general, there are three mechanisms of ion transport to and from the electrode/electrolyte interface: convection,
diffusion and migration. From Table 2-1, it can be seen that the three modes of ionic transport are driven by a form of gradient near the electrode surface. This gradient gradually changes the particular property with distance from the electrode surface and results in boundary layers.

Table 2-1: Modes of mass transport (Walsh, 1993)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Driving Force</th>
<th>Nature of Force</th>
</tr>
</thead>
<tbody>
<tr>
<td>Convection</td>
<td>Velocity gradient $dv/dx$</td>
<td>Density differences (if natural convection) or external mechanical forces (in forced convection)</td>
</tr>
<tr>
<td>Diffusion</td>
<td>Concentration gradient $dc/dx$</td>
<td>Physical</td>
</tr>
<tr>
<td>Migration</td>
<td>Potential Gradient $d\phi/dx$</td>
<td>Electrostatic</td>
</tr>
</tbody>
</table>

Thus, the layers of electrolyte near the electrode surface have a different velocity, concentration or potential than the electrode surface and the bulk electrolyte. The forms of mass transport in electrochemical reactions are illustrated schematically in Figure 2-8.

Figure 2-8: Schematic of an electrochemical system showing the transport processes and one dimensional distribution of electrical potential
**Diffusion** is the movement of a species down a concentration gradient and it is induced by a chemical change at the electrode solution, such as the conversion from the oxidised species (O) to the reduced species (R). This results in a lower concentration of O at the electrode surface than in the bulk solution and a higher concentration of R at the electrode surface.

The rate of material transport by diffusion is governed by Fick’s first law. The law states that the diffusion flux of a dissolved species $i$ to a surface depends on the diffusion coefficient of the species in the electrolyte $D_i$ and is proportional to the concentration / activity gradient.

$$N_{diff,i} = -D_i \nabla c_i$$

(2.55)

Where the Del operator for gradients in three dimensions is:

$$\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$$

(2.56)

Where $D$ is the diffusion coefficient (m$^2$ s$^{-1}$) and $x, y, z$ represent the distance from the electrode (m).

Under non-steady state conditions, Fick’s second law can be used to predict how the diffusion causes the concentration to change with time. It states that the change of concentration with time is equal to the difference of the diffusive fluxes in and out of a given volume element (Bard, 2003)

$$\frac{dc_i}{dt} = D_i \nabla^2 c_i$$

(2.57)

In the case of a dissolved species reacting chemically, Fick’s second law is modified to take into account homogeneous chemical reactions. For example, if the species is being consumed by an irreversible first-order chemical reaction with a rate constant $k_i$, the resulting equation is:

$$\frac{dc_i}{dt} = D_i \nabla^2 c_i - k_i c_i$$

(2.58)

**Convection** is the movement of a species down a velocity gradient due to mechanical forces such as pressure, density, or temperature gradient (Jones, 1996, Bard, 2003). There are two
types of convection, natural and forced convection. Natural convection results in small
differences in solution density due to chemical changes at the electrode surface or by localised
temperature fluctuations. (Walsh, 1993) Forced convection is usually the main mode of mass
transport and may be brought on by electrode or electrolyte movement.

The flux of a species $i$ due to convection $N_{\text{conv},i}$ (mol m$^{-2}$ s$^{-1}$) is the product of the bulk
concentration of that species ($c_i$) and the velocity of the solution ($v_{\text{sol}}$):

$$N_{\text{conv},i} = c_i v_{\text{sol}} \quad (2.59)$$

*Migration* is the movement of a charged species in response to a potential gradient caused by
the presence of an electric field which results in ionic currents passing through the electrolyte.
It is the preferential drift of ions toward the electrode of the opposite sign. This type of ionic
transport is driven by electrostatic forces and it takes the ion size and charge into account. Ions
will move in a field with a net drift velocity $v_d$ (m s$^{-1}$) that is proportional to the potential
gradient $\nabla \Phi$ (V m$^{-1}$).

$$v_d = -u_e \nabla \Phi \quad (2.60)$$

Where $u_e$ (m$^2$ V$^{-1}$ s$^{-1}$) is the electric mobility and it is a measure of the velocity the ion would
acquire in an electric field of 1 V m$^{-1}$. The induced flux of species $i$, due to migration is:

$$N_{\text{migr},i} = z_i F u_i c_i \nabla \Phi \quad (2.61)$$

In this expression, mobility $u_i$ is the velocity that one mole of species $i$ would acquire under the
effect of a force of 1 N. $z_i F$ (C mol$^{-1}$) is the charge per mole of the ionic species. $z_i$ is positive
for cations and negative for anions.

Therefore, the total flux for a charged electro-active species, $N_i$ (mol m$^{-2}$ s$^{-1}$) to an electrode
surface is the sum of the three different modes of mass transport:

$$N_i = N_{\text{diff},i} + N_{\text{migr},i} + N_{\text{conv},i} \quad (2.62)$$

$$J_i = -D_i \nabla c_i - z_i F u_i c_i \nabla \Phi + c_i v_{\text{sol}} \quad (2.63)$$
The diffusion coefficient \(D_i\) can be expressed in terms of mobility by the Nernst-Einstein equation:

\[
D_i = u_i \frac{RT}{z_i F}
\]  

(2.64)

From the Faraday’s law, the current density can be calculated from equation (2.65).

\[
j = F \sum_i z_i N_i
\]  

(2.65)

Where the current density at an electrode with area \(A_e\):

\[
j = I / A_e
\]  

(2.66)

In the absence of significant concentration gradients, substitution of (2.65) equation (2.64) results in ohm’s law:

\[
j = -\kappa \nabla \phi
\]  

(2.67)

\[
\kappa = F \sum_i |z_i| u_i c_i
\]  

(2.68)

Where, \(\kappa\) is the conductivity of the solution and with the assumption of electroneutrality in the bulk solution:

\[
\sum_i z_i c_i = 0
\]  

(2.69)

The movement of ions due to an electric field may cause re-distribution of the charge in the solution adjacent to the electrode interface which will cause the potential drop at the interface to be altered. This could result in fluctuations in the localised driving force for electrochemical reactions which is particularly detrimental during kinetic measurements during which \(\eta\) should be measured or controlled as accurately as possible (Fisher, 1996). However, if there is an abundant concentration of charged species also known as a ‘supporting electrolyte’ in addition to the primary reactant species, then the field fluctuations can be stabilised as they carry the most of the charge in the bulk solution (Pletcher, 1984). Mass transport limiting current densities \((j_{lim})\) are also lower in the presence of a supporting electrolyte, because increasing the electrode potential has no effect on the migrational contribution to the transport rate of the
electroactive species, the majority of the current being carried in the bulk solution by the supporting electrolyte. Thus, it is common practice in electrochemical systems to add a supporting electrolyte to increase the conductivity of the solution and decrease the ohmic potential drop between the electrodes. A supporting electrolyte also serves to improve uniformity in the current density distribution across electrochemical reactors with larger electrodes and in some cases can be used to adjust the solution pH.

In the presence of excess supporting electrolyte, the migrational contribution in equation (2.62) is negligible. For the following discussion, it is assumed that near the electrode surface there is a stagnant layer of electrolyte of thickness $\delta_N$, called the Nernst diffusion layer. In reality, this stagnant layer near the electrode surface of a finite thickness does not exist as the solution velocity $v_{sol}$ decreases gradually closer to the electrode surface becoming zero at the electrode surface. However, the concept of a Nernst diffusion layer is important when considering the convective mass transport at electrodes and allows for distinction between the contributions due to convection and diffusion. Within the stagnant Nernst diffusion layer, the net flux of the species is due only to diffusion, while beyond the diffusion layer, ohm’s law applies in a well-stirred bulk electrolyte in which there are essentially no concentration gradients, so convection is the only relevant mass transport mechanism.

The thickness of the Nernst diffusion layer is dependent on the convection rate as convection has the effect of decreasing the hydrodynamic boundary layer at the electrode | solution interface. Rotating disk electrodes are often employed in electrochemical laboratory experiments to provide a well-characterised system for controlling mass transport rates due to convection, as will be discussed further in Chapter 4.

According to Fick’s law for one dimensional steady state diffusion, the flux to a plane is proportional to the concentration gradient

$$N = -D_i \frac{dc_i}{dx}$$

(2.70)
where the diffusion coefficient $D_i$ (ca. $10^{-9} \text{ m}^2 \text{ s}^{-1}$ for species in aqueous solution at 298 K) is assumed to be independent of the concentration. Integration of equation (2.70) over the Nernst diffusion layer gives the following equation for the current density.

$$j = -nFD_i \frac{(C_i - C_{i,x=0})}{\delta_N} \tag{2.71}$$

Where the current density is linearly related to the flux via Faraday’s law, equation (2.72). $c_i$ and $c_{i,x=0}$ are the bulk and surface concentrations respectively and $\delta_N$ is the Nernst diffusion layer thickness.

$$j = -nFN_i \tag{2.72}$$

Solving equation (2.71) for the absolute value of the surface concentration of species $i$ results in:

$$C_{i,x=0} = C_i - \frac{\frac{1}{nF}N_i}{nFD_O} \tag{2.73}$$

The surface concentration of the species $C_{i,x=0}$ continues to decrease with increasing current density until it reaches a value of $C_{i,x=0} = 0$ at the maximum possible rate. The current density at this point is called the mass transport limiting current density, $j_{lim}$.

$$j_{lim} = \frac{-nFD_iC_i}{\delta} = nFk_mC_i \tag{2.74}$$

Where $k_m$ is the mass transport rate coefficient. Dividing by (2.71):

$$\frac{j}{j_{lim}} = 1 - \frac{C_{i,x=0}}{C_i} \tag{2.75}$$

Thus the concentration polarization which arises due to the changes in concentration of the electroactive species in the electrode | electrolyte interface can be expressed as (Jones 1996)

$$\eta_{conc} = \beta \log \left(1 - \frac{j}{j_{lim}}\right) \tag{2.76}$$

With increasing electrode potential from its equilibrium value, the current density increases until it approaches the limiting current density $j_{lim}$, which is independent of potential, unless
another reaction such as solvent decomposition occurs. As the current reaches the limiting current, the concentration polarisation goes to negative infinity. The limiting current density, \( j_{\text{lim}} \), increases with solution velocity, temperature, and bulk concentration of the species.

Mass transport considerations are particularly significant in corrosion rate measurements in where there is a limited concentration of oxidant species. For example, in a case of iron corrosion occurring in a neutral solution with oxygen as the primary oxidant, then the maximum corrosion rate will be determined by the limiting current density of the cathodic reactant to the iron surface.

### 2.3.2. Electrochemical Reaction Coupled to Mass Transport

Electrode reactions typically involve a series of steps: the transport of the reactant species to the solution | electrode interface, the transfer of charge at the electrode and the transport of the product species formed away for the surface. The charge transfer and mass transport processes are interlinked in series, i.e. the charge transfer can occur only after transport of reactants species to the electrode surface. At low overpotentials, the mass transport rates are fast compared to the electrochemical reaction kinetics i.e., electron transfer is the rate determining step. The extended Butler-Volmer takes into account both the kinetically controlled overpotential and the mass transfer controlled overpotential, which arise due to the changes in the concentration of the electroactive species in the electrode-electrolyte interface. (Bard and Faulkner, 2001). The activation and concentration polarisations combine in the case of the cathodic branch by substituting equation (2.76) into equation (2.43) which results in:

\[
 j = j_o (1 - \frac{j}{j_{\text{lim}}}) \times \exp \left[ \frac{-(1-a)F(E-E^{\text{rev}})}{RT} \right] 
\]

This can be rearranged to give the equation which describes the \( j-E \) relationship for the cathodic reaction controlled by charge transfer kinetics as well as the mass transport kinetics.

\[
 j = \frac{j_o \exp \left[ \frac{-(1-a)F(E-E^{\text{rev}})}{RT} \right]}{1 - \frac{j_o}{j_{\text{lim}}} \exp \left[ \frac{-(1-a)F(E-E^{\text{rev}})}{RT} \right]} 
\]

(2.78)
Figure 2-9: Regions of Cathodic Current density-Overpotential Relationship
In the kinetically controlled potential region, the activation overpotential dominates over concentration overpotential as \( j_{lim} > j_0 \exp \left[ -\frac{(1 - \alpha)F}{RT} (E - E^{rev}) \right] \) so the denominator of equation (2.78) goes to 1 and the equation simplifies to the Tafel equation. However, larger overpotentials result in an exponential increase in current density according to the Bulter-Volmer Equation, the reactant species being progressively depleted at the interface, resulting in a concentration gradient in the boundary layer (\( \delta \)). In this potential region, the rate the reaction is influenced by both charge transfer and mass transport and the reaction occurs under mixed control.

In the mass transport controlled region, further increase in the overpotential results in the surface concentration of the reactant species tending to zero, \( j_{lim} < j_0 \exp \left[ -\frac{(1 - \alpha)F}{RT} (E - E^{rev}) \right] \) the equation becomes \( j = j_{lim} \) and the reaction rate becomes independent of potential.

The influence of charge transfer and mass transport can also be seen by rearranging equation (2.78):

\[
E - E^{rev} = \eta = -\frac{RT}{(1 - \alpha)F} \ln \frac{j}{j_0} - \frac{RT}{(1 - \alpha)F} \ln \left( 1 - \frac{j}{j_{lim}} \right)
\]  
(2.79)

The total polarisation is a sum of the charge transfer polarisation (the first term) and the concentration polarisation (second term).

\[
\eta_T = \eta_{act} + \eta_{conc}
\]  
(2.80)

The whole Butler-Volmer equation, equation (2.43), can be extended to take all the regions in the polarization curve (Figure 2-9) into account.

\[
I_{net} = \frac{j_0 \exp \left[ \frac{\alpha F \eta_a}{RT} \right] - j_0 \exp \left[ -\frac{(1 - \alpha)F \eta_a}{RT} \right]}{1 + \left( \frac{j_0}{j_L} \right) \exp \left[ \frac{\alpha F \eta_a}{RT} \right] - j_0 \exp \left[ -\frac{(1 - \alpha)F \eta_a}{RT} \right]}
\]  
(2.81)
2.4. References


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3. Chapter 3

Literature Review

This chapter presents a general overview of the amine scrubbing process, including a discussion on the different types of amines currently used for the CO\(_2\) absorption process, their chemical properties and chemical reactions with CO\(_2\). This is followed by a discussion on the operation difficulties commonly encountered on amine plants, with a particular focus on corrosion. This chapter also gives an in-depth literature survey of the current views on the corrosion mechanisms in aqueous CO\(_2\) systems and a description of the various forms that such corrosion damage can take. The important parameters influencing or exacerbating the rate of CO\(_2\) corrosion in amine scrubbing systems will then be discussed. Next, a review on the occurrence and characteristics of corrosion product films formed on the steel surfaces in CO\(_2\)-H\(_2\)O environments, such as protective iron carbonate, will be presented. Finally, a review of the mechanisms of iron dissolution and hydrogen evolution on iron is presented, including data for exchange current densities and Tafel slopes at various pHs and temperatures.
3.1. The CO₂ Absorption Process

As discussed briefly in Chapter 1, existing coal-fired power plants provide about 30% of the total power generated and represent more than 25% of CO₂ emissions in the United Kingdom. In the United States, coal-fired power plants have a power capacity of more than 300,000 MW, providing about 50% of the total power generated nationally resulting in more than 30% of CO₂ emissions (Rochelle, 2009). A sensible strategy for mitigating anthropogenic climate change must address the issue of CO₂ emissions without shutting down these plants. At present, CO₂ capture by amine scrubbing is the only technology for post combustion capture that is available to tackle this issue and will be discussed in detail in the following section.

CO₂ removal by amine absorption is a robust, well understood and widely used technology. The first amine scrubbing process was invented and patented by (Bottoms, 1930). The absorption plant typically consists of an absorber and a stripper in which the absorbent is regenerated at a high temperature. The continuous amine scrubbing process is based on a temperature-dependent-reversible reaction between a weak base (amine) and a weak acid (CO₂) to form a soluble carbonate salt. In the absorber, which is operated at low temperatures, (ca. 40 °C), CO₂ reacts with the amine exothermically to form protonated amine (RNH₃⁺), hydrogen carbonate (HCO₃⁻), and carbamate (RNHCO₂⁻) (Isaacs et al., 1980). Impurities such as sulfur and nitrogen oxides are first removed from the flue gas, prior to its entering the absorber, to prevent their preferential reaction with the amines, which could reduce the capacity for CO₂ or irreversibly contaminate the solvent. Acid gases such as SO₂, SO₃ and NOₓ react with amines to form heat-stable salts, which would reduce the CO₂ absorption capacity of the solvent, so extremely low concentrations (less than 10 ppm in total) of these contaminant gases are required to prevent excessive loss of solvent (Department of Trade Industry, 2005). The flue gas enters a packed bed absorber from the bottom and is contacted counter-currently with the aqueous amine solution. The amine proceeds to selectively absorb the CO₂. When the amine solution has been loaded with CO₂, it is passed to a stripper and is regenerated with water vapour at
100°C to 120°C to reverse the chemical reaction and release CO₂. After regeneration, the CO₂-lean solvent is then recycled back to the absorber to absorb more CO₂. The pure CO₂ captured from the stripper is then compressed to 10 to 15 MPa for transportation and geological sequestration. The schematic (Figure 3-1) below shows a more detailed description of the absorption/desorption process.

![Figure 3-1: Amine CO₂ capture system flow diagram](image)

1. The flue gas from the power plant enters through the bottom of the absorption column and flows upward.

2. The absorber operates at a pressure of 0.1 MPa and a temperature range of 40-60°C. A mixture of water and amine-based solvent flows down the absorber and CO₂ reacts with the amine to form carbamate salt. The absorber is filled with packing to maximise the contact between both fluids and ensure adequate residence time for the reaction to occur.

3. CO₂-free gas leaves at the top of the absorber.

4. The ‘rich’ amine solvent, with a CO₂ loading ($\alpha$) of around 0.40 leaves through the bottom of the absorber and is preheated by a hot stream of ‘lean’ regenerated solvent (from the stripper / reboiler) in a heat exchanger.
5. The now heated ‘rich’ solvent is passed to the top of the stripping column. The stripper also operates at a pressure of 0.1 MPa but at a higher temperature range of 100-120°C. As the solvent flows down the column, CO\(_2\) is released gradually until it is further heated to saturation in the reboiler, which completes the CO\(_2\) removal process.

6. The hot ‘lean’ amine formed, \(\alpha \approx 0.15\), then flows back to the heat exchanger, in which it is cooled before being recycled into the absorption column.

7. The CO\(_2\) leaves through the top of the stripping column at about 80°C, saturated with water vapour. The mixture is then cooled and condensed before compressing the CO\(_2\) to prepare for transportation.

For over 30 years, amine scrubbing with aqueous monoethanolamine solutions has been used to capture CO\(_2\) from flue gas streams resulting from various processes ranging from fossil-fuelled boilers to petrochemical process heaters. The first large scale CO\(_2\) capture plant in the United States was the Searles Valley Minerals Plant, Trona, California which has been in continuous operation since 1978, capturing 400 ton day\(^{-1}\) of CO\(_2\) from flue gas resulting from a coal-fired boiler. Presently, there are hundreds of other plants employing this technology to remove CO\(_2\) from natural gas, hydrogen and other gases with low oxygen concentrations (Rochelle, 2009). There are over 20 pilot-scale coal-fired plants with power outputs of 6 to 40 MW using 20% -30% monoethanolamine to separate CO\(_2\) from flue gas with substantial oxygen content (Rochelle, 2009). In addition to MEA, other solvents such as aqueous ammonia and proprietary hindered amines such as KS-1, have also been used successfully to capture CO\(_2\) from dilute gas streams (Global CCS Institute, 2012). According to the (Global CCS Institute, 2012) there are several near-term solvent-based technologies involving either ammonia or proprietary amines which include Fluor’s Econamine FG PLUS, Mitsubishi Heavy Industries KS1 solvent, Cansolv Technologies, Aker Clean Carbon and Alstom’s Chilled Ammonia Process (ACAP).
The Fluor Econamine FG Plus\textsuperscript{SM} technology is a monethanolamine-based process but also employs proprietary inhibitors to control corrosion, oxidative degradation and thermal degradation (Fluor, 2016). The addition of inhibitors permits higher concentrations of MEA to be used (30-35 wt\% versus 18-20 wt\% used previously) which, in combination with process optimisation such as heat integration, absorber intercooling and split flow configuration, is said to increase the CO\textsubscript{2} absorption rate and reduce the steam consumption of Fluor Econamine FG Plus\textsuperscript{SM} by over 30\% in comparison to ‘generic’ MEA technology. Thus, Econamine FG Plus\textsuperscript{SM} is frequently used as a representative technology for economic evaluation of post-combustion CCS technologies.

Another near-term technology for coal-fired power plants is the Mitsubishi Heavy Industries (MHI) KS-COR process that uses KS-1, a proprietary sterically-hindered solvent (Mitchell, 2008). KS-1, developed by MHI and Kansai Electric Power Company, is claimed to be advantageous in comparison to conventional MEA for a number of reasons, including higher CO\textsubscript{2} loading, lower circulation rate (60\% of MEA), lower stripping energy requirements (68\% of MEA) and lower solvent loss and degradation (10\% of MEA). However, the unit cost of KS-1 is higher than that of MEA by a factor of 5. The KS-1 solvent also requires significantly lower levels of SO\textsubscript{x} and NO\textsubscript{x} (typically 1 ppm), so has higher pre-treatment and upstream polishing requirements.

The Alstom’s Chilled Ammonia Process (ACAP) is a more recent technology based on exploiting the changes in chemical equilibrium of ammonia, ammonium carbonate and ammonium hydrogen carbonate with changes in temperature (Alstom, 2016). Being a low-cost solvent and resistant to degradation, ammonia allows for stripping at higher temperatures and exposure to NO\textsubscript{x} and SO\textsubscript{x}. The AEP’s Mountaineer presently employs this technology and is able to achieve CO\textsubscript{2} capture with 80-90\% efficiency and at 99.9+ \% purity (AEP, 2016). However, the ACAP process typically requires a significantly larger absorber, due to the relatively low absorption rate and CO\textsubscript{2} loading capacity. Another issue commonly encountered
with the use of ammonia for CO$_2$ capture is ammonia slip, which results from the high volatility of ammonia leading to large amounts of ammonia evaporating and leaving the absorber with the flue gases.

The Powerspan ECO$_2$TM process was reformulated to use a proprietary solvent, which incorporates a mixture of amines (Powerspan Clean Technology, 2016). With this solvent, Powerspan announced in May 2010 that the technology was ready for scale up with a cost of less than $40 per ton of CO$_2$ captured and compressed (Powerspan Clean Technology, 2016).

Cansolv, owned by Shell Global Solutions International B.V, developed aqueous diamine solvents for the selective removal of CO$_2$, SO$_x$, and NO$_x$ and mercury. With this technology, 90% CO$_2$ capture rates have been achieved and it has since been chosen for the retrofit of a 150 MWe unit at SaskPower’s Boundary Dam.

In addition to the technologies mentioned above, Just Catch Technology was developed by Aker Clean Carbon and had undergone several refinements throughout the slipstream testing phase in a flue gas plant at Scottish Power’s Longannet station. In 2009, Scottish Power announced that Just Catch could achieve a one-third reduction in energy requirements in comparison to reference plants by using of low-energy solvents. Alstom and Dow Chemical Company are also collaborating on the development of DOW UCARSOL™ FGC 3000, a proprietary Dow amine solvent for removal of CO$_2$ from flue gas streams from a coal-fired boiler at a DOW chemical plant in South Charleston, West Virginia. The Dow amine is also claimed to have a higher CO$_2$ capture efficiency, higher tolerance to oxygen and other trace contaminants and to be less susceptible to degradation. Doosan Babcock Energy and HTC Purenergy are working jointly on the commercialization of a mixed amine solvent process that was originally developed and field tested at the University of Regina, Saskatchewan (Global CCS Institute, 2012). HTC also claims a reduced regeneration energy of less than 1.0 ton steam per ton CO$_2$ which is about 30% less than conventional 30 wt% MEA.
Apart from amine technologies, Siemens Energy and TNO are also working on developing an amine acid salt based technology (Alston, 2016). Amino acid salts are considered to offer several advantages over amine solvents, such as rapid CO₂ absorption kinetics, higher CO₂ loading capacity, lower solvent flow rate, lower regeneration requirements, degradation resistance, lower volatility and less environmental impact (Brouwer, 2005). The different types of amines and their respective properties are discussed below.

3.2. Solvents for CO₂ Absorption

The most extensively used group of amine solvents for CO₂ capture are alkanolamines, which are compounds that contain both hydroxyl (-OH) and amino functional (-NH₂, -NHR and -NR₂) groups on an alkane backbone. The attractive advantage of alkanolamines is that, while the amino group provides the alkalinity to absorb CO₂, the hydroxyl group reduces their vapour pressure and increases their solubility in aqueous solutions (Strazisar et al., 2002). Alkanolamines can be classified structurally as primary, secondary or tertiary, based on the number of carbon-containing groups attached to the nitrogen atom or the number of hydrogen atoms that have been replaced by the organic functional groups. Amines such as monoethanolamine (MEA) and diglycolamine (DGA) with only one carbon containing group, are classified as primary amines, while secondary amines such diethanol amine (DEA) and diisopropyl amine (DIPA) have two carbon containing groups and methyldiethanol amine (MDEA) with three carbon containing groups falls into the tertiary amine category. Some of the most commonly used amines in CO₂ capture and the relevant chemical structures are listed in Table 3-1.

3.2.1. CO₂ Absorption Reactions

Alkanolamines have been found to exhibit varying reaction rates, equilibrium absorption characteristics as well as different degradation and corrosion rates (Global Climate & Energy Project, 2005). The reactivity of amines to CO₂ has been found to have a strong dependence on
the structure, with primary amines displaying the fastest reaction kinetics, followed by secondary, then tertiary amines. For example, the reaction constants for MEA, DEA and MDEA with CO$_2$ are 7000, 1200 and 3.5 mol m$^{-3}$ s$^{-1}$ kmol$^{-1}$ respectively at 25°C (Sada et al., 1976; Hikita et al., 1979; Bishnoi and Rochelle, 2000). MEA, developed over 70 years ago, is at present the most extensively used amine and acts as the benchmark for the CO$_2$ absorption process (Isaacs, 1980). It has several notable advantages such as fast reaction kinetics, achieved due to low steric hindrances around the nitrogen atom. MEA is also readily available at a relatively low cost, has a high solubility in water and a low absorption of hydrocarbons when used for natural gas cleaning processes (Isaacs, 1980; Lepaumier et al., 2009). However, it also suffers from the severe drawback of a high enthalpy of solution leading to high energy requirements in the stripper, and a susceptibility to degradation, as well as being corrosive in nature. The secondary amine DEA has greater steric hindrance, which ultimately slow down the reaction kinetics. This in turn implies that the energy requirements for the release of CO$_2$ in the stripper are much less than that required with the use of MEA, so is less parasitic.

![Reaction Scheme of Alkanolamines with CO$_2$](image)

Figure 3-2: Reaction Scheme of Alkanolamines with CO$_2$
While the chemistry of the reactions of amines with CO\textsubscript{2} is not fully understood, a series of reactions were identified by (Danckwerts and McNeil, 1967) and have been generally accepted. Alkanolamine-CO\textsubscript{2}-H\textsubscript{2}O solutions at equilibrium undergo a series of reactions to form the carbamate anion (RNHCO\textsubscript{2}O\textsuperscript{-}), protonated cation (RNH\textsubscript{3}\textsuperscript{+}), hydrogen carbonate ion (HCO\textsubscript{3}\textsuperscript{-}) and carbonate ion (CO\textsubscript{3}\textsuperscript{2-}) (where R stands for hydrogen or an organic group such as CH\textsubscript{3} or CH\textsubscript{2}CH\textsubscript{2}OH).

(Isaacs et al., 1980) found that the most commonly used primary and secondary amines MEA, DEA, DIPA and DGA exhibit limited thermodynamic capacities to absorb CO\textsubscript{2}. The inability of these common alkanolamines to absorb CO\textsubscript{2} much beyond 0.5 mol CO\textsubscript{2} (mol amine\textsuperscript{-1}) is due to the stability of the carbamates formed with amines in which the amino nitrogen is attached to a primary alkyl group (Park et al., 2003). In the case that formation of carbamate is the only reaction (reaction path 1), the reaction stoichiometry indicates that 2 moles of amine are required for each mol of CO\textsubscript{2}. However, the formation of hydrogen carbonates by hydrolysis (reaction path 3) creates free amines, which can then further react with the CO\textsubscript{2} molecules and enhance the loading capacity. The reaction stoichiometry for the reaction involving hydrogen carbonate ions shows a one to one ratio.
Table 3-1: Chemical Structures of the amines commonly used in CO₂ capture

<table>
<thead>
<tr>
<th>Class of Amine</th>
<th>Alkanolamine</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Amines</td>
<td>Monoethanolamine (MEA)</td>
<td>HO-CH₂-CH₂-NH₂</td>
</tr>
<tr>
<td></td>
<td>Diglycolamine (DGA)</td>
<td>HO-CH₂-CH₂-O-CH₂-CH₂-NH₂</td>
</tr>
<tr>
<td>Secondary Amines</td>
<td>Diethanolamine (DEA)</td>
<td>HO-CH₂-CH₂-NH</td>
</tr>
<tr>
<td></td>
<td>Diisopropanolamine (DIPA)</td>
<td>OH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃-CH-CH₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃-CH-CH₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OH</td>
</tr>
<tr>
<td>Tertiary Amines</td>
<td>Methyldiethanolamine (MDEA)</td>
<td>HO-CH₂-CH₂-NH</td>
</tr>
<tr>
<td>Sterically Hindered Amines</td>
<td>2-amino-2-methyl-1-propanol (AMP)</td>
<td>CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HO-CH₂-C-NH₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃</td>
</tr>
<tr>
<td></td>
<td>Piperazine (PZ)</td>
<td>NH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-OH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH</td>
</tr>
</tbody>
</table>
While the reaction of primary and secondary amines with CO$_2$ leads to the formation of carbamates, tertiary amines such as MDEA exhibit a different limiting behaviour as they are able to form hydrogen carbonate ions, but unable to form carbamates due to the absence of available hydrogen atoms. (Jou et al., 1995) found that the absorption of CO$_2$ in MDEA can reach 1.0 mol of CO$_2$ (mol of amine)$^{-1}$. Although this quality of high CO$_2$ loading capacity is highly desired, the low absorption rate due to steric hindrance limits the attractiveness of MDEA. On a positive note, they require much less heat in the reverse reaction, due to their inclination to release the absorbed CO$_2$.

In more recent years, sterically hindered amines such as AMP (2-amino-2-methyl-1-propanol) and piperazine (a cyclic diamine with the molecular formula C$_4$H$_{10}$N$_2$) have been developed due to their high CO$_2$ loading capacity and ease of regeneration. The stability of the carbamate formed from AMP is decreased, due to steric hindrance of the bulky substituent group adjacent to the amino nitrogen (Park et al., 2003). The unstable carbamate can undergo hydrolysis to form hydrogen carbonate ions via reaction scheme 3 while still maintaining a relatively high absorption rate for CO$_2$. Despite advantages such as AMP having an 80% higher CO$_2$ release rate than MEA (Yeh and Pennline, 2001), it has been found that sterically hindered amines do not always have a higher CO$_2$ loading capacity than the more commonly used amines such as MEA. The energy savings that are achievable from using sterically hindered amines are balanced out by the higher capital costs associated with the larger scrubbing equipment required, due to slower absorption rates. Experimental results show that under certain conditions such as low CO$_2$ partial pressures, the solubility of CO$_2$ is lower in hindered amines than in the MEA solutions (Park et al., 2003). The absorption of CO$_2$ usually takes place at atmospheric pressure or at low CO$_2$ partial pressures, so it is particularly important to select an absorbent with a high solubility of CO$_2$ even at low pressures.
It has proven to be extremely difficult to identify any single amine that has all the desirable properties, such as rapid absorption kinetics, low energy requirements for desorption, high chemical stability, low vapour pressure, resistance to degradation and low corrosion rates etc. This issue has led newer technology to involve the use of a mixture of a number of amines. It has been suggested that the combination of primary or secondary amines with tertiary amines might actually synergise their individual advantages (Park et al., 2003). The aim is to have a mixture of amines retaining the reactivity of the primary or secondary amines at comparable or lower circulation rates, but reducing regeneration costs in a similar manner to tertiary amines.

Several blends have been studied experimentally such as MEA/MDEA, DEA/MDEA, MEA/AMP, DEA/AMP, MDEA/AMP, MDEA/DEA/AMP, PZ/MDEA, DIPA/MDEA, and DIPA/PZ (Park et al., 2003). There have been significant reductions in energy requirements, as well as circulation rates that have been reported for amine blends in comparison to a single amine system (Strazisar et al., 2003).

In addition, traditionally used amines have been blended with amines that are less corrosive and require less steam to regenerate or involve the use of the additive piperazine (PZ) (Global Climate & Energy Project, 2005). Examples of such include MEA-PZ blends, MDEA-PZ blends, blends of Nmethyldiethanolamine and triethylene tetramine (Shao and Stangeland, 2009). While PZ is less soluble in water and more volatile than MEA, its presence increases CO₂ absorption and allows the use of smaller concentrations of MEA (Dang and Rochelle, 2003). Research has also shown that solvents based on PZ-promoted K₂CO₃ can have reaction rates similar to that of MEA, but their capacity has been found to be significantly lower (Cullinane and Rochelle, 2003).

Degradation of alkanolamine-based solvents on contact with oxygen is a great disadvantage. Typical flue gas streams contain oxygen in the order of 3-12% which can bring about the oxidative degradation of the amines (Goff and Rochelle, 2004). This will cause a reduction in
their CO₂ absorption capacity and lead to the production of unwanted degradation products, leading eventually to the amine solution having to be discarded. These degradation products often lead to severe corrosion (Goff and Rochelle, 2004). The operational cost savings that have been reported with blended amines would only be possible if the loss of amine due to degradation and the corrosion of the equipment is less than or comparable with losses from single amine systems. Presently, there is very little information on the degradation of mixed amines and steel corrosion behaviour. (Dawodu and Meisen, 1996) studied the absorption of CO₂ with MEA/ MDEA and DEA/MDEA mixtures and found that higher circulation rates were required for DEA in the MDEA/DEA blend than the MEA in the MDEA/MEA blends. They also reported that the blends affected the rate of degradation, but were unable to establish a firm relationship between the blends and the degradation rates (Strazisar et al., 2003).

3.3. CO₂ Induced Corrosion in Amine Plants

Amine absorption-desorption is the process of choice for CO₂ capture, because coal power plants can be retrofitted easily and have been reported to be comparatively free from operational difficulties. However, there are several issues apart from solvent degradation that can lead to additional costs and result in a significant decrease in capacity for CO₂ capture. From an economic perspective, the major sources of such operational difficulties are corrosion, amine loss, foaming and plugging of equipment.

Corrosion can be defined as an irreversible reaction of a material with the environment, which usually results in the degradation of the material or its properties and is thought to be the most severe of the operational difficulties facing the equipment used in alkanolamine treating plants (Kohl and Nielsen, 1997; Veawab and Aroonwilas, 2002). It is a natural potential hazard associated with amine scrubbing plants, due to CO₂ being dissolved in the aqueous solution phase, the inherent corrosivity of which, is dependent on the concentration of CO₂ and the water
chemistry. CO₂ corrosion or ‘sweet corrosion’ is also the predominant form of attack and is a serious cause of concern in many other applications using carbon and low alloy steels, such as oil and gas production and transportation facilities. The occurrence of such corrosion can lead to unscheduled downtime, loss of products, reduced equipment life and in extreme cases injury or death.

Despite extensive previous experimental research and the development of predictive models, the corrosion process is still not fully understood and there are still ambiguities with respect to the parameters that affect it. Whilst it would be impractical to eliminate corrosion completely, it is possible to minimise or mitigate its occurrence; to achieve this, a good understanding of the corrosion chemistry is required, involving the kinetics, product identification, stoichiometry, and mechanisms.

3.3.1. Plant Experience

Being the most serious operational setback presently faced on alkanolamine gas purification plants, corrosion has been given the most consideration and research. There has been a considerable amount of information and reports in the open literature about amine scrubbing plants and the experiences with corrosion issues under a wide range of conditions. Table 3-2 lists a summary of the plants, amine type, details about the type of corrosion and the ensuing issues. Corrosion occurs in various units within the plant, such as the bottom of the absorber, the heat exchanger, the stripper, the overhead condenser, pumps and valves where the acid gas loading and temperatures are high (Soosaiprakasam and Veawab, 2008).

Several factors have been attributed to aggravating corrosion issues, such as poor plant design and operation, i.e. high amine solution velocity in pipelines, high operating temperatures in the stripper and reboiler, as well as the presence of contaminants and degradation products. The construction material is also an important factor in determining the susceptibility to corrosion.
Whilst it is less costly in terms of the initial up-front capital investment to construct the plant entirely from carbon steel, it is common practice to use stainless steel or other corrosion-resistant alloys in certain sections, which allows for plant operation under more ‘aggressive’ operating conditions, such as high amine concentrations and CO₂ loadings.

Corrosion in amine scrubbing plants has been reported as uniform thinning or as a localised attack, such as pitting, erosion, intergranular and stress corrosion cracking. As listed in Table 3-2, general or uniform corrosion has been observed to occur at various parts of the plant such as the bottom of the absorber or in the regenerator trays, but the occurrence has been noted with other localised attacks such as pitting and galvanic corrosion (Heisler and Weiss 1975; DuPart et al., 1993). Although uniform corrosion of metals in aqueous CO₂ environments has received more attention by researchers, localised attacks are actually of greater concern as they are more likely to result in unexpected failures. Localised forms of corrosion are characterised by loss of metal at distinct areas of the metal surface, while other surrounding areas are seemingly unaffected or undergo general corrosion. These forms of localised corrosion may appear on the metal surface in various geometrical shapes. Pitting corrosion presents itself as circular depressions, usually with tapered or smooth sides. Messa type corrosion attack is characterized by a deep and sometimes flat-bottomed local attack which covers a large surface area with very sharp edges. Localised corrosion can also take other geometrical shapes such as slits, also known as knifeline attack. Flow induced localised corrosion can be identified by localised attacks in the form of parallel or shallow grooves related to the direction of flow.

Localised forms of corrosion are connected strongly to the formation of passive layers on the metal surface. The presence of the passive layer acts to protect the metal surface against degradation and dissolution; however, the presence of aggressive anions can lead to local breakdown in the passive layer and the formation of corrosion pits. Pitting formation has long been recognized in CO₂ systems from field observations (American Petroleum Institute, 1958;
Habler and Schonewolf, 1974; Hackerman and Schmidt, 1949) with a relatively small number of experimental investigations on pitting phenomena and localized attack (Schmitt and Rothman, 1978; DeBerry et al., 1980). This may be due to the long induction period, sometimes on the order of several months, required for pit initiation. For pitting corrosion to occur, the passive layers formed on the surface of the metal must have local defects. These imperfections may be as a result of a non-uniform growth of passive layers and/or the mechanical disruption by hydromechanic attack (high fluid shear stress, erosion, cavitation) or by scratches on the coating, uneven surface coverage of the corrosion inhibitor, scale formation, dust and other impurities. The non-uniform growth of the passive layers is influenced by alloy effects, metallurgical factors, the presence of certain chemicals, CO₂ partial pressure, pH and temperature. The pit then grows due to differences in the chemical compositions of the aqueous solution below the pit and the directly surrounding steel surface. The bottom of the pit acts as the anode and the nearby steel acts as the cathode. It is also known that all steels may undergo pitting corrosion in CO₂ environments under the enabling conditions (American Petroleum Institute, 1958; Schmitt and Rothman, 1978; DeBerry et al., 1980; Hackerman and Schmidt, 1949). Whilst stainless steels become susceptible to pitting corrosion only in the presence of aggressive anions like chlorides and small quantities of oxygen, medium and especially low alloy carbon steels need only the CO₂ aqueous system. Generally aggressive operating conditions, such as high temperature have been found to exacerbate the formation of pitting corrosion and to decrease the time it takes to occur (Hausler and Goddard, 1984). Pit formation was observed frequently in the dead zones and hot regions, such as the bottom of the absorber, the regenerator valve trays and the tube bundles of the reboiler (DuPart et al., 1993; Litschewski, 1996). So far, the existence of a critical CO₂ partial pressure below which pitting formation does not occur, has not yet been identified. However, in practice, it is the rule of
thumb that corrosion damage from pitting is unlikely below 50 kPa CO₂ (American Petroleum Institute, 1958).

Mesa type corrosion occurs mainly when protective passive layers such as iron carbonate form, but are not very stable and do not offer complete protection. As film formation generally occurs at elevated temperatures, typically above 60°C, mesa type corrosion is less likely to occur at temperatures below this. According to (Nyborg, 1998), the attack starts as several small pits beneath a porous passive film, which continue to grow beneath the film until the top of the passive film is torn away by mechanical forces such as turbulent flow. As the attack progresses, the pit continues to grow both laterally and in depth and the original passive film is removed stepwise by flow and with dissolution of the underlying metal. As several pits are initiated, they start to grow together into a wider mesa attack of nearly uniform depth. As long as the protective films are not reformed, the mesa attack continues to grow with a high corrosion rate both laterally and in depth. However, on reaching a certain scale, initiation of new pits ceases, due to galvanic effect between the underlying corroding metal at the bottom of the mesa attack and the film-covered metal surrounding the mesa attack. Whilst the initiation of pits is independent of the flow, the growth from small pits into a larger mesa attack is dependent on the flow conditions.

Galvanic corrosion or dissimilar metal corrosion occurs when two dissimilar metals are in electrical and ionic contact. This type of corrosion typically occurs in the junction between two metals; the metal with the lower electrode potential acts as the anode and corrodes preferentially, while the metal with the higher electrode potential acts as the cathode and is protected from corrosion. The degree of corrosion is most intense at the contacting point and decreases further away from the point of contact. Galvanic corrosion in amine treating plants has been observed in parts where both stainless steel and carbon steel were utilised. Examples of locations in which galvanic corrosion occurred are in the stainless steel valve coupled with
a carbon steel disk (DuPart et al., 1993) and in the stainless steel regenerator trays in contact with a carbon steel regenerator wall. The carbon steel (anode) preferentially corrodes while the stainless steel (cathode) remains protected.

As the metal owes its corrosion resistance to the formation and resistance of protective scales, the removal of such scales in localised areas can lead to accelerated attack. Erosion corrosion is the deterioration of the metal caused by high amine solution velocities, solution turbulence and impingement of gas and amine on metal surfaces. Rapid motion of the solution and any abrupt changes in the direction of flow could either erode the surface of the metal directly or remove any protective film protecting the piping and equipment from corrosion and finally corrode the underlying metal. Similarly to the case of pitting corrosion, solid impurities such as scale, dust and amine degradation products aggravate erosion. In parts of the plant in which there is a considerable loss of pressure, ‘cavitation’ erosion can occur. Low pressure (below the saturation vapour pressure of the flowing amines) causes vapour or gas bubbles to be nucleated from the flowing solution which then bombard the metal surface. Areas that are at risk of erosion-corrosion are piping with bend fittings, and amine pumps, while the areas damaged by the cavitation are the absorber bottom, the flash drum, the rich amine pump, the heat exchanger tubes, the regenerator and the reboiler (Dingman et al., 1966, Smith and Younger, 1972; Heisler and Weiss, 1975; Gerus 1981; Dupart et al., 1993)

Four types of carbon steel cracking mechanisms have been identified in amine scrubbing plants. The first three cracking mechanisms are associated with the entry of hydrogen atoms into the carbon steel lattice. These mechanisms are known as the sulfide stress cracking (SSC), hydrogen induced cracking (HIC) and the stress-orientated hydrogen induced cracking (SOHIC) and they all are associated with the production of hydrogen from aqueous–H$_2$S solutions. However, in such environments, CO$_2$ is considered to be a contributing factor rather than a principal factor and as the removal of H$_2$S is not of particular concern in this work, it
will not be discussed further. The fourth mode of cracking, stress corrosion cracking (SCC), occurs as a result of a combined influence of tensile stress and a corrosive environment. Examples of such tensile stress include residual stress from welding and fabrication or externally applied stress. The most common type of stress-corrosion cracking thought to occur on an amine plant is the Alkaline Stress-Corrosion Cracking (ASCC) (Kohl & Nielsen, 1997). ASCC occurs due to a film rupture mechanism, and areas that are prone to high residual stress slip, causing the protective passive film to break, exposing bare underlying metal, which then undergoes corrosion and forms cracks. The passive film may re-form, but the residual stress causes the film to rupture repeatedly leading to cracking. An explosion and a fire caused by the rupture of an amine LPG treater in 1984, resulted in the death of 17 people (McHenry et al., 1986) and was found to have been most likely caused by stress corrosion cracking. This unfortunate disaster and reports of cracking within other amine systems, led to a detailed investigation of carbon steel cracking within amine units. A survey of 294 units conducted by the National Association of Corrosion Engineers (NACE) in 1992 showed that 70% of the SCC cases were found in MEA plants, 24 % due to the use of DEA, while the residual 6 % were from plants utilising the other amine solvents (Dupart et al., 1993). Cracks were found to occur in every type of equipment, even at low temperatures, but no correlations were established between cracking and operating conditions, such as amine concentration, CO₂ loading, use of corrosion inhibitors or types of carbon steel etc.
Table 3-2: Summary of Amine Scrubbing Plant Experience on Corrosion

<table>
<thead>
<tr>
<th>Plant</th>
<th>Solvent</th>
<th>Corrosion Type</th>
<th>Susceptible area</th>
<th>Reported cause</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sour gas treating plant in Texas</td>
<td>MEA</td>
<td>Erosion</td>
<td>• Rich lean heat exchanger</td>
<td>• High solution velocity</td>
<td>(Dingman, 1966)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Letdown valve</td>
<td>• Changes in direction of fluid flow</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Piping downstream of letdown valve</td>
<td>• Contamination with solids such as iron oxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 sour gas treating plants in Western Canada</td>
<td>DEA</td>
<td>Erosion, SCC</td>
<td>• Rich lean heat exchanger</td>
<td>• Contaminants in the amine solution</td>
<td>(Smith, 1972)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Stripper</td>
<td>• High velocity flowrates</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Reboiler</td>
<td>• Chloride ions evolved gasket fabrication material between heat exchanger plates</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Rich solution piping</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Stainless steel heat exchanger plate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural gas treating plants at Aderlas, Austria</td>
<td>MEA</td>
<td>Uniform, Pitting, Erosion</td>
<td>• Stripper, weld seam, joints and tray</td>
<td>• Cavitation due to vapour flash</td>
<td>(Heisler and Weiss 1975)</td>
</tr>
<tr>
<td>Sour gas treating plants</td>
<td>DIPA</td>
<td>Pitting</td>
<td>• Absorber bottom</td>
<td>• Acid gas flashing</td>
<td>(Schmeal et al., 1978)</td>
</tr>
<tr>
<td>Ram river gas plant located at Fronthills</td>
<td>DEA</td>
<td>N/A</td>
<td>• Stripper</td>
<td>• N/A</td>
<td>(Hall and Barron 1981)</td>
</tr>
</tbody>
</table>
Table 3-3: Summary of Amine Scrubbing Plant Experience on Corrosion (Continued)

<table>
<thead>
<tr>
<th>Plant</th>
<th>Solvent</th>
<th>Corrosion Type</th>
<th>Susceptible area</th>
<th>Reported cause</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas treating plants</td>
<td>N/A</td>
<td>• Pitting</td>
<td>N/A</td>
<td>• N/A</td>
<td>(Gerus 1981)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Erosion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MDEA</td>
<td></td>
<td>• Absorber bottom</td>
<td></td>
<td>• Aqueous CO$_2$ flashing • Cavitation • High velocity impingement</td>
<td>(Dupert et al., 1993)</td>
</tr>
<tr>
<td>MDEA</td>
<td></td>
<td>• Erosion</td>
<td>• Wall of absorber bottom</td>
<td>Turbulent flow</td>
<td>(Dupert et al., 1993)</td>
</tr>
<tr>
<td>MEA</td>
<td></td>
<td>• Uniform</td>
<td>• Absorber bottom</td>
<td>Oxygen contaminants</td>
<td>(Dupert et al., 1993)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Galvanic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MDEA</td>
<td></td>
<td>• Pitting</td>
<td>• Stripper at carbon steel; tray and 304 stainless steel valve opening • Shell side of the heat exchanger • 304 stainless steel valve connected to carbon steel disk</td>
<td>• Aqueous CO$_2$ flashing • High CO$_2$ loading • Insufficient stripping steam</td>
<td>(Dupert et al., 1993)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Erosion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Galvanic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4. Corrosion Mechanisms in Amine Plants

As depicted in Table 3-2, most of the equipment and piping in alkanolamine treating plants is typically constructed of carbon steel. (Kohl & Nielsen, 1997) suggested that it might be possible to build the entire alkanolamine plant completely from carbon steel by maintaining a low amine stripper temperature, minimizing amine solution concentration and CO₂ loading. However, it is common practice to construct the parts of the plant that are more susceptible to corrosion with stainless steel or more corrosion–resistant alloys, to allow for operation under more aggressive conditions. The parts of the plant schematically shown in Figure 3-3 marked in the bold line show the parts that are typically constructed from stainless steel as opposed to carbon steel. The red and blue dotted lines represent the units susceptible to wet acid gas corrosion and amine solution corrosion respectively.

Figure 3-3: Flow diagram of a typical amine plant showing principal areas of corrosion and suggested materials of construction (Kohl & Nielsen, 1997).
(Kohl & Nielsen, 1997) suggested that corrosion within amine scrubbing plants can be classified into two broad categories:

- **Wet acid gas corrosion** of the carbon steel is the reaction of CO$_2$ with iron in an aqueous environment, in which little or no amine is present.
- **Amine solution corrosion** is the corrosion of carbon steel in the presence of aqueous amine.

These two mechanisms will be discussed in detail below.

### 3.4.1. Wet Acid Gas Corrosion

Wet acid gas corrosion is most likely to occur in the parts of the plant in contact with aqueous phases with a high concentration of acid gases such CO$_2$, e.g., at the top of the regenerator and at the bottom of the absorber (Veawab and Aroonwilas, 2002). Due to the severe corrosion issues associated with oil and gas production and transportation facilities, the corrosion mechanisms of carbon steel in CO$_2$–H$_2$O systems under varying conditions, such as pressure, temperature and pH, has been reported extensively in recent literature. Some of the most important findings feature the works of (Bockris et al., 1961, de Waard & Milliam, 1975; de Waard et al, 1991; Dugstad et al, 1991; Drazic et al and Nesic et al, 1996). Thus, most of the publications on corrosion within the context of amine scrubbing technology have drawn conclusions from the vast research conducted on carbon steel corrosion in other CO$_2$-H$_2$O systems, rather than strictly in CO$_2$ loaded amine systems.

In spite of the immense amount of research on CO$_2$ corrosion phenomena, including experimental research and the development of predictive models, the corrosion process is yet to be fully understood and there are still some ambiguities about the corrosion mechanisms and the effect of operating parameters. The mechanisms that have been proposed for wet acid
gas corrosion in amine systems differ depending on the operating conditions such as type of amine being used and absence or presence of oxygen.

The corrosion of carbon steel in CO\textsubscript{2} - H\textsubscript{2}O environments is considered to be a heterogeneous process with a number of chemical, electrochemical and transport processes occurring simultaneously and the overall corrosion rate is controlled by the slowest of these steps. When the transport processes occur at a faster rate than the interfacial electrochemical reactions, the corrosion rate is governed by the electrode kinetics and is said to be under ‘activation’ or ‘charge transfer’ control. On the other hand, when the electrochemical reactions proceed at a higher rate, the corrosion rate is controlled by mass transport processes and the overall process is under transport control.

3.4.1.1. Chemical reactions

Whilst dry carbon dioxide gas itself is not corrosive, on dissolving in water it forms a weak carbonic acid. This aqueous phase in contact with the carbon steel equipment enables electrochemical reactions to occur, resulting in corrosion of the steel. Different mechanisms have been proposed for the CO\textsubscript{2} induced corrosion process, but they all involve either carbonic acid (H\textsubscript{2}CO\textsubscript{3}) or hydrogen carbonate ions (HCO\textsubscript{3}\textsuperscript{-}).

The concentration of the aqueous CO\textsubscript{2} at a given CO\textsubscript{2} partial pressure and temperature can be calculated from Henry’s law:

\[ CO_{2(g)} \leftrightarrow CO_{2(aq)} \]  \hspace{1cm} \text{(3.1)}

\[ [CO_2] = H \cdot P_{CO_2} \]  \hspace{1cm} \text{(3.2)}

here, \([CO_2]\) is the concentration of CO\textsubscript{2} in the aqueous phase, \(H\) is the Henry’s constant and \(P_{CO_2}\) is the partial pressure of CO\textsubscript{2} in the gas phase.
When CO$_2$ is the only acid gas present, it is hydrated in water to form carbonic acid according to the following reaction:

$$ CO_{2(g)} + H_2O_{(aq)} \leftrightarrow H_2CO_3_{(aq)} \quad (3.3) $$

The carbonic acid then partially dissociates to form hydrogen carbonate ion (HCO$_3^-$) which then dissociates to carbonate ion via the following two steps:

$$ H_2CO_3_{(aq)} \leftrightarrow HCO_3^-_{(aq)} + H^+_{(aq)} \quad (3.4) $$

$$ HCO_3^-_{(aq)} \leftrightarrow CO_3^{2-}_{(aq)} + H^+_{(aq)} \quad (3.5) $$

### 3.4.1.2. Electrochemical Reactions at the Carbon Steel Surface

The corrosion of carbon steel occurs by the oxidation of iron via reaction (3.6):

$$ Fe \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad (3.6) $$

The electrons released by the anodic reaction must then be consumed by a cathodic reaction of equal rate. Earlier studies conducted by researchers in the field have shown that the corrosion rate of carbon steel in aqueous CO$_2$ environments, in the absence of oxygen and at ambient temperature, is controlled primarily by the kinetics of one or several reactions resulting in the evolution of hydrogen. (Schwenk, 1974) concluded that H$^+$ ions are reduced via reaction (3.7).

$$ 2H^+ + 2e^- \leftrightarrow H_2 \quad (3.7) $$

The hydrogen evolution reaction is considered to be the dominant reduction reaction, the rate of which is limited by the mass transfer of H$^+$ ions to the iron surface from the bulk solution. However, it has been established that the mechanism in which H$^+$ ions are supplied to the electrode surface in CO$_2$-containing solutions differs from that occurring in strong acid
solutions, in which diffusion of H\(^+\) ions from the bulk solution is the principal rate controlling reaction. There have been several additional electrochemical reactions proposed and several inconsistencies in the open literature about the species reacting at the electrode to form hydrogen. While there are still several different mechanistic interpretations of CO\(_2\) corrosion, there appears to be a general agreement on the corrosion rates observed under similar conditions (Eriksrud and Sontvedt, 1983; Ikeda et al., 1984; Schmitt, 1983; Dunlop et al., 1984; Murata et al., 1985). The corrosion of steel was found to obey the relationship developed by (de Waard and Milliams, 1975).

\[
\log v = 0.67 \left( \log P_{\text{CO}_2} \right) + C
\]  

(3.8)

For this relationship, different validity limits were established by each researcher: (Schmitt, 1983) \( P_{\text{CO}_2} < 0.2 \text{ MPa} \); (Eriksrud and Sontvedt, 1983) \( P_{\text{CO}_2} < 0.1 \text{ MPa}, 20^\circ \text{C} \); (Dunlop et al., 1984) \( 82^\circ \text{C}, \text{ velocity below critical} \ (V_C = 7.6/\sqrt{p}) \); (Ikeda et al., 1984) \( P_{\text{CO}_2} = 0.2 \text{ MPa}, 60^\circ \text{C} \); (Murata et al., 1985) \( P_{\text{CO}_2} = 0.7 \text{ MPa}, 60^\circ \text{C} \).

(Schwenk, 1974; Schmitt and Rothman, 1977; Fisher and Siedlarek, 1978) each observed a limiting cathodic current density, in solutions fully saturated with CO\(_2\), at pH 4, that was several orders of magnitude higher than could be expected in solutions of equal pH in the absence of CO\(_2\). At the low temperature conditions under which the measurements were conducted (\( \leq 20^\circ \text{C} \)), varying the solution flow rate was found to have little to no effect on the corrosion rate, so excluding the diffusion of H\(^+\) ions as the rate controlling step. As a result, it was concluded that it was not strictly the hydrogen evolution reaction in the sense of a Volmer or Bockris mechanism (Section 3.11) which acts as the rate controlling reaction, instead it was a reaction which precedes the charge transfer reaction. It is possible that the presence of carbonic acid and hydrogen carbonate ions formed from the hydration of CO\(_2\) provides a reservoir of H\(^+\) at a particular pH, thereby increasing the corrosion rate by serving as a source
of $H^+$ via reactions (3.4) and (3.5), which are subsequently reduced according to the hydrogen evolution reaction equation (3.7) (Schwenk, 1974). Thus for a solution of $pH > 4$, $CO_2$ being present would also lead to a much higher corrosion rate than would be found in a strong acid of equal $pH$.

(Schwenk, 1974) proposed that the limiting current is determined by the diffusion of $CO_2$ to the surface of the steel. However, this appears to be improbable as the concentration of $CO_2$ in $CO_2$-saturated solutions is approximately 27 mol m$^{-3}$ and the diffusion coefficient at 298 K is about $10^{-9}$ m s$^{-1}$ (Schmitt, 1983; Schwenk, 1974). This results in a diffusion limiting current density of 52 A m$^{-2}$, which is in the order a factor higher than the limiting current density observed experimentally in quiescent solutions (Eriksrud and Sontvedt, 1983). As the observed current densities were lower than the predicted limiting currents due to diffusion of $CO_2$, a purely diffusion controlled limiting by the diffusion of $CO_2$ is improbable.

The corrosion rate at 20°C was found to be independent of solution flow rate, suggesting that the rate-determining step was either a chemical or electrochemical reaction. If a chemical reaction was the rate-determining step, then the corrosion rate would be determined by a limiting current that was reaction controlled and independent of solution flow. However, (Eriksrud and Sontvedt, 1983) discovered that the corrosion rate was independent of the limiting current density, which increased with solution flow, so the corrosion rate was not controlled completely by a chemical reaction. As a chemical rate determining reaction was excluded, (Eriksrud and Sontvedt, 1983) and (Schmitt and Rothman, 1977) suggested that it was more likely that a flow independent electrochemical reaction acts as the rate determining step. As there was a small effect of solution flow rate on the limiting current at low flow rates, they assumed that diffusion was partly controlling and there was a change from partial diffusion control at low flow rates to charge-transfer control at higher flow rates. As the
diffusion rate increases with flow rate, on attaining a certain flow rate, the charge transfer reaction becomes the slow step, making the corrosion rate independent of flow rate.

According to studies by (Eriksrud and Sontvedt, 1983), there also appeared to be a change in mechanism with change in temperature from 20°C to 60°C. Whilst at low temperatures (≤ 20°C), the corrosion rate was flow independent, at higher temperatures (≥ 60°C) it appeared to be mass transport limited. This suggested that the corrosion process was controlled by the kinetics of a reaction that increased with temperature. As the rate of the charge transfer controlled reaction increases significantly more with temperature than diffusion rates, so at 20°C the rate determining step was the charge transfer reaction but at elevated temperatures, diffusion became the slowest step and therefore rate-determining.

According to studies by (Gray et al., 1990; Stern, 1955), the slow hydration of CO₂ to form carbonic acid was considered to be the rate determining step, due to its slow chemical reaction kinetics. Based on an assumption of the hydration of CO₂ as the rate determining step, with the rate coefficient for the forward-going reaction at room temperature given as 3×10⁻² s⁻¹ (Fisher and Siedlarek, 1978), (Eriksrud and Sontvedt, 1983) calculated a limiting current density of 10 mA m⁻², a value that is closer to the observed value for the limiting current density at 20°C in stagnant solutions. However, this theory can also be discounted, as the limiting current was found to be dependent of the hydrodynamic conditions of the test solution, i.e. the rotation rate of the electrode, as mentioned previously. This led (Schmitt and Rothman, 1977) to suggest that the observed limiting current results from both limiting transport rates of H⁺ ions and a rate limited chemical reaction. The interpretation of this ‘rate limited reaction’ is also a source of discrepancies in the literature. Based on observed and calculated limiting current densities, (Eriksrud and Sontvedt, 1983) suggested that the hydration of CO₂ to form carbonic acid is a homogeneous reaction, while (Schmitt and Rothman, 1977) proposed that
the overall cathodic reaction was controlled by the heterogeneously catalysed hydration of chemisorbed CO₂.

Three different reaction mechanisms were proposed by (Schmitt, 1983):

1) Hydrogen evolution by the reduction of H⁺ ions from the bulk solution after the dissociation of H₂CO₃ and diffusion to the metal surface. The hydrogen ions resulting from the dissociation of carbonic acid are transported from the bulk solution to the metal surface. Adsorbed molecular hydrogen yields from chemical recombination according to the Tafel reaction or electrochemical recombination according to the Heyrovsky reaction (Section 3.11) and desorbs from the surface to allow subsequent adsorption and reduction of hydrogen ions. In this reaction sequence, there is no significant difference between the hydrogen evolution reaction in CO₂ solutions and diluted acid solutions.

\[
CO_2^{(sol)} + H_2O \leftrightarrow H_2CO_3^{(sol)} \quad (3.9)
\]

\[
H_2CO_3^{(sol)} \leftrightarrow H^+^{(sol)} + HCO_3^-^{(sol)} \quad (3.10)
\]

\[
H^+^{(sol)} \leftrightarrow H^+^{(ads)} \quad (3.11)
\]

\[
H^+^{(ads)} + e^- \leftrightarrow H^{(ads)} \quad (3.12)
\]

2) CO₂ molecules adsorb on the metal surface and subsequent hydration yields chemisorbed carbonic acid. These species then dissociate while still adsorbed to give hydrogen ions, which are subsequently reduced to yield adsorbed hydrogen atoms. It is important to note a significant difference of reaction sequence (2) from sequence (1) is that the hydration of CO₂ occurs as a heterogeneous reaction on the metal surface.
\[ CO_{2(sol)} \leftrightarrow CO_{2(ads)} \]  
(3.13)

\[ CO_{2(ads)} + H_2O \leftrightarrow H_2CO_3(ads) \]  
(3.14)

\[ H_2CO_3(ads) \leftrightarrow H^+(ads) + HCO_3^-(ads) \]  
(3.15)

3) Hydrogen evolution from the direct reduction of adsorbed carbonic acid:

\[ H_2CO_3(ads) + e^- \leftrightarrow H(ads) + HCO_3^-(ads) \]  
(3.16)

The direct reduction of carbonic acid to form hydrogen carbonate ions and hydrogen (reaction scheme 3) was also proposed by (de Waard and Milliams, 1975) as an explanation for higher rates of corrosion in CO\(_2\) containing solutions. The charge transfer reaction (3.16) was also assumed to be the rate determining step. From their experimental data (de Waard and Milliams, 1975) concluded that hydrogen evolution in CO\(_2\) solutions proceeds in a ‘catalytic’ manner, in which adsorbed hydrogen carbonate from reaction (3.15) is neutralized by a hydrogen ion to re-form adsorbed H\(_2\)CO\(_3\) from which more hydrogen can be directly or indirectly produced.

\[ HCO_3^- (ads) + H^+ (ads) \leftrightarrow H_2CO_3(ads) \]  
(3.17)

(Schmitt and Rothman, 1977) also concluded that the adsorption of CO\(_2\) on the metal surface must occur prior to hydration. This restriction seems unlikely as radiotracer studies conducted by (Wieckowski et al., 1983) indicated that CO\(_2\) absorption is not required for the corrosion reactions to proceed.

(Wieckowski et al., 1983) suggested an alternative scheme in which H\(_2\)CO\(_3\) and HCO\(_3^-\) reactions occur on the metal surface, by a catalytic mechanism in which the reactant is regenerated by water.
\begin{align}
H_2CO_3 + e^- & \leftrightarrow H(ads) + HCO_3^- & (3.18) \\
HCO_3^- + OH^- & \leftrightarrow CO_3^{2-} + H_2O & (3.19)
\end{align}

Or

\begin{align}
HCO_3^- + e^- & \leftrightarrow CO_3^{2-} + H(ads) & (3.20) \\
CO_3^{2-} + H_2O & \leftrightarrow HCO_3^- + OH^- & (3.21)
\end{align}

Whilst (Schmitt, 1983) favoured a heterogeneously catalysed hydration of chemisorbed CO\textsubscript{2} as the rate controlling step, on the basis that the limiting cathodic current densities were strongly affected by the type of steel, (Eriksrud and Sontvedt, 1983) argued otherwise. They were able to support their claims of a homogeneous hydration of CO\textsubscript{2} on the basis that the observed cathodic limiting current in CO\textsubscript{2} solutions was the same as that found by (Schwenk, 1974) and others for platinum and steel. They remarked that a chemical reaction in solution would be independent of the type of metal, while a heterogeneous adsorption reaction will often depend on the metal type, since some sort of bonding is involved. They also noted this as the reason for the influence of metal type on the hydrogen evolution rate, due to the difference in the binding energy of adsorbed H atoms.

(Berry, 1982) gave an alternative explanation for the higher rates of corrosion observed for CO\textsubscript{2} solutions than those in strong acidic solutions with the same bulk pH values. The depletion of hydrogen ions from the solution at the iron surface caused the solution adjacent to the corroding steel surface to become less acidic, which in turn decreased the rate of corrosion. (Berry, 1982) suggested that this decrease in local H\textsuperscript{+} ion concentration is counterbalanced by the evolution of gases which increases turbulence of the liquid, thereby decreasing the alkalinity by providing fresh acid solution to the metal surface. It was also proposed that in a weakly ionized acid such as carbonic acid, there is a large amount of dissolved but un-ionized
CO₂ in the solution, which can then go on to react via reaction (3.3) to provide hydrogen ions, replacing those consumed by the corrosion reaction. On the other hand, only relatively low concentrations of a strongly ionized acid are required to produce the same pH as the weakly ionized solution and the depletion of hydrogen ions can reduce the corrosion rate.

(Ogundele and White, 1986) suggested that due to the large hydrogen carbonate concentrations the direct reduction of the hydrogen carbonate ion may also be significant. However, their experiments covered only a narrow pH range under quiescent solution conditions.

\[
2\text{HCO}_3^- + 2e^- \leftrightarrow H_2(g) + \text{CO}_3^{2-}(aq)
\]  

(Gray et al., 1990) also proposed the same electrochemical reduction of hydrogen carbonate ions with different electrochemical reactions being dominant in different pH regions. They proposed that in CO₂ containing solutions at low pH (pH < 4), that hydrogen evolution from H⁺ reduction is dominant and the hydration of CO₂ is not thermodynamically favourable and a very small concentration of carbon dioxide is present as carbonic acid. At an intermediate pH range (4 < pH < 6), they proposed the direct reduction of carbonic acid in addition to hydrogen ions. At a higher pH range (6 < pH < 10) in which hydrogen carbonate ions are present in significantly higher concentrations, they expected HCO₃⁻ to be directly involved in the reduction reaction. However, it is still debatable which one or more of the numerous proposed mechanisms is appropriate, so the debate continues.

3.4.2. Amine Solution Carbon Steel Corrosion

(Lang and Mason, 1958; MacNab and Treseder, 1971 and Kohl and Riesenfeld, 1985) each proposed that while alkanolamines contribute to corrosion by reacting with CO₂, they are not corrosive themselves. Amines are not intrinsically corrosive due to their high pH, they become so only when they absorb CO₂, leading to the second type of corrosion encountered: amine
solution corrosion. This corrosiveness is due partly to CO₂-loaded amines having a significantly lower pH. This type of corrosion is most prominent in the hot bottom section of the stripper and the rich solution side of the heat exchanger. (Riesenfeld and Blohm, 1951) firstly noted that substantial amine corrosion is usually accompanied by the evolution of acid gases from the rich amine solution. Based on their observations, (Riesenfeld and Blohm, 1951) identified the presence of CO₂ as the principal cause of carbon steel corrosion in amine solutions.

CO₂ is evolved from the rich amine solution via the following reactions:

\[
RNH_3^+ + \text{HCO}_3^- \leftrightarrow RNH_2 + CO_2 + H_2O \tag{3.23}
\]

\[
RNH_3^+ + R_2NCO_2^- \leftrightarrow CO_2 + RNH_2 \tag{3.24}
\]

(Kosseim et al., 1984) suggested an explanation for amine acid gas corrosion that provides an alternative source for the proton required for the corrosion reaction. They suggested that due to the high concentration of protonated amine (RNH₃⁺) resulting from the CO₂ absorption reaction, it is likely that RNH₃⁺ can provide protons for the corrosion reactions. Thus, they proposed the following corrosion mechanism involving the protonated amine via reaction (3.25); however, it has not been featured in any other work.

\[
Fe + RNH_3^+ \leftrightarrow Fe^{2+} + H_2 + RNH_2 \tag{3.25}
\]

The reaction scheme implies that the corrosion rate should increase in proportion to the concentration of protonated amine(s).

### 3.5. Factors Affecting CO₂ Corrosion in Amine Plants

Certain trends have been identified concerning the corrosive nature of amines used in CO₂ absorption. The following factors have been shown to influence amine solution corrosion (Kohl & Nielsen, 1997):
• High operating temperature
• High rich and lean amine loading
• Type of amine
• Amine solution concentration
• Amine solution contaminants such as degradation products and heat-stable salts
• Surface films

3.5.1. Temperature

The amine solution temperature has been identified as one of the most important factors influencing steel corrosion rates. Increasing the solution temperature enhances corrosion reaction kinetics with rates doubling with temperature increases of 10 - 20°C (Kittel et al., 2010). However, measuring the effect of temperature within the amine treating plant is made complex by the temperature difference between the absorber which operates at 40°C and the reboiler at 120°C. The difference in temperature has a considerable effect on the chemistry of the amine, in particular the CO₂ loading. Hence, a great difference in corrosion rates can be found throughout the amine scrubbing plants. Based on plant experience, the most susceptible areas to corrosion have been observed as the sections operated at elevated temperatures, such as the heat exchanger and the stripper. (Veawab et al., 1999) made potentiodynamic measurements on carbon steel in three different amines, MEA, DEA and AMP under varying temperature conditions (25-80°C) and found that increasing the solution temperature accelerated the corrosion rate. (Kladkaew et al., 2009) also carried out similar tests on carbon and stainless steel samples in 5 M MEA solutions, obtaining similar results.

(de Waard and Milliams, 1975) observed that corrosion rates in CO₂ containing solutions increased with temperature up to 60°C, reaching a maximum between 60°C to 70°C and then decreased with additional increases in temperature. (De Waard and Lotz, 1993), Nesic and
Lunde, 1993) and (Vuppu and Jepson, 1994) also observed similar effects of temperature on corrosion rates. Figure 3-4 depicts the effect of temperature and CO\textsubscript{2} partial pressure on the corrosion rate of carbon steel in aqueous CO\textsubscript{2} systems as observed by (De Waard and Lotz, 1993). It was observed that the corrosion rate at any particular CO\textsubscript{2} partial pressure initially increases with temperature until it reaches a maximum then starts to decrease with further increases in temperature. Whilst the initial increase in corrosion rates was attributed to increases in mass transfer and charge transfer rates, (De Waard and Lotz, 1993) suggested that the observed decrease at elevated temperatures (> 70\textdegree{}C) was due to the formation of a protective film of corrosion products such as siderite (FeCO\textsubscript{3}) or magnetite (Fe\textsubscript{3}O\textsubscript{4}) on the steel surface which act as barriers to the oxidising species in the solution and restricts access to the metal surface. At temperatures above 80\textdegree{}C, the iron carbonate solubility decreases, making the formation of FeCO\textsubscript{3} scales more likely (Ikeda et al., 1984). (De Waard and Lotz, 1993) also proposed a method for the prediction of carbon steel corrosion rates in aqueous CO\textsubscript{2} solutions, by converting the data they collected to the form of a nomograph, as shown in Figure 3-5. The decrease in corrosion rates at elevated temperatures was also taken into account in the nomograph by a scale factor from 0.1 to 1, which is used as a multiplier to decrease the corrosion rate calculated from the chart in the temperature region beyond the temperature predicted to correspond to the maximum corrosion rate.
Figure 3-4: Effects of temperature and CO₂ partial pressures on carbon steel corrosion rates (de Waard and Lotz, 1993).

Figure 3-5: Nomograph for corrosion rates of carbon steel in aqueous CO₂ environments (de Waard and Lotz, 1993).
3.5.2. CO$_2$ Loading

CO$_2$ loading has been identified as one of the other primary factors affecting steel corrosion rates in amine scrubbing plants (Pearce and DuPart, 1987). Increasing the CO$_2$ loading increases the amine solution’s aggressiveness, so accelerating corrosion rates (Polderman et al., 1955; Fochtman et al., 1963). This was supported by evidence that rich amine solutions are more corrosive than lean amine solutions (Kohl & Nielsen, 1997). Thus, there have been a few recommended guidelines for the CO$_2$ loading that should keep the corrosion rates in amine scrubbing plants to acceptable levels (Kohl & Nielsen, 1997). The maximum CO$_2$ loading in the rich amine solutions should be limited to 0.25 - 0.40 mol CO$_2$ (mol amine)$^{-1}$ for MEA, 0.33 - 1.00 mol CO$_2$ (mol amine)$^{-1}$ for DEA, 0.45 - 0.50 mol CO$_2$ (mol amine)$^{-1}$ for MDEA, 0.25 - 0.45 mol CO$_2$ (mol amine)$^{-1}$ for DGA and 0.50 – 0.85 mol CO$_2$ (mol amine)$^{-1}$ for DIPA.

The increase in corrosion rates can be attributed partly to the decrease in the amine solution pH with increasing CO$_2$ loading. The pH is considered to impact both the rates of electrochemical reactions at the steel surface and the precipitation of corrosion products.

The total carbonate species in the aqueous solution can be represented by:

$$[C_T(IV)] = [CO_2(aq)] + [RNHCOO^-(aq)] + [H_2CO_3(aq)] + [HCO_3^-(aq)] + [CO_3^{2-}(aq)] \quad (3.26)$$

At 25°C, in an aqueous CO$_2$ environment within a low pH range (2 < pH < 4), the corrosion of steel is considered to be limited by the diffusion of H$^+$ to the surface (Gray et al., 1989).

$$2H^+ + 2e^- \leftrightarrow H_2 \quad (3.27)$$

At the intermediate pH range, the direct reduction of carbonic acid is thought to occur at the steel surface (de Waard and Milliams, 1975). Reaction (3.28) is considered to be limited by the hydration of carbon dioxide to form carbonic acid.
\[ 2H_2CO_3(aq) + 2e^- \leftrightarrow 2HCO_3^-(aq) + H_2(g) \]  

(3.28)

It has also been suggested that the direct reduction of hydrogen carbonate ions and water can become important at a higher pH range \((6 < \text{pH} < 10)\).

\[ 2HCO_3^-(aq) + 2e^- \leftrightarrow CO_3^{2-}(aq) + H_2(g) \]  

(3.29)

\[ 2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \]  

(3.30)

Where reactions (3.29) and (3.30) are thought to be charge transfer controlled. The concentration of \(HCO_3^-\) increases with pH, and at pH 6 and 0.1 MPa \(CO_2\), the concentration of \(HCO_3^-\) becomes more than 300 times the \(H_2CO_3\) concentration. Although the concentration of \(HCO_3^-\) is significantly higher \(\geq 6\), the low dissociation constant makes hydrogen carbonate \((pK_a2 \text{ ca. } 10)\) a poor proton donor, so it has also been deliberated that the contributions from these reactions might be insignificant. It is also important to note that it is difficult to distinguish experimentally between any of the mechanisms for hydrogen evolution.

The solubility of iron carbonate is also strongly dependent on the pH and \(CO_2\) partial pressure, and decreases with pH for the pH range \((4 < \text{pH} < 7)\). The solubility of \(FeCO_3\) decreases by a factor of about 5 with a pH increase of 4-5, and a factor of 100 per unit pH increase at pH > 5 (Dugstad, 1992). A lower solubility results in a higher \(FeCO_3\) supersaturation on the steel surface, so accelerating the precipitation and deposition processes (Dugstad, 1992). The probability of \(FeCO_3\) formation on the steel surface is dramatically increased at pHs > 5, and many reports confirm this by indicating significantly lower corrosion rates in the pH range 5.5-6.

Based on experimental studies, (Veawab et al., 1999) found that in MEA solutions, increasing the \(CO_2\) loading from unloaded solutions to 0.40 mol \(CO_2\) (mol amine)\(^{-1}\) resulted in increases
in corrosion rates from negligible values to 0.6 mm a\(^{-1}\). They attributed this increase in corrosion rates with CO\(_2\) loading to the increasing concentrations of RNH\(_3^+\) and HCO\(_3^-\) that dissociate via reaction (3.31) and (3.32) to produce more hydrogen ions.

\[
RNH_3^+ \leftrightarrow RNH_2 + H^+ \quad (3.31)
\]

\[
HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (3.32)
\]

(Veawab et al., 1999) also proposed that corrosion rates increased due to a corrosion mechanism involving the direct reaction of Fe with hydrogen carbonate ions via reaction (3.33). Whilst this reaction scheme is indeed plausible, the formation of passive FeCO\(_3\) due to increasing CO\(_2\) loading as they had proposed, would lead to an overall decrease not increase in corrosion rates as they had observed.

\[
Fe + 2HCO_3^- \leftrightarrow FeCO_3 + CO_3^{2-} + H_2 \quad (3.33)
\]

(Sun et al., 2011) also observed an increase in corrosion rates with CO\(_2\) loading and suggested that this was because hydrogen carbonate ions act as the primary oxidising agent in aqueous amine-CO\(_2\) solutions and are reduced via reaction (3.33).

### 3.5.3 Amine Type

The type of amine also has an important effect on corrosion rates in amine scrubbing plants. Pure unloaded amine solutions are not corrosive and are even likely to offer corrosion inhibition to the carbon steel surface (Lang and Mason, 1958; Kohl and Riesenfeld, 1985; DuPart et al., 1993). Several studies have also shown that there is no difference in corrosion rates between the different types of amines in the absence of CO\(_2\) (MacNab and Treseder, 1971; Dow Chemical Company, 1962; Lang and Mason, 1958; Froning and Jones, 1958; Blanc, Grall, Demarais, 1982). However, amine solutions containing even the smallest concentrations of dissolved CO\(_2\) become corrosive. In loaded solutions, different amines have been found to
exhibit varying degrees of corrosiveness to the carbon steel equipment, with MEA having the worst reputation for corrosion issues. Primary amines have been found to be the most corrosive, followed by secondary amines, with tertiary amines being the least corrosive (Kohl and Riesenfeld, 1985). Although DEA has been found to be less corrosive than MEA, similar results have been obtained with its use, in terms of increasing corrosion rates with CO₂ loading and temperature. Measurements conducted with MDEA indicated that it was favourable from a corrosion standpoint, as it has significantly lower corrosion rates than MEA and DEA. The reason for this is not yet fully understood.

It is considered that the difference in the corrosion behaviours may be partly due to the nature of the degradation products formed in the different amines. MEA and DEA solutions form degradation products on absorption of CO₂, while MDEA solutions do not. There are still several questions arising from this, such as if MEA, DEA and MDEA have similar corrosion rates in unloaded solutions and with basic degradation products in the absence of CO₂, why is MEA more corrosive than DEA and DEA more corrosive than MDEA? (Teevens, 1990) suggested that reactivity plays a strong role and the difference in the corrosion rates in the amines might be related to the fact that MEA is a stronger Lewis base than DEA and MDEA is the weakest (Dupart et al., 1993). The formation of basic degradation products can be attributed to the reaction of CO₂ with primary amines and secondary amines to form intermediate amides and subsequently their carbamates (RNHCOO’), which then undergo dehydration to yield various degradation products (Section 3.5.7.). As MEA is a stronger Lewis base than DEA, it is more likely to form carbamate. The ratio of carbamate to hydrogen carbonate is 3:1 in MEA, 1:1 in DEA, while MDEA, being a tertiary amine does not form carbamates and only forms hydrogen carbonate ions (Veldman, 2000). Thus, the relationship between carbamate and hydrogen carbonate ion concentrations is considered to be a major factor that determines corrosion (Veldman, 2000) and the presence of carbamates as
intermediary salts may somehow influence the corrosivity of MEA and DEA solutions, whilst the inability of tertiary amines to form carbamates is an important clue for its less corrosive nature. It is also possible than in tertiary amines, the only intermediary product, hydrogen carbonate ions react with iron to form a uniform layer of FeCO₃ which provides a passive barrier against additional corrosion, even with high loadings of CO₂. However, with primary and secondary amines that selectively form carbamates over hydrogen carbonates, the layer of FeCO₃ will be less uniform.

(Veawab et al., 1999) also conducted studies to compare corrosion rates in various amines and found that at full CO₂ saturation, MEA was the most corrosive followed by AMP, then DEA and MDEA. They suggested that the influence of amine type on corrosion behaviour is due to differences in the amount of CO₂ absorbed by the amine solution at full saturation. They supported this hypothesis by calculating the CO₂ loading in the amines and they also determined that MEA had the highest CO₂ loading followed by AMP, then DEA and MDEA. (Veawab et al., 1999) subsequently attempted to eliminate the influence of CO₂ loading by comparing the corrosion rates in the different amines all with a CO₂ loading of 0.20 mol CO₂ (mol amine)⁻¹. They also observed that amine type had an effect on corrosion rates, even though the influence of CO₂ loading was eliminated and proposed that it might be due to the difference in HCO₃⁻ ion concentrations in the solutions. However, this hypothesis is unlikely to be valid, as MDEA has a higher CO₂ loading capacity than primary and secondary amines. According to (Jou et al., 1995), the absorption of CO₂ in MDEA can reach 1.0 mol CO₂ (mol amine)⁻¹, whilst (Veawab et al., 1999) calculated a CO₂ loading of 0.243 mol CO₂ (mol amine)⁻¹. The hypothesis of (Veawab et al., 1999) also fails to explain why higher rates of corrosion are not experienced in MDEA solutions, which form only HCO₃⁻ ions, than in primary and secondary amines, which also form carbamates as intermediary products.
3.5.4. Amine Concentration

The concentration of the amine solution has also been found to influence steel corrosion rates. Generally, on amine scrubbing plants, it would be desirable to employ high amine concentrations for energy saving purposes. However, from an industrial standpoint, high amine concentrations have been found to increase the corrosion rates. In order to control and limit the corrosion rates to acceptable and manageable levels, most amine scrubbing plants are operated within the recommended guidelines for maximum amine concentrations. Typical amine concentrations are 10 - 20 wt% for MEA, 20 – 40 wt% for DEA, 50-55 wt% for MDEA, 50-65 wt% for DGA and 20 - 40 wt% for DIPA (Nielsen et al., 1995). However, the experimental results on the effect of amine concentration have ranged from significant (DuPart et al., 1993; Veawab et al., 1999), to moderate, to no effect at all (Guo and Tomoe, 1999; Vazquez, et al., 2000).

3.5.5. Effect of Oxygen

The effects of oxygen has been the source of debate by researchers. In experimental studies conducted by (Veawab et al., 1999), corrosion rates were found to increase with the presence of O₂, as expected for such an oxidising agent in amine solutions, oxidizing steel surfaces to form oxide films as in the reactions:

\[ 2Fe + 2H₂O + O₂ \rightarrow 2Fe(OH)₂ \]  \hspace{1cm} (3.34)

\[ 2Fe(OH)₂ + H₂O + \frac{1}{2}O₂ \rightarrow 2Fe(OH)₃ \]  \hspace{1cm} (3.35)

(Kladkaew et al, 2009) also observed increases in corrosion rates and proposed an alternative reaction scheme (3. 36), in which higher corrosion rates resulted from higher reduction rates of dissolved oxygen by:
\[ O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \]  \hspace{1cm} (3.36)

Then, iron oxidation products, Fe(OH)$_2$ and Fe(OH)$_3$ are formed via reaction (3.34) and (3.35) respectively.

On the contrary, (Kittel et al., 2010) observed no significant impact of oxygen on the corrosion rates of carbon steel in CO$_2$-loaded MEA solutions.

### 3.5.6. Effect of Surface Films

Another important parameter that determines the corrosion rate is the ability of the carbon steel to form iron carbonate by reaction with any of the forms of dissolved CO$_2$. Under the right operating conditions of temperature and pH, FeCO$_3$, an insoluble scale can precipitate on the steel and act as a protective barrier. As the corrosion reaction advances, once the Fe$^{2+}$ and CO$_3^{2-}$ ions exceed the solubility limit, they react to form solid FeCO$_3$ films according to reaction (3.37). Based on experimental evidence, it seems clear that the rates of corrosion can be decreased significantly by precipitation of FeCO$_3$ that is adherent to steel surfaces (Dugstad, 1998; Nyborg, 1998; Nyborg, and Dugstad, 1998).

\[ Fe^{2+} + CO_3^{2-} \leftrightarrow FeCO_3(s) \]  \hspace{1cm} (3.37)

The iron carbonate decreases corrosion rates by presenting a diffusion barrier for the species involved in the corrosion process, by blocking a portion of the steel and preventing the underlying steel from undergoing any further dissolution. (Kohl & Nielsen, 1997; Kladkaew et al., 2009a) suggested an alternative scheme for ferrous carbonate formation in amine scrubbing plants which occurs from the reaction of the ferrous ions produced from dissolution of iron and the hydrogen carbonate ions in solution.
Whilst (DuPart et al., 1993) and (Rooney and Bacon, 2000) were able to identify the presence of some insoluble corrosion products such as iron carbonate and iron hydroxide in several parts of the plant, they were also able to identify soluble corrosion products, such as Fe$^{II}$. However, there are no studies in the open literature which, quantify these corrosion products. (Burnstein and Davies, 1980) proposed an alternate reaction scheme which, could account for the formation of such products as outlined in reactions (3.39) to (3.42):

\[
Fe + 2HCO_3^- \rightarrow FeCO_3 + CO_3^{2-} + H_2 \quad (3.38)
\]

\[
Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^- \quad (3.39)
\]

\[
Fe + HCO_3^- \rightarrow FeCO_3 + H^+ + 2e^- \quad (3.40)
\]

\[
Fe(OH)_2 + HCO_3^- \rightarrow FeCO_3 + H_2O + OH^- \quad (3.41)
\]

\[
FeCO_3 + HCO_3^- \rightarrow Fe(CO_3)_2^{2-} + H^+ \quad (3.42)
\]

The reduction of undissociated carbonic acid has also been proposed via the following schemes (Kladkaew et al., 2009):

\[
Fe + H_2CO_3 \rightarrow FeCO_3 + H_2 \quad (3.43)
\]

\[
Fe + 2H_2CO_3 \rightarrow Fe(HCO_3)_2 + H_2 \quad (3.44)
\]

(Riesenfeld and Blohm, 1951) also suggested that the dissolved CO$_2$ in the amine solutions could react directly with carbon steel to form iron carbonate (FeCO$_3$) via the following reaction (Kladkaew et al., 2009):

\[
Fe + CO_{2(aq)} + 2H_2O \leftrightarrow FeCO_3(s) + H_2 \quad (3.45)
\]

Another common surface product found in CO$_2$ corrosion of mild and low alloy steels is iron carbide (Fe$_3$C), which is part of the steel microstructure, so its quantity increases with the
carbon content of the steel (Avner, 1997). \( \text{Fe}_3\text{C} \) is a metallic conductor with a low hydrogen overpotential and a much lower overpotential than iron for other cathodic reactions, so it is more difficult to dissolve and is often left on the steel surface as a consequence of the corrosion reaction. Its presence can enhance the corrosion rate by up to a reported factor of 3-10 (Crolet et al., 1996) by establishing a galvanic effect and acting as a cathodic site for the hydrogen evolution reaction (Crolet et al., 1996; Videm et al., 1996). However, \( \text{Fe}_3\text{C} \) does not always have a detrimental and corrosive effect. Under the right conditions such as high pH, temperature, it has been reported by (Dugstad, 1998) and (Palacios and Shadley, 1991) that \( \text{Fe}_3\text{C} \) may enhance \( \text{FeCO}_3 \) precipitation by preventing the diffusion of ferrous ions from the surface. If the iron carbide layer blends into the iron carbonate film in a well distributed manner, it can also act as an anchor to the protective \( \text{FeCO}_3 \) layer. Both the \( \text{FeCO}_3 \) and \( \text{Fe}_3\text{C} \) films will be discussed in more detail in section 3.6.

### 3.5.7. Amine Degradation Products

Whilst the main reaction between amines and \( \text{CO}_2 \) is reversible, irreversible side reactions could also occur, resulting in degradation products from which the amines cannot be easily recovered. There are several mechanisms through which the amines can degrade and the degradation products depend on a number of factors such as the degradation mechanism and the type of amine used for the \( \text{CO}_2 \) capture process.

- Oxidative degradation
- Thermal degradation
- Heat stable salts
- Degradation caused by carbonyl sulfide (COS) and carbon disulfide (CS\(_2\))
- Degradation by carbon monoxide (CO)
Sulfur and polysulfide degradation

As the solvents must be replaced after degradation due to the decrease in CO₂ absorption capacity, there are concerns about amine loss, the adverse environmental effects of disposal and the inevitable operating costs of dealing with the degradation. Whilst these are issues that can be dealt with relatively easily, the corrosion of the carbon steel equipment is another major concern closely related to amine degradation that is of a more complex nature. According to (Gregory and Scharmann, 1937) degradation products enhance the corrosion issue in MEA plants. On the other hand, the link between corrosion and degradation for other amines remains inconclusive. (Blanc et al, 1982) attempted to study degradation-induced corrosion in DEA solutions and concluded that DEA degradation products had little to no effect on carbon steel corrosion, whilst others (Moore, 1960 and Chakma and Meisen, 1986) argued otherwise and established that there was a correlation between the two operational issues.

Although the presence of degradation products and contaminants, particularly heat stable salts, has been reported to increase corrosion rates (DuPart et al., 1993), there is still very limited relevant information in the open literature. Heat stable salts are the products of alkanolamines and acids stronger than CO₂ and H₂S, such as carboxylic acids. There are various sources of these acids such as makeup water and feed gas streams. They can also be generated within the plant by chemical reactions with contaminants such as O₂, CO, HCN and SO₂.

In general, the acids react with the amine by the proton transfer reaction (Veldman, 2000):

\[ RNH₂ + HA \leftrightarrow RNH₃⁺ A^- \]  \hspace{1cm} (3. 46)

where \( HA \) is the acid form of the heat stable salt anion and \( A^- \) is the heat stable salt anion.

They are called heat stable salts (HSS) since they cannot be regenerated and separated from the amine through typical regeneration conditions; instead they remain and accumulate in the
absorbent. The accumulation of these contaminants within the system has been found not only to decrease the CO₂ absorption capacity of the amines but also to increase corrosion rates significantly (Tanthapanichakoon et al., 2006). HSSs typically induce corrosion in the system by decreasing the pH, increasing the conductivity of the amine solution and may also act as chelating agents, dissolving the protective film on the metal surface (Rooney et al., 1996). (McCullough and Nielsen, 1996) also suggested the possibility that with some of the weaker HSS such as formic acid, as the operating temperatures increases during the amine regeneration, the acids also become less bound to the amine and are temporarily un-neutralized to release the free acid that could then react directly with the steel. It has been found that areas involved with high temperature processes such as the reboiler, reboiler piping, lower trays of the regenerator and the hot side of the heat exchanger, are the most affected by this type of corrosion, especially pitting.

Whilst it is has been generally accepted that the presence of heat stable salts and amine degradation products exacerbate corrosion rates, there is no consensus on the corrosion mechanism. (Tanthapanichakoon and Veawab, 2006) investigated the effect of fourteen heat stable amine salt compounds on the corrosion of both carbon steel and stainless steel, using MEA and CO₂. The corrosion rates increased in the presence of oxalate, formate, malonate, glycolate, succinate, and acetate, sulfate and hydrogen chloride; oxalate was the most corrosive of these heat stable salts followed by formate and malonate. These results were in agreement with those of (Nainar and Veawab, 2009). The other HSSs investigated such as sulfite, sodium chloride, sodium thiosulfate, ammonium thiosulfate, sodium thiocyanate, and ammonium thiocyanate, either decreased corrosion rates or acted as inhibitors.
3.6. **Review of Corrosion Product Films**

Based on experience in the oil and gas industry, uniform protective scales at the bottom of deep gas wells have been found to result in less severe corrosion rates (Burke and Hausler, 1985). Chemical analysis of these protective scales revealed that they consisted predominantly of iron carbonate (Burke and Hausler, 1985). Experimental studies showed consistently that even a thin adherent layer of FeCO$_3$ deposited on the surface of corroding iron or steel can result in significant decreases in corrosion rates (Dunlop et al., 1984; Ikeda et al., 1984; Videm and Dugstad, 1989).

The nature of this protective scale and the stability of the film determines the rate of corrosion, as well as the type of corrosion i.e. general corrosion or mesa attack. The structure, porosity and morphology, as well as its adherence to the underlying steel surface are much more important than the thickness in diminishing corrosion rates. The composition of the corrosion layer can also have a substantial effect on its ability to protect the steel surface (Crolet, 1994). In some cases, corrosion product layers can be extremely protective, whilst in others not very (Crolet et al., 1995) and in some cases have been found to actually enhance corrosion rates (Crolet et al., 1994).

Corrosion product films in CO$_2$-water systems can be divided into four main categories, each of which will be discussed below:

- Iron carbonate
- Iron carbide
- Iron carbonate and Iron carbide
- Iron carbonate and iron oxide
3.6.1. Iron Carbide Films

When steel corrodes in an aqueous CO$_2$ system and ferrous ions are produced via the anodic dissolution of iron, the Fe$^{II}$ ions dissolve leaving uncorroded iron carbide (Fe$_3$C) accumulating on the surface. Fe$_3$C is a metallic conductor with a low hydrogen overpotential, which forms an electrically conductive, porous, sponge-like layer on which the cathodic reaction can occur. It is characterised by a non adherent, black surface film with a thickness typically in the order of 100 µm (Crolet et al., 1994). The flow rate of the aqueous solution affects the amount of Fe$_3$C formed; at high solution flow rates (turbulent flow conditions, Reynolds number $\geq$ 4000), the surface film will principally consist of iron carbide and possibly some other unidentified constituents of alloying constituents. Decreasing flow rates results in an increase in the amount of Fe$_3$C accumulating on the steel surface, as well as an enhancement in the rate of formation of FeCO$_3$ in the product layer. According to (Dugstad and Videm, 1990), it is possible that the diffusion of Fe$^{II}$ ions away from the steel surface is slowed down by the Fe$_3$C film, allowing the solubility of FeCO$_3$ to be exceeded locally.

The presence of Fe$_3$C can increase the corrosion rate by a factor of 3-10 through galvanic effects (Crolet et al., 1996). As Fe$_3$C has a significantly lower overpotential for the cathodic reaction than iron, it can establish a galvanic effect with the uncorroded steel surface thereby enhancing the corrosion of the metal by accelerating the cathodic reaction. At low Fe$^{II}$ ion concentration of $<<$ 1 ppm, pure Fe$_3$C films will be formed, causing an increase in the corrosion potential and the corrosion rate. As the cathodic reactions occur at the Fe$_3$C film and the anodic reaction is the dissolution of iron as ferrous ions, there is a distance between the site of occurrence of the two reactions. The cathodic reaction typically consists of the reduction of protons resulting in the region around the Fe$_3$C film becoming less acidic or more alkaline. On the other hand, the region around the anodic site (the steel surface) becomes more acidic.
(Crolet et al., 1994; Crolet et al., 1995; Dugstad and Videm, 1990). It has been suggested that this is due to a number of hydrolysis reactions such as equation (3.47).

\[
Fe^{2+}_{(aq)} + H_2O \rightarrow Fe(OH)^+_{(aq)} + H^+_{(aq)} \tag{3.47}
\]

The iron carbide layer will have the effect of slowing down the diffusion of the ferrous ions to the bulk solution, causing their accumulation in the porous film structure. This in turn leads to supersaturation of the Fe\textsuperscript{II} locally and on exceeding the solubility, precipitation of FeCO\textsubscript{3}. However, it is possible that the steel surface may be too acidic for FeCO\textsubscript{3} precipitation, in spite of high local Fe\textsuperscript{II} ion concentrations (Crolet et al., 1994; Crolet et al., 1995; Dugstad and Videm, 1990). The FeCO\textsubscript{3} will precipitate in the more alkaline cathodic regions. Thus, the iron carbonate layer will precipitate in or on top of the iron carbide layer, forming a corrosion layer with poor adherence to the metal surface. Such surface films result in inadequate corrosion protection resulting in high corrosion rates. The inception of high corrosion rates leads to an increase in the difference in local pH between the cathodic and anodic sites that in turn aggravates the formation of the non-protective film.

Under certain conditions, it is possible for iron carbide and iron carbonate to mix and form an adherent surface film. Fe\textsubscript{3}C acts as the framework for the film and anchors the FeCO\textsubscript{3} layer, providing a greater resistant to the shear forces caused by turbulent flow conditions. The formation of such films can significantly decrease the effect of localised forms of corrosion, such as erosion corrosion.

In summary, it is apparent that the accumulation of Fe\textsubscript{3}C on the steel surface can have either a favourable or detrimental effect on corrosion of steel in CO\textsubscript{2}-H\textsubscript{2}O systems, depending on the structure of the film and the conditions under which it is formed. If the iron carbide structure slows down the diffusion of the Fe\textsuperscript{II} ions from the steel surface, it promotes FeCO\textsubscript{3} precipitation. If it blends into the film, it can enhance the strength of the film formed.
3.7. Iron carbonate Film

FeCO$_3$ also known as siderite or chalybite was discovered by (Baylis, 1926) to play an significant role in the corrosion process. The precipitated FeCO$_3$ film forms a layer that is impermeable and retards the corrosion process by leading to diffusion control. In CO$_2$ containing aqueous systems, the corrosion rate is highly dependent on the precipitation rate of FeCO$_3$ and the morphology of the film, both of which are determined by the FeCO$_3$ supersaturation and the temperature of the system. The morphology and composition of the film govern the nature of the corrosion process from the worst case scenario to low corrosion with protective films or mesa type corrosion.

The supersaturation of FeCO$_3$ is the key driving force for precipitation. The precipitation rate is usually slow; a high level of FeCO$_3$ supersaturation is required to obtain sufficient deposits on the steel surface. The likelihood of FeCO$_3$ depositing on the surface depends on the kinetics of precipitation and the way in which it is anchored to the underlying steel surface.

In principle, film precipitation occurs in two steps: nucleation and particle growth so the morphology of the film is most likely subject to the relative kinetics of these two processes (Dugtsad et al., 1993; Davis, 1993). It is assumed that the rates of these processes are dependent on the relative supersaturation ($RS$) where $S$ is the supersaturation, $Q$ is the concentration of the solute at any instant, $Q_{eq}$ is the equilibrium solubility and $K_{sp}$, the solubility product for FeCO$_3$.

$$Relative\ Supersaturation = RS = \frac{(Q-Q_{eq})}{Q_{eq}}$$

The nucleation rate is considered to increase exponentially with supersaturation i.e.:

$$Rate\ of\ nucleation = k_1 \left(\frac{(Q-Q_{eq})}{Q_{eq}}\right)^n$$

Whereas the rate of particle growth depends approximately linearly on the supersaturation:
The value of $K_2$ is typically significantly larger than $K_1$, so growth is predominant at low relative supersaturation, while at higher supersaturation, the exponential dependence of nucleation rate causes this process to occur to the near exclusion of particle growth. During the nucleation process, a colloidal dispersion forms close to the steel surface or inside the film in which settling is prevented as a result of Brownian motion and electrical repulsion between the colloid particles. In order to form a stable film, coagulation must occur. Coagulation of these colloidal dispersions can be accelerated by an increase in temperature, stirring and increasing ionic strength and decreasing the surface charge. A high supersaturation is required for the precipitation of FeCO$_3$ (Dugstad, 1992), so it is important to control the degree of supersaturation on the steel surface to achieve the desired film precipitation rate and properties.

![Figure 3-6](image.jpg)

Figure 3-6: Calculated growth rate of iron carbonate as a function of temperature and supersaturation (Jonson and Tomson, 1991).
Based on their studies on the precipitation of FeCO₃, (Jonson and Tomson, 1991) calculated FeCO₃ growth rates as shown in Figure 3-6; they then proposed equation (3. 51) to describe the kinetics of FeCO₃ precipitation in pure CO₂ corrosion of steel:

$$PR = k_r \frac{A}{V} K_{sp} (SS^{0.5} - I)^2$$  \hspace{1cm} (3. 51)

In this expression, the precipitation rate ($PR$) in kmol m⁻³ s⁻¹ is a function of the iron carbonate supersaturation ($SS$), the solubility product ($K_{sp}$), the temperature (via the rate constant $k_r$ which obeys Arrhenius law) and the surface area to volume ratio ($A/V$). The supersaturation ratio is given by equation (3. 52), in which $[\text{Fe}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the time-dependent species concentrations:

$$SS = \frac{[\text{Fe}^{2+}][\text{CO}_3^{2-}]}{K_{sp}}$$  \hspace{1cm} (3. 52)

From Figure 3-6, it is clear that the FeCO₃ growth rate is very low at low temperatures, but significantly increases with increasing temperature. (van Hunnik et al., 1996) extended the work of (Jonson and Tomson, 1991) on the precipitation kinetics of iron carbonate and found that equation (3. 51), which describes the effect of temperature on the precipitation kinetics of FeCO₃, did not provide a good fit over a wide range of supersaturation levels. This was due to (Jonson and Tomson, 1991) having fitted the equation only to experimental data at low levels of supersaturation i.e. $SS < 2$; (van Hunnik et al., 1996) considered that the precipitation rate based equation (3. 51) would be overestimated, especially at larger values of SS.

The supersaturation varies from typically above one for high temperature systems to values as high as 1000 at low temperatures. Hence, the experimental work conducted by (van Hunnik et al., 1996) investigated the effect of supersaturation over a wide range, resulting in a nominally more accurate expression referred to as the ‘KSLA’ equation:
In deriving this expression, (van Hunnik et al., 1996) assumed that the precipitation rate for FeCO$_3$ was controlled by the kinetics of the particle growth, as opposed to nucleation. In support of this assumption, they were able to model their experimental results sufficiently using equations describing precipitation growth only, regardless of the steel microstructure involved.

The rate constants $k_r$ for all the experiments were obtained from the measured precipitation rates via the precipitation equations and appeared to obey Arrhenius’s law for temperature dependence.

\[ k_r = A \exp\left(\frac{-B}{RT}\right) \]  

(3.54)

The values for A and B measured by (Jonson and Tomson, 1991; van Hunnik et al., 1996) are listed in Table 3-4.

Table 3-4: growth kinetics of FeCO$_3$, $2\sigma = 95\%$ confidence level

<table>
<thead>
<tr>
<th>Johnson and Tomson equation</th>
<th>KSLA equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>$2\sigma$</td>
</tr>
<tr>
<td>A</td>
<td>56.3</td>
</tr>
<tr>
<td>B</td>
<td>127.3</td>
</tr>
</tbody>
</table>

The equation proposed by (van Hunnik et al., 1996) has been shown to give a better overall fit for the precipitation rate, regardless of the level of supersaturation, whilst the (Jonson and Tomson, 1991) equation gives a more precise prediction at lower levels of supersaturation.

(van Hunnik et al., 1996) observed that the scale formed was protective only if the precipitation rate was of the order of the corrosion rate. If the precipitation rate was much less than the rate of iron dissolution, then the steel substrate would be removed at a higher rate than a dense FeCO$_3$ film can form.
The increase in precipitation rate with temperature has been observed to affect FeCO$_3$ film properties. At temperatures higher than 60°C, when the precipitation rate is high whilst the supersaturation is low result in dense, protective, crystalline films. At lower temperatures (< 40°C), the precipitation rate is much lower and so the relative supersaturation can become very high when dissolved Fe$^{II}$ and CO$_3^{2-}$ accumulate; hence, corrosion films are formed with low crystallinitities. If the crystal growth rate is less than the rate of dissolution, the difference between the two reactions will result in an iron carbonate film that is porous and non-adherent. Thus, films formed at temperatures less than 40°C are generally porous, not very adherent, non-crystalline in nature and considerably less protective than those formed at higher temperatures. For example, at 40°C, a supersaturation ratio of 50 would be required to obtain a precipitation rate which matches a corrosion rate of 3 mm a$^{-1}$ (van Hunnik et al., 1996). It is likely that such a high supersaturation occurs close to the steel surface when a corrosion film layer restricts diffusion rates of reactants and products. The maximum supersaturation will then be a balance between the rate of dissolution, nucleation, precipitation and transport (Dugstad, 1998).

This general precipitation mechanism is supported by many of the observations found in literature. Between 80°C-100°C, the precipitation is fast and the supersaturation low, hence dense protective crystalline carbonate layers have been observed, as shown in Figure 3-7.
At temperatures between 20°C and 60°C, a Fe₃C film is formed that possibly may be filled with FeCO₃, depending on the supersaturation. If the supersaturation ratio is between 10 and 100, then the Fe₃C film will be partially filled with FeCO₃ as shown in Figure 3-7.

Figure 3-8: FeCO₃ embedded in a Fe₃C film; 60°C, 10-100 supersaturation ratio (Dugstad, 1998).
The film formed will have a porous structure and the FeCO$_3$ is unlikely to form on the actual surface of the steel. The FeCO$_3$ will probably precipitate within the outer carbide layer, gradually precipitating inwards towards the steel surface as time progresses. At supersaturation ratios between 1-3, the iron carbonate is unlikely to precipitate within the porous iron carbide structure, leaving an unfilled iron carbide film as shown in Figure 3-9.

![Figure 3-9: FeCO$_3$ embedded in a Fe$_3$C film; 60°C, 1-3 supersaturation ratio (Dugstad, 1998).](image)

Iron carbonate precipitation has not been observed within the iron carbide structure at temperatures slightly below 40°C, even when the solution is highly supersaturated with FeCO$_3$. However, increasing the temperature significantly increases the growth rate, so much more FeCO$_3$ has been observed in corrosion films formed at 40°C (Dugstad et al., 1993). It is also important to note that at higher temperatures (ca. 120°C), the corrosion films formed are frequently less protective than those formed between 80°C and 100°C.

At temperatures > 150°C, the iron dissolution is prevented by the formation of a compact and adhesive film layer, which consists primarily of FeCO$_3$. According to (Ikeda et al., 1984), the steel corrosion is controlled by a high precipitation rate and slow dissolution of the protective FeCO$_3$ film. They conducted X-ray diffraction analysis of the steel surface and detected only
FeCO$_3$ and not Fe$_3$O$_4$, even though the latter phase would have been predicted as the more thermodynamically stable phase at high pHs ($\geq 9$).

(van Hunnik et al., 1996) also presented a concept of scaling tendency, which is defined as the ratio between the precipitation rate and the corrosion rate. They suggested that when the scaling tendency reached a critical value called ‘the critical scaling tendency’, an iron carbonate film will start to grow and start to decrease the corrosion rate. For all the experiments conducted by (van Hunnik et al., 1996), the critical scaling tendency was a value higher than 0.4. They also proposed that for a scaling tendency of $> 0.5$, then the protective FeCO$_3$ film would be self-repairing. The concept of the scaling tendency is useful, but it is subject to several drawbacks, such as the lack of consideration of the film adherence or the steel microstructure, as it assumes a smooth surface.

The temperature also has been found to influence the adherence of the corrosion film. According to (Videm and Dugstad, 1989), the FeCO$_3$ film formed at 40$^\circ$C can be wiped off easily with a cloth, whilst at 60$^\circ$C the films are more adherent and at 90$^\circ$C the films were so tough that they could not be scraped off even with a plastic knife.

Table 3-5: Standard State Formation Properties of FeCO$_3$ at 298.15 K and 0.1 MPa.

<table>
<thead>
<tr>
<th>$\Delta H^0$/kJ mol$^{-1}$</th>
<th>$\Delta G^0$/kJ mol$^{-1}$</th>
<th>$S^0$/J mol$^{-1}$ K$^{-1}$</th>
<th>$C_p^0$/J mol$^{-1}$ K$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>92.9</td>
<td>83.35</td>
<td>(Anderson, 1934)</td>
</tr>
<tr>
<td>-747.60</td>
<td>-673.75</td>
<td>92.9</td>
<td>82.09</td>
<td>(Kelly and Anderson, 1935)</td>
</tr>
<tr>
<td>-744.8</td>
<td>-673.88</td>
<td>92.9</td>
<td></td>
<td>(Latimer, 1952)</td>
</tr>
<tr>
<td>-748.9</td>
<td></td>
<td></td>
<td></td>
<td>(Wilcox and Bromley, 1963)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>96.1</td>
<td>(Kostryukov and Kalinkina, 1964)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>105.0</td>
<td>(Robie, 1965)</td>
</tr>
<tr>
<td>-743.965</td>
<td>-673.749</td>
<td>105.0</td>
<td></td>
<td>(Robie and Wladbaum,</td>
</tr>
</tbody>
</table>
The solution pH also affects the corrosion rate strongly by affecting the solubility of FeCO$_3$, which decreases at high solution pHs. Therefore, increasing the pH has the effect of increasing both the supersaturation and precipitation rate. FeCO$_3$ formation is unlikely to occur at a pH value of less than between 5-6, although the exact value will depend on the other conditions such as temperature, dissolved Fe$^{II}$ activity etc.

Several researchers have published and reviewed standard FeCO$_3$ thermodynamic properties such as entropy, enthalpy of formation, solubility constant and Gibbs energy of formation, for corrosion modelling and the computation of potential-pH diagrams (Ghosh et al., 1996; Dresel et al., 1989; Hem, 1967). These thermodynamic properties also have been used in kinetic models to predict the formation of FeCO$_3$. (Fosobol et al, 2010) presented a comprehensive review of the thermodynamic properties of FeCO$_3$ by comparing and discussing the most reliable values, which are summarised in Table 3-5.
3.7.1. Mixed Iron Carbonate and Iron Carbide Film

The most common film found on steel surfaces in CO$_2$ containing environments is a structure consisting of both iron carbonate and iron carbide, as the corrosion of the iron component leaves a Fe$_3$C layer on the steel surface. If FeCO$_3$ precipitation occurs, it mixes within the Fe$_3$C layer to form a mixed film. The structure and degree of protectiveness of the mixed corrosion film is dependent on the location of the iron carbonate precipitation within the film. If the FeCO$_3$ precipitation occurs inside the carbide layer, then a protective and adherent film will form that can often endure the stress of high solution flow.

The structure and nature of the mixed film will also depend on the structure of the porous Fe$_3$C layer, which is a function of the steel microstructure. Pre-treatments such as heat treatment can influence the formation and structure of the iron carbide layer (Palacios and Shadley, 1991). Experimental studies conducted by (Dugstad et al., 1993) on the effect of heat treatments on the corrosion of carbon steel showed that both corrosion rate and the likelihood of protective film formation decreased with increasing tempering temperature, so supporting the hypothesis that the Fe$_3$C structure has a significant effect on protective film formation.

The carbon content of the steel also plays a significant role in the formation and protectiveness of the mixed films. Mesa attacks are more prevalent in carbon steels with a low carbon content (< 0.05 %) than in carbon steels with a carbon content of 0.15-0.20 %. Steels with a higher carbon content have a carbide structure that offers a framework for the precipitation and accumulation of a dense and adherent mixed (iron carbonate and iron carbide) film, offering protection to the underlying steel. Conversely, carbon steels with a low carbon content have a much more porous and open carbide structure, which does not provide an adequate framework for protective FeCO$_3$ precipitation. The shape and distribution of the carbide phase has an impact on the adherence of corrosion films, with spherical Fe$_3$C particles resulting in little
adherence to the carbon steel surface (Dugstad, 1991). The structure of the mixed film has a substantial effect on the corrosion behaviour of the steel; the effects of different types of corrosion product orientation have been summarised by (Crolet et al., 1996) as shown schematically in Figure 3-10.

![Diagram showing the composition of protective and non-protective iron carbide and iron carbonate films (Crolet et al., 1996).]

**Figure 3-10:** The composition of protective and non-protective iron carbide and iron carbonate films (Crolet et al., 1996).

### 3.7.2. Iron Carbonate and Iron Oxide Film

The potential-pH diagram for Fe-CO₂-H₂O systems is shown in Figure 3-11. Based on thermodynamic predictions (Figure 3-11) and data from the literature (Ikeda et al., 1984), there is a comparatively wide region in which oxides and hydroxides such as magnetite (Fe₃O₄) are also expected to dominate. However, there is no direct evidence of the presence of magnetite in corrosion films produced in CO₂ containing environments at 100-150°C. The corrosion films
formed at 120°C are reportedly less protective than films formed within the temperature region of 80-120°C. Based on studies conducted by (Dugstad et al., 1993; Ikeda et al., 1984) at 120°C, despite expectations of Fe$_3$O$_4$ within the corrosion film formed at this high temperature, it was not observed. At 150°C and pH 4.8, the corrosion product formed was found to consist of only iron carbonate, whilst at 250°C magnetite was detected as the predominant product (70% Fe$_3$O$_4$ and 30% FeCO$_3$) (Shanon, 1978), so providing evidence for magnetite formation only at sufficiently high temperatures. However, it is also important to note that the electrode potential in which these films were formed was not reported.

Figure 3-11: Potential-pH diagram for Fe-CO$_2$-H$_2$O System, showing the lines for dissolved iron activity of $10^{-4}$ and (0.1 MPa CO$_2$, 298 K) (Kelsall 2013).
In summary, the most important component in corrosion films on steel is FeCO$_3$. A dense and adherent film of FeCO$_3$ can provide protection to the underlying steel, by decreasing corrosion rates to $< 0.1 \text{ mm a}^{-1}$. However, a mixed FeCO$_3$ and Fe$_3$C film offers the most protection against localised forms of corrosion, such as erosion or mesa attack. Based on reports from the open literature, the ideal operating conditions for the formation of a protective film are pH $\geq 5.5$, and an elevated temperature $60 \degree C < T < 150 \degree C$ and a supersaturation ($SS \geq 1$) of Fe$^{II}$. The different types of corrosion films formed in aqueous CO$_2$ environments over a temperature range of 25$\degree$C- 150$\degree$C are summarised in Table 3-6.

Table 3-6: Types of corrosion films formed from 30-150$\degree$C in steel-CO$_2$-H$_2$O systems

<table>
<thead>
<tr>
<th>Type</th>
<th>Category</th>
<th>Manifestation</th>
<th>Temperature</th>
<th>Effect on corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Carbide/ Cementite (Fe$_3$C)</td>
<td>Porous</td>
<td>Porous, sponge like appearance</td>
<td>$(T &lt; 150\degree C)$</td>
<td>Increase corrosion rate</td>
</tr>
<tr>
<td>Ferrous Carbonate/Siderite (FeCO$_3$)</td>
<td>Dense</td>
<td>Grey black or golden- brown</td>
<td>$(60\degree C &lt; T &lt; 150\degree C)$</td>
<td>Not Protective</td>
</tr>
<tr>
<td>Mixed film (Iron Carbide + Ferrous Carbonate)</td>
<td>Mixture throughout the film</td>
<td>Fe$_3$C on top, FeCO$_3$ at the bottom</td>
<td>$(60\degree C &lt; T &lt; 150\degree C)$</td>
<td>Not Protective</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FeCO$_3$ on top and Fe$_3$C at the bottom</td>
<td></td>
<td>Protective</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Protective and provides resistance to localised corrosion as a result of additional anchoring by Fe$_3$C film framework</td>
</tr>
</tbody>
</table>
3.8. Corrosion Inhibitors for Amine Absorption Plants

Inhibitors are frequently employed to decrease corrosion rates in closed systems such as amine gas treating plants. It has been found that a corrosion inhibitor is unnecessary in systems operating with relatively low CO\textsubscript{2} loading, low amine degradation or heat stable salt formation, low amine concentrations and amine solution velocities of ca. 1 m s\textsuperscript{-1}. However, in systems which do not meet these low corrosion rate requirements, it is necessary to inhibit corrosion.

The corrosion inhibitors function via different methods:

i) Adsorbed as a thin film on the metal surface;

ii) Promoting the formation of a thick layer of corrosion products;

iii) Altering the conditions of the corrosive environment by removing or reacting with corrosion-promoting species.

There are different ways in which corrosion inhibitors can be classified: by their chemical nature and termed as organic or inorganic, or they could be divided into oxidising passivators and adsorption inhibitors, based on their inhibiting function.

There has been extensive research into developing corrosion inhibitors and a few have been commercialised and patented for amine scrubbing plants. Organic inhibitors include cyclic amines and salicylic acid, while inorganic inhibitors are vanadium(V), copper(II), antimony(V), cobalt(II) and sulfur-containing compounds. Inorganic inhibitors are generally preferred to organic corrosion inhibitors due to the superior inhibiting properties.

The most extensively and successfully used inorganic corrosion inhibitors contain vanadium(V), in particular sodium metavanadate (NaVO\textsubscript{3}). These class of corrosion inhibitors work by raising the steel’s potential to the passive region, so that surfaces are covered by passive films, thereby decreasing corrosion rates. Such passive films that adhere to steel surfaces,
forming protective barriers against corrosion, have been postulated to be Fe$_2$O$_3$. The barrier is often only a few molecular layers thick and has been found to be effective in decreasing corrosion rates in general corrosion, but inadequate in preventing localised forms of corrosion. Film forming corrosion inhibitors have had varying reports about their success and commercial viability. While the use of inorganic inhibitors have been reported to be effective in the vapour phase regions of the stripper, they have not worked as well in other areas, especially in the piping and reboiler, in which corrosion occurs from heat stable salts or CO$_2$. In recent years, environmental concerns have been expressed about the use of heavy metals, because of their toxicity.

(Nainar and Veawab, 2009) investigated the effectiveness of sodium metavanadate (NaVO$_3$) and copper carbonate (CuCO$_3$) as corrosion inhibitors; the latter being a potential substitute for the more toxic NaVO$_3$. Although CuCO$_3$ was able to constrain corrosion rates of carbon steel below the acceptable level of 0.254 mm y$^{-1}$, NaVO$_3$ proved to be a superior inhibitor. Both inhibitors were more effective in the presence of O$_2$ than in its absence, because O$_2$ is required to maintain active Cu$^{II}$ or V$^V$ in the inhibited solutions, to prevent the formation of other oxidation states of vanadate and copper. Increasing the concentration of NaVO$_3$ also increases the inhibition, more protective films are produced, so decreasing corrosion rates. The presence of heat stable salts decreased the inhibitive capabilities of both NaVO$_3$ and CuCO$_3$.

Oxygen scavengers or reducing agents are also used to reduce dissolved oxygen, thereby inhibiting corrosion. They are particularly effective if they are able to enhance the formation and stability of the passive film on the metal surface. In the case of iron, magnetite (Fe$_2$O$_3$-FeO/Fe$_3$O$_4$) and hematite (Fe$_2$O$_3$) are the most stable films, believed to consists of a layer of Fe$_2$O$_3$-FeO in the inner layer and Fe$_2$O$_3$ in the outer layer. It has been proposed that these passive layers are formed through the following reaction schemes (Veldman, 2000):
\[ Fe + H_2O \rightarrow (FeOH) + H^+ + e^- \]  \hspace{1cm} (3.55)

\[ (FeOH)_{ads} \rightarrow (FeO)_{ads} + H^+ + e^- \]  \hspace{1cm} (3.56)

\[ (FeO)_{ads} + H_2O \rightarrow (FeOO)_{ads} + 2H^+ + 2e^- \]  \hspace{1cm} (3.57)

The adsorbed species then combine to form the more passive oxides:

\[ (FeO)_{absorbed} + (FeOO)_{absorbed} \leftrightarrow Fe_2O_3 \]  \hspace{1cm} (3.58)

\[ 2 (FeO)_{absorbed} + (FeOO)_{absorbed} \leftrightarrow Fe_2O_3 - FeO \]  \hspace{1cm} (3.59)

Thus, the removal of oxygen at the metal surface would shift the overall equilibrium to favour the formation of the passive oxides. The selection of an ideal oxygen scavenger must be based on its ability to remain reactive at all amine unit operating temperatures and work well in both liquid and vapour phases, while not being unfavourable to the operation. In applications where passive oxide formation does not occur easily, scavengers complicate the process further and accelerate corrosion. While oxygen scavengers have been found to be effective, they are not very useful for preventing pitting or stress cracking and corrosion due to heat stable salts.

(Veawab et al., 1997) investigated the corrosion rates of carbon steel in AMP solutions for comparison with MEA. While they found that the AMP systems were less corrosive to carbon steel than MEA, they concluded that the use of inhibitors was still necessary. For this purpose, they employed sodium metavanadate (NaVO₃) and an oxygen scavenger, sodium sulfite (Na₂SO₃). The corrosion products formed were observed to adhere to the metal surface and act as a protective barrier against other corroding agents. They observed that the corrosion products in the AMP system were more tenacious than the loose products formed in the MEA system. NaVO₃ proved to be the more superior of the inhibitors with more than 94% protection, as compared to the 90% achieved by Na₂SO₃ (Veawab et al., 1997). They proposed that this was
due to Na$_2$SO$_3$ acting only to remove the dissolved oxygen and does not have that same effect on the corroding agents such as hydrogen carbonate and water which may have played a vital role in the corrosion process. (Veawab et al., 1997) also observed that high solution flow rates resulted in breaking up of the protective film formed by the inhibitors or preventing the film from being formed completely. The potential-pH diagram for vanadium-water systems is shown in Figure 3-12. Whilst NaVO$_3$ is soluble in neutral and alkaline solutions, it’s inhibitive action is attributed to the competitive adsorption of monovanadate anions on the metal surface and reduction to form insoluble lower oxides (salts) with dissolved metal ions, which act as a passive layer and consequently decreases the rate of iron dissolution.

![Potential-pH diagram for the V-H$_2$O system at 298K. Activity of dissolved species = 0.01 (Kelsall et al., 1992).](image)

Figure 3-12: Potential-PH diagram for the V-H$_2$O system at 298K. Activity of dissolved species = 0.01 (Kelsall et al., 1992).
3.9. **Equilibrium Models for Aqueous Amine CO\textsubscript{2} Systems**

A quantitative understanding of the chemical and phase equilibria within amine-CO\textsubscript{2}-H\textsubscript{2}O systems is vital for the prediction of corrosion within an amine scrubbing plant. Thermodynamic modelling of the aqueous amine systems enables the speciation and redox behaviour to be predicted as functions of solution composition and operating parameters such as CO\textsubscript{2} loading and temperature. Whilst experimental data are important in terms of offering direct knowledge on the solubility of CO\textsubscript{2} in amine systems, at ‘extreme conditions’ such as lean CO\textsubscript{2} loading, high operating temperature or very high amine concentrations, it is sometimes difficult to obtain accurate data because of analytical constraints. Thermodynamic models have been used to complement experimental data, and the models usually require experimental data to feed in the parameter regression. Thermodynamic models can then be used to predict the solution chemistry for an entire range of operating conditions beyond the experimental measurements.

3.9.1. **Solution Chemistry**

The equilibrium between the amines, CO\textsubscript{2} and H\textsubscript{2}O is assumed to be governed by the following chemical reactions:

- **Dissolution of carbon dioxide**

  \[ CO_{2(g)} \leftrightarrow CO_2 \]  
  \[ (3.60) \]

- **Formation of carbamate**

  \[ 2RNH_2 + H_2O + CO_2 \leftrightarrow RNHCOO^- + RNH_3^+ + H_2O \]  
  \[ (3.61) \]

- **Dissociation of protonated amine ion**

  \[ RNH_3^+ \leftrightarrow RNH_2 + H^+ \]  
  \[ (3.62) \]
- Hydrolysis of carbamate

\[ \text{RNHCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_2 + \text{HCO}_3^- \]  
(3.63)

- Hydrolytic ionization of CO\(_2\)(aq)

\[ \text{CO}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]  
(3.64)

- Water dissociation

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]  
(3.65)

- Dissociation of hydrogen carbonate ion

\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \]  
(3.66)

As remarked by Austgen et al., other side reactions can also take place, in addition to the ones outlined above. However, they also noted that these side reactions are negligible on a laboratory scale and can be ignored in vapour-liquid equilibrium (VLE) studies.

### 3.9.2. Thermodynamic Framework

The thermodynamic framework for the VLE of amine-carbon dioxide-water systems should cover both the chemical and phase equilibria. The chemical equilibria is described by the reactions (3.60) - (3.66) and can be summarised with the mass action law in equation (3.67).

\[ K(T) = \prod a_i^{v_i} = \prod (m_i \gamma_i)^{v_i} \]  
(3.67)

where \( K(T) \) is the temperature-dependent equilibrium constant, \( a_i \) is the activity of species \( i \), \( v_i \) is the reaction stoichiometry of species \( i \), \( m_i \) is the molality of species \( i \) and \( \gamma_i \) is the activity coefficient of species \( i \).

Henry’s law is usually employed to relate the CO\(_2\) partial pressure, \( P_{\text{CO}_2} \), to the dissolved gas concentration in the amine solution, [CO\(_2\)], via equation (3.68).
\[ P_{CO_2} = H_{CO_2}[CO_2] \]

where \( H_{CO_2} \) is the Henry’s law constant.

The equilibrium equations (3.69) to (3.73) corresponding to reactions (3.60) – (3.66) are:

\[
K_1 = \frac{[RNH_2][H^+]}{[RNH_3^+]},
\]

(3.69)

\[
K_2 = \frac{[RNH_2][HCO_3^-]}{[RNHCOO^-]},
\]

(3.70)

\[
K_3 = \frac{[H^+][HCO_3^-]}{[CO_2]}
\]

(3.71)

\[
K_4 = [H^+][OH^-]
\]

(3.72)

\[
K_5 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}
\]

(3.73)

Apart from the equilibria equations, the system is also subject to mass and charge balance constraints:

Amine material balance:

\[ [MEA] = [RNH_2] + [RNH_3^+] + [RNHCOO^-] \]

(3.74)

Carbon material balance:

\[ [MEA]\alpha_{CO_2} = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RNHCOO^-] \]

(3.75)

Charge balance:

\[ [RNH_3^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [RNHCOO^-] \]

(3.76)

Where \([MEA]\) is the initial amine concentration in kmol m\(^{-3}\), \([CO_2]\) is concentration of dissolved \(CO_2\) kmol m\(^{-3}\) and \(\alpha_{CO_2}\) is the \(CO_2\) loading (mol \(CO_2\) (mol amine\(^{-1}\)).
There have been several attempts by various researchers to develop predictive models, built upon a large body of VLE data (Atwood et al., 1957; Danckwerts and McNeil, 1967; Edwards et al., 1978; Deshmukh and Mather, 1981; Austgen et al., 1989; Arcis et al., 2009) Thus, there are a number of approaches that can be employed to correlate experimental VLE data. Initially, curve-fitting attempts were adopted (Mason and Dodge, 1936) which then progressed to more rigorous thermodynamic models. The major equilibrium models for aqueous CO₂-amine systems are i) The Kent-Eisenberg model ii) The model of (Edwards et al., 1978) iii) Deshmukh- Mather method (Deshmukh and Mather, 1981) iv) Electrolyte- NRTL (e-NRTL) model (Chen et al., 1986) v) SAFT-VR model (Gaëtan, 1998) and other types of model such as the electrolyte –UNIQUAC model used by (Kaewsichan et al, 2001). The Kent-Eisenberg model was used in this thesis and is described below.

3.9.2.1. Kent-Eisenberg Model

(Kent and Eisenberg, 1976) proposed the first well-accepted VLE model for aqueous amine absorption processes. They developed a simple correlation method, which included all the non-ideality in the liquid phase into definite assigned equilibrium constants. Whilst it was not developed initially to be a predictive model, it is frequently used especially in industrial settings.

(Kent and Eisenberg, 1976) made the assumption that provided the MEA-CO₂-H₂O system behaves ideally, the Henry’s law constant and equilibrium constants should only be temperature dependent. The activity coefficients of all the species were set to unity. Initially, they fitted available published data to determine empirical expressions for the Henry’s law constant and the equilibrium constants \(K_3 – K_5\). Then they fitted published equilibrium partial pressure data for H₂S- MEA and CO₂-MEA systems to obtain an expression for \(K_1\), which represents the amine protonation and to obtain a similar expression for \(K_2\), which represents the
carbamate formation. Although only MEA or DEA solutions used for the selective absorption of mixed CO\textsubscript{2} and H\textsubscript{2}S gases were studied in the original paper by (Kent and Eisenberg, 1976), this model can easily be extended to other amines, even mixed amine systems. The temperature-dependent equilibrium constants K\textsubscript{i} (i = 1-5) and Henry’s constant H\textsubscript{CO2} are represented by the following empirical expression:

\[
\ln K_i(\text{or} H_{CO_2}) = a_i + b_i/T + c_i/T^2 + d_i/T^3 + e/T^4
\]  

(3. 77)

Where \(a_i\) to \(d_i\) are constants for T in °R. The values of these constants obtained by (Kent and Eisenberg, 1976) are listed in Table 3-7.

Table 3-7: Equilibrium constants used in the Kent-Eisenberg model (Kent and Eisenberg, 1976).

<table>
<thead>
<tr>
<th>Equilibrium Constant / mol L\textsuperscript{-1}</th>
<th>a</th>
<th>b \times 10\textsuperscript{-4}</th>
<th>c \times 10\textsuperscript{-8}</th>
<th>d \times 10\textsuperscript{-8}</th>
<th>e \times 10\textsuperscript{-8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>K\textsubscript{1}</td>
<td>-3.3636</td>
<td>-1.0532</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K\textsubscript{2}</td>
<td>6.69425</td>
<td>-0.556349</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K\textsubscript{3}</td>
<td>241.818</td>
<td>53.6855</td>
<td>-4.8123</td>
<td>1.94</td>
<td>-2.96445</td>
</tr>
<tr>
<td>K\textsubscript{4}</td>
<td>39.5554</td>
<td>-17.7822</td>
<td>1.843</td>
<td>-0.8541</td>
<td>-1.4292</td>
</tr>
<tr>
<td>K\textsubscript{5}</td>
<td>-294.74</td>
<td>65.5893</td>
<td>-5.9667</td>
<td>2.4249</td>
<td>-3.7192</td>
</tr>
<tr>
<td>H\textsubscript{CO2}</td>
<td>22.2819</td>
<td>-2.48951</td>
<td>0.223996</td>
<td>-0.090918</td>
<td>0.12601</td>
</tr>
</tbody>
</table>

The Kent-Eisenberg model has proven to be extremely popular amongst industry experts, due to its relative simplicity and reasonable accuracy. Several researchers in academia have also used this model to correlate their experimental data. (Kritpiphat and Tontiwachwuthikul, 1996) employed this model for their solubility data of CO\textsubscript{2} in AMP, whilst (Park et al., 2002) fitted their data for CO\textsubscript{2} solubility in MEA, DEA, AMP, MEA + AMP and DEA + AMP to obtain empirical expressions for the equilibrium expressions for the amine protonation (K\textsubscript{i}) and carbamate formation (K\textsubscript{2}). The correlations obtained by (Park et al., 2002) were then
compared with experimental data obtained by (Tontiwachwuthikul et al., 1991) which, achieved reasonable results within an average deviation of $\leq 14.9\%$.

The Kent-Eisenberg model has been found to be accurate within the CO$_2$ loading range of 0.20 – 0.70 mol CO$_2$ (mol amine)$^{-1}$ (Weiland et al., 1993), but is inaccurate at more extreme CO$_2$ loadings.

3.10. Review of the mechanisms of iron dissolution and hydrogen evolution

This section reviews the literature on the proposed mechanisms for iron dissolution, as well as the reported exchange current densities and the corresponding Tafel slopes. Studies conducted on the exchange current densities and Tafel constants for hydrogen evolution on Fe will also be discussed. Finally, a review on the few experimental studies of Tafel slopes and exchange current densities in CO$_2$-H$_2$O systems will be presented.

3.10.1. Mechanism of the dissolution of iron

3.10.1.1. Catalytic mechanism

(Drazic, 1989) provides a comprehensive review of the mechanisms for the dissolution of iron. (Roiter et al, 1939) published the first set of studies on the anodic dissolution of iron, which were carried out in acidic iron (II) sulfate (FeSO$_4$) solutions. The experiments were conducted by anodic constant - current (galvanostatic) measurements, from which they obtained a Tafel slope of $\approx 60$ mV dec$^{-1}$ and an exchange current density ($j_0$) of $10^{-8}$ A cm$^{-2}$. Subsequently (Kuznetsov and Iofa, 1947) studied the anodic dissolution of iron in 1 M hydrochloric acid (HCl) and recorded an anodic Tafel slope of $\beta_a \approx 60$ mV dec$^{-1}$. In a following report (Kuznetsov et al., 1947), anodic dissolution measurements were conducted in alkaline 2 M sodium hydroxide (NaOH) and they reported an anodic slope $\beta_a \approx 40$ mV dec$^{-1}$. Thus, a reaction mechanism in which a second-order reaction dependence on OH$^-$ ions was proposed. By
comparing their results with those conducted in acidic media, they concluded that these two reactions either occur via different mechanisms or are strongly affected by the solution pH.

The influence of pH on the anodic dissolution of iron was the motivation behind the first detailed suggestion for the iron dissolution mechanism. (Hoar and Hurlen, 1959) found the reaction order with respect to [OH\(^-\)] \(p_{\text{OH}} = 1\), with \(\beta_a = RT / 2F\) in sulfuric acid solutions. Soon after, (Bonhoeffer and Heusler, 1956) reported \(p_{\text{OH}} = 1.6\) which they took to be 2 and \(\beta_a = RT/2F\). Based on this, (Heusler, 1957) proposed a mechanism for Fe dissolution in which they suggested the participation of a species (FeOH\(_\text{ad}\)) as a catalyst. The mechanism suggests the simultaneous transfer of two electrons in one reaction step, which had not been previously featured in electrode kinetics. This mechanism will be described in more detail in section 3.10.1.2.

(Bockris, Despic and Drazic, 1961) also conducted studies of Fe dissolution in acid sulfate, chloride, perchlorate and nitrate solutions and obtained anodic slopes \(\beta_a = 2RT/3F\) and cathodic slopes \(\beta_c = 2RT/ F\) and the reaction order in [OH\(^-\)] was \(= 1\). Based on this and other observation, (Bockris, Despic and Drazic, 1961) proposed the well known ‘BDD mechanism’, a consecutive electrode mechanism established upon the existence of an intermediate species (Fe(OH))\(^+\)), produced from (FeOH) which participated in the mechanism sequence but no longer acted as a catalyst. Unlike the mechanism proposed by (Heusler, 1958), only single electron steps were considered to be involved.

Table 3-7 summarises the results obtained by various authors on the dissolution of iron in acidic, neutral and alkaline media, respectively. It appears that amongst other factors, the condition of the metal surface, the type and the content of the steel also play a significant role (Akiyama et al., 1970; Felloni, Cozzi and Cammarota, 1967; Burnstein and Kearns, 1984). Based on a comprehensive collection of Fe dissolution kinetic data, there is a clear dependence
of the experimental results on the properties of the iron surface, such as the type of impurities, the dislocation density and internal stresses and crystallinity. (Lorenz & Eichkorn, 1965; Hilbert et al., 1971) observed that the same sample of iron can produce diverse kinetic data, depending on both the surface and internal structure of the metal. (Akiyama et al., 1970) found that annealing of the iron sample could shift the Tafel slope for the anodic dissolution ($\beta_a$) from 30 to 40 mV dec$^{-1}$, while the duration for which the iron surface was in contact with the electrolyte could decrease the slope from 60 to 40 mV dec$^{-1}$.

(Drazic and Vorkapic, 1978) proposed a ‘branching mechanism’ to account for the observed changes in the rate determining step in the BDD reaction mechanism. (Schweickert et al., 1980) and (Keddam et al., 1981) proposed an alternative but similar branching mechanism.

In terms of experimental measurements for corrosion in the aqueous amine-CO$_2$ solutions, it is important to determine if the kinetic data for pure iron can be used reliably as an acceptable surrogate for those on carbon steel, from which the typical amine scrubbing equipment are fabricated. As for the anodic reaction, the answer is yes; however, for the cathodic reaction, evidence exists that the presence of Fe$_3$C may affect the mechanism and may also change the rate-determining step from that on pure iron (Flitt and Bockris, 1982).

The effect of pH on amine-CO$_2$-H$_2$O systems is a fundamental process parameter, so the effect of pH on the kinetics and mechanisms of Fe dissolution and passivation will be discussed below.
Table 3-8: Compilation of diagnostic criteria for Fe dissolution and deposition reactions obtained under different experimental conditions (Drazic, 1989).

<table>
<thead>
<tr>
<th>Solution</th>
<th>T / °C</th>
<th>pH</th>
<th>$\beta_a$ / mV dec$^{-1}$</th>
<th>$j_a$ / A cm$^{-2}$</th>
<th>Reaction order in [OH$^-$]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25 M FeSO$_4$</td>
<td></td>
<td></td>
<td></td>
<td>60</td>
<td>10$^8$</td>
<td>(Roiter et al., 1939)</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ + 0.5 M Fe$_2$(SO$_4$)$_3$</td>
<td></td>
<td>1.2 - 4.9</td>
<td></td>
<td>35 – 45</td>
<td></td>
<td>(Bockris, Despic and Drazic, 1961)</td>
</tr>
<tr>
<td>H$_2$SO$_4$ + K$_2$SO$_4$</td>
<td></td>
<td>0.3 - 2</td>
<td></td>
<td>40</td>
<td></td>
<td>Hilbert et al., 1971</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$</td>
<td>40</td>
<td></td>
<td></td>
<td>10$^{-13}$</td>
<td></td>
<td>(Foroulis, 1966)</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ + 0.5 M Na$_2$SO$_4$</td>
<td>45</td>
<td></td>
<td></td>
<td>0.8</td>
<td></td>
<td>(Aksut, 1983)</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ Un-annealed</td>
<td>38 - 45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Akiyama et al., 1970)</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ Annealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$SO$_4$ + Na$_2$SO$_4$</td>
<td>0</td>
<td>60</td>
<td>0.75 - 1.2</td>
<td>40</td>
<td>1</td>
<td>(Bala, 1984)</td>
</tr>
<tr>
<td>1 M H$_2$SO$_4$ + Na$_2$SO$_4$</td>
<td>2.1</td>
<td>30</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ + 0.5 M Fe$_2$(SO$_4$)$_3$</td>
<td>2.4</td>
<td>85</td>
<td>1.2 - 4.9</td>
<td>34</td>
<td>1.75</td>
<td>(Bockris and Kita, 1961)</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ + Na$_2$SO$_4$</td>
<td>3.3</td>
<td>36</td>
<td>1 - 3.3</td>
<td>40</td>
<td>1.4</td>
<td>(Kelly, 1961)</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$ + (0.01 - 0.5) M Na$_2$SO$_4$</td>
<td>28</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
<td>(Shemenski et al., 1965)</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$</td>
<td>40</td>
<td>45</td>
<td>&lt; 3.5</td>
<td>38</td>
<td>1.0</td>
<td>(Abdul et al., 1972)</td>
</tr>
<tr>
<td>1.5 M H$_2$SO$_4$ + K$_2$SO$_4$</td>
<td></td>
<td></td>
<td>&gt; 3.5</td>
<td>40</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>0.25 M H$_2$SO$_4$ + 1 M K$_2$SO$_4$</td>
<td>25</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td>(Felloni, 1968)</td>
</tr>
<tr>
<td>FeCl$_2$ + KCl + HCl</td>
<td>1 - 4</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td>(Hurlen, 1962)</td>
</tr>
<tr>
<td>1 M HCl + KCl</td>
<td>1.5 – 3</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td>(Frankenthal, 1971)</td>
</tr>
<tr>
<td></td>
<td>0 - 1.5</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Neutral Media

<table>
<thead>
<tr>
<th>Solution</th>
<th>T</th>
<th>pH</th>
<th>$\beta_a$ / mV dec$^{-1}$</th>
<th>$j_0$ / A cm$^{-2}$</th>
<th>Reaction order in [OH$^-$]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Lorenz and Vilche, 1972)</td>
</tr>
<tr>
<td>No stirring</td>
<td>25</td>
<td>4.7-6</td>
<td>64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Drazic and Hao, 1982)</td>
</tr>
<tr>
<td>Stirring</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 Na$_2$SO$_4$</td>
<td>20</td>
<td>6.2-7.9</td>
<td>60</td>
<td>0</td>
<td></td>
<td>(Hoar, 1961)</td>
</tr>
<tr>
<td>0.5 Na$_3$BO$_3$ + NaOH + 2.5 M Na$_2$SO$_4$</td>
<td>20</td>
<td>6-10</td>
<td>60</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Alkaline Media

<table>
<thead>
<tr>
<th>Solution</th>
<th>T</th>
<th>pH</th>
<th>$\beta_a$ / mV dec$^{-1}$</th>
<th>$j_0$ / A cm$^{-2}$</th>
<th>Reaction order in [OH$^-$]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 – 3M NaOH</td>
<td>20</td>
<td>$&gt;$ 3.5</td>
<td>30-40</td>
<td></td>
<td></td>
<td>(Kabanov et al., 1947)</td>
</tr>
<tr>
<td>0.1- 3 M NaOH</td>
<td>25</td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td>(Hurlen, 1963)</td>
</tr>
<tr>
<td>0.1 KOH + 1M KCl</td>
<td>25</td>
<td></td>
<td>65</td>
<td></td>
<td></td>
<td>(Asakura, Nobe, 1971)</td>
</tr>
<tr>
<td>0.05 – 5M KOH</td>
<td>25</td>
<td></td>
<td>65-70</td>
<td></td>
<td></td>
<td>(Drazic and Hao, 1982)</td>
</tr>
</tbody>
</table>
3.10.1.2. The mechanism of Fe dissolution in Acidic solutions

(Heusler, 1958) suggested a mechanism for iron dissolution based on the results of steady-state measurements with a recorded anodic and cathode Tafel slope, $\beta_a = \beta_c = 30$ mV dec$^{-1}$ and $p_{OH^-} = 2$ and $\beta_a = \beta_c = 30$ mV dec$^{-1}$ from transient measurements in perchlorate solutions.

The rate determining step was proposed as:

$$Fe + (OH^-) + (FeOH)_{ads} \rightarrow FeOH^+ + (FeOH)_{ads} + 2e^- \quad (3.78)$$

followed by a fast equilibrium reaction

$$FeOH^+ \leftrightarrow Fe^{2+} + OH^- \quad (3.79)$$

(FeOH)$_{ads}$ is considered as a catalyst, formed via a slow parallel reaction:

$$Fe + H_2O \leftrightarrow (FeOH)_{ads} + H^+ + e^- \quad (3.80)$$

The transient Tafel lines from galvanostatic peak potentials were thought to involve the catalyst (FeOH)$_{ads}$, such that:

$$j_{a,in} = F(FeOH)_{ads}(FeOH)_{ads,cat}[OH^-] \exp \left( \frac{E^\eta}{RT} \right) \quad (3.81)$$

The catalyst (FeOH)$_{ads}$ slowly accumulates and the steady state current density is given by:

$$j_{a,ss} = k_{SS}[OH^-]^2 \exp \left( \frac{2E^\eta}{RT} \right) \quad (3.82)$$

giving $\beta_a = 29$ mV dec$^{-1}$ and $p_{OH^-} = 2$.

For the cathodic reaction:

$$FeOH^+ + Fe(FeOH)_{ads} + 2e^- \rightarrow Fe + OH^- + Fe(FeOH)_{ads} \quad (3.83)$$

Fe(FeOH)$_{ads}$ is the adsorbed catalyst formed from the reaction:
\[
Fe + FeOH^+ + e^- \leftrightarrow Fe(FeOH)_{ads}
\]  
(3.84)

The steady state current density would be represented by:

\[
ij_{c,SS} = k_{SS}[OH^-]^2[Fe^{2+}] \exp\left(\frac{2\phi}{RT}\right)
\]  
(3.85)

giving \( \beta_c = 30 \text{ mV dec}^{-1} \) and \( p_{Fe^{2+}} = 2 \) and \( p_{OH^-} = 2 \)

The foundation of this mechanism was the observation by (Heusler, 1958) of the transient Tafel slopes \( \beta_a = 60 \text{ mV dec}^{-1} \), with an anodic steady-slope of \( \beta_a = 30 \text{ mV dec}^{-1} \) observed by (Hoar and Hurlen, 1959) and also by (Heusler, 1957) although it was not published. (Heusler, 1958) found the coefficient \( \delta \log j_{corr} / \delta \text{pH} \) to be zero while the mechanism predicts -2/5. Subsequently, (Heusler, 1958) suggested a physical interpretation for the catalysts \( \text{FeOH}_{ads} \) and \( \text{Fe(FeOH)}_{ads} \), in that they represent activities at kink sites. The catalytic mechanism is based on an assumption that the surface morphology of iron is independent of the electrode potential; whereas there is evidence from electron microscopic studies that the distance between edge sites is dependent on the potential (Bockris et al., 1961).

(Bockris et al., 1961) found several inconsistencies with the catalytic mechanism. Firstly, highlighted that (Heusler, 1958) neglected the fact that the pH at the interface differs from that in the bulk solution and depends upon potential. They also pointed out that the mechanism involves a single reaction step with the simultaneous transfer of two electrons, which results in calculated heats of reaction that are significantly larger than was observed. Thus, Bockris, Despic and Drazic, proposed the BDD mechanism, which is based on the concept that Fe dissolution occurs in two consecutive one-electron-transfer steps. The reaction sequence shown in equations (3.86) – (3.88) was suggested as representing the mechanisms under the conditions resulting in a reaction order of unity with respect to OH\(^-\) and \( \beta_a = 2RT/3F \) (38 mV dec\(^{-1}\)).
\[
Fe + H_2O \leftrightarrow (FeOH)_{ads} + H^+ + e^- \quad (3.86)
\]
\[
(FeOH)_{ads} \xrightarrow{rd} FeOH^+ + e^- \quad (3.87)
\]
\[
FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O \quad (3.88)
\]

The mechanism was established from experimental data measured in sulfate solutions within a pH range of 1-5 and the effect of other anions was also studied. (Bocrkis et al., 1961) also made measurements to obtain the cathodic data for Fe deposition, which included the co-deposition of H and the resulting pH change. They accomplished this by making parallel measurements of the hydrogen evolution rate, so the total current density \(j_{fe}\) could be deconvoluted from \(j_{total}\) and the interfacial pH could be calculated. The cathodic slope \(\beta_c\) was calculated to be 38 mV dec\(^{-1}\) (2RT/3F) which corresponded with the experimental results.

The BDD mechanism was used by several researchers to elucidate their experimental results. However, there was a significant issue, which was frequently raised about the amount and stability of the hydroxo intermediate in the proposed mechanism when the reaction occurs in acidic media. (Batrakov et al., 1968) conducted faradaic impedance measurements and calculated that the surface coverage (\(\theta\)) of (FeOH)\(_{ads}\) in sulfuric acid solutions varies between 0.1 - 4% for the potential range of -0.2 to +0.12 V (versus standard hydrogen electrode (SHE)).

The BDD mechanism predicts an anodic slope of 40 mV dec\(^{-1}\), but as can be seen from Table 3-7, a few other researchers reported \(\beta_a\) of 30 mV dec\(^{-1}\) for steady state measurements that corresponds with the catalytic mechanism by (Hesuler, 1958). Hilbert et al., (1971) attempted to explain the inconsistency between the results obtained by the different researchers. They conducted a series of experiments from which they recorded a \(\beta_a\) of 40 mV dec\(^{-1}\) and a reaction order of 1 with respect to OH\(^-\) for annealed iron wire, \(\beta_a\) of 30 mV dec\(^{-1}\) and a reaction order of 1.70 with respect to OH\(^-\) when the wire was subjected to a large strain. (Hilbert et al., 1971)
proposed that this was due to a change in mechanism from the BBD to the catalytic mechanism, resulting from the manifestation of a sizeable amount of ‘active sites’ as a result of the strain on the wire. Hence, it was concluded that the annealed and less strained material undergoes anodic dissolution via the BDD mechanism, while heavily strained materials undergo the catalytic mechanism proposed by (Hesuler, 1958).

(Drazic and Vorkapic, 1978) suggested that the adsorption energy of the hydroxo intermediate \((\text{FeOH})_{\text{ads}}\) increases with strain, leading to a rate-determining desorption reaction (reaction (3.89)) and the anodic Tafel slope \(\beta_a\) shifts to \(RT/2F\).

\[
(\text{FeOH})_{\text{ads}} \rightarrow (\text{FeOH})_{\text{solt}}
\]  

(Drazic and Vorkapic, 1978) suggested that the change in kinetic parameters was less likely to result from a change in mechanism but from a change in the rate determining step in the same reaction sequence. They then proposed a modified version of the BDD mechanism after taking into account the possibility of the presence of adsorbed \(\text{FeOH}, \text{FeOH}^+\) and \(\text{Fe(OH)}_2\) species even in acidic media and also the possibility that the desorption of these adsorbed species could be activated and hence the rate determining step. This modified version of the BDD mechanism, called the branching mechanism, is shown in Figure 3-12. Consequently, for an activated surface, the anodic slope \(\beta_a\) tends to \(RT/2F\) and the reaction order with respect to \(\text{OH}^-\) can shift towards 2, if the rate constants for the two parallel desorption reactions are of the same order. (Drazic and Vorkapic, 1978) suggested that there are conditions under which the branching mechanism occurs and the diagnostic criteria are shown in Table 3-9.
Table 3-9: Diagnostic Criteria for the ‘Branching Mechanism’ at Low and High Surface Coverages if Step 2, 3 or 4 is Rate-Determining’ (Drazic and Vorkapic, 1978).

<table>
<thead>
<tr>
<th>Rate determining step</th>
<th>( \theta &lt;&lt; 1 )</th>
<th>( \theta &gt;&gt; 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_a )</td>
<td>( \beta_a / \text{mV dec}^{-1} )</td>
<td>Reaction order in [OH(^-)]</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>30</td>
</tr>
</tbody>
</table>

(El Miliguy et al., 1975) suggested that there are three different possible states that can occur: the activated dissolution, a transition range, pre-passive behaviour and a passive state. In the activated dissolution region, the BDD mechanism is operative, in the transition range, Fe(OH)\(_2\) affects the dissolution process by acting as a membrane inhibitor. The branching mechanism by (Drazic and Vorkapic, 1978) applies to the activated dissolution and pre-passive regions.

### 3.10.2. The influence of halide ions on dissolution kinetics

Several researchers such as (Hurlen, 1962; Lorenz, 1965; Heusler and Cartledge, 1961; Darwish et al., 1973) studied the effect of anions on the dissolution of iron. They all reported that anions, particularly halide ions in concentrations of < 1 M in mixtures of sulfate or perchlorate, exhibited some sort of inhibitive effect on Fe dissolution. Anodic polarization curves obtained by (Heusler and Cartledge, 1961; Schwabe and Voigt, 1969) exhibited an “S” shape with a degree of hysteresis and a strong dependence on the method of surface preparation, while the polarization curves obtained by (Hurlen, 1962; Lorenz, 1965; Darwish et al., 1973) had well defined Tafel regions with higher slopes than in halide-free perchlorate solutions. The reason for this discrepancy was considered to be that the second group of results arose from electrode surfaces that have been anodically treated previously for some time,
although some of the experimental details are not well defined. The adsorption of halide ions is relatively slow and the results of the Tafel measurements will depend on the rate at which the experimental studies are conducted, which explains the reason for a spread in experimental results.

There have been several mechanisms proposed for the effects of halide ions, all of which make the assumption that these halide ions are specifically adsorbed and compete with other species for the surface. The reaction mechanism also incorporates a step in which adsorbed halide ions form a particular kind of adsorbed complex with Fe and OH species that subsequently desorbs from the surface. This was incorporated to avoid the argument that the adsorption of halide ions should become stronger at more positive potentials, while also explaining the reason for the negative reaction order for halide ions and the S-shaped polarization curves.

(McCafferty and Hackermann, 1972) studied the Fe dissolution kinetics over a wide concentration range of chloride ions (1 – 6 M). The OH$^{-}$ accelerated mechanism proposed by (Lorenz, 1965) was assumed with a reaction order of -1 with respect to [H$^{+}$] and adapted to take into account the competitive adsorption of OH$^{-}$ and Cl$^{-}$ ions. The proposed reaction sequence is outlined from (3. 90) – (3. 93).

\[
\begin{align*}
Fe + H_{2}O & \leftrightarrow Fe \cdot H_{2}O_{ads} \leftrightarrow FeX^{-}_{ads} + H_{2}O \quad (3. 90) \\
Fe \cdot H_{2}O_{ads} + X^{-} & \leftrightarrow FeOH^{-}_{ads} + H^{+} + X^{-} \quad (3. 91) \\
FeX^{-}_{ads} + FeOH^{-}_{ads} & \rightarrow FeOH^{+} + Fe + X^{-} + 2e^{-} \quad (3. 92) \\
FeOH^{+} + H^{+} & \leftrightarrow Fe^{2+} + H_{2}O \quad (3. 93)
\end{align*}
\]
Then at higher H\(^+\) concentrations for which the reaction order with respect to [H\(^+\)] was 2, a different, H\(^+\) accelerated mechanism was proposed and outlined from (3. 94) – (3. 97).

\[
Fe + H_2O \leftrightarrow Fe \cdot H_2O_{\text{ads}} \quad (3. 94)
\]

\[
Fe \cdot H_2O_{\text{ads}} + X^- \leftrightarrow FeX^-_{\text{ads}} + H_2O \quad (3. 95)
\]

\[
FeX^-_{\text{ads}} + H^+ \leftrightarrow FeX^- \cdot H^+ \equiv \text{complex} \quad (3. 96)
\]

\[
FeX^- \cdot H^+ + H^+ \stackrel{r_{ds}}{\rightarrow} FeX^+ + 2H^+ + 2e^- \quad (3. 97)
\]

(Chin and Nobe, 1972) proposed an alternative mechanism based on measurements in chloride ions within a concentration range of (0.01 – 1.9 M) and a pH range of 0.0 – 1.8.

\[
Fe + Cl^- + H_2O \leftrightarrow (FeClOH)^-_{\text{ads}} + H^+ + e^- \quad (3. 98)
\]

\[
(FeClOH)^-_{\text{ads}} \stackrel{r_{ds}}{\rightarrow} FeClOH + e^- \quad (3. 99)
\]

\[
FeClOH + H^+ \rightarrow Fe^{2+} + Cl^- + +H_2O \quad (3. 100)
\]

The adsorption of (FeClOH\(^-\))\(_{ads}\) was assumed to follow a Langmuir isotherm.

For concentrated chloride solutions and very small acid concentrations, (Chin and Nobe, 1972) modified the reaction sequence and suggested the mechanism below:

\[
Fe \cdot H_2O_{\text{ads}} + Cl^- \leftrightarrow FeCl_{\text{ads}} + H_2O + e^- \quad (3. 101)
\]

\[
FeCl_{\text{ads}} + H^+ \leftrightarrow FeClH^+ \quad (3. 102)
\]

\[
FeClH^+ + Cl^- \stackrel{r_{ds}}{\rightarrow} FeCl_2 + H^+ + e^- \quad (3. 103)
\]
For this mechanisms it is assumed that the surface coverage adsorbed species FeCl, $\theta_{\text{FeCl}} \rightarrow 1$ and that of FeClH$^+$, $\theta_{\text{FeClH}^+} \rightarrow 0$ and they follow the Langmuir isotherm.

3.10.3. **Mechanisms for Dissolution of Iron in Solutions in the Mid-pH range**

There have been only a select number of reports on the mechanistic analysis of the anodic dissolution of iron in neutral solutions, in spite of the fact that most natural corrosion occurs in solutions with a close to neutral bulk pH. This may be due to several complications such as the fact that the pH at the iron | solution interface is particularly dependent on the current density and surface coverage with adsorbed oxide or hydroxide films is significantly higher in acid and varies with time and potential.

(Hoar and Ferrer, 1965) and (Lorenz and Vilche, 1972) conducted some of the earliest studies within neutral solutions in which (Hoar and Ferrer, 1965) obtained an anodic Tafel slope $\beta_a$ of 60 mV dec$^{-1}$ in dilute solutions of several anions, whilst (Lorenz and Vilche, 1972) recorded $\beta_a$ as 66 mV dec$^{-1}$ and a reaction order of 0.7 with respect to [OH$^-$] in stirred sulfate solutions within the pH range of 5-6. The active dissolution of iron in both studies was interpreted by the BDD mechanism and it was also assumed that increases in the local pH led to higher surface coverage with intermediate species, following a Tempkin adsorption isotherm and resulting in a Tafel slope of RT/F.

(Drazic and Hao, 1982) carried out a more in-depth study on the effect of pH in neutral sulfate solutions (pH 6 - 8). They found that the rate of the anodic reaction was independent of pH and recorded an anodic Tafel slope of 60 mV dec$^{-1}$ at lower current densities and 120 mV dec$^{-1}$ at higher current densities, the latter also determined by (Freiman and Kolotyrkin, 1965). Thus, (Drazic and Hao, 1982) proposed an extension to the BDD branching mechanism to accommodate neutral solutions which corresponds to the surface coverage by intermediate
species FeOH\textsubscript{ads} $\theta_{\text{FeOH}} \rightarrow 1$, a reaction order of 0 with respect to OH$^-$ ions and $\beta_a$ as 120 mV dec$^{-1}$.

3.10.4. Mechanisms of Iron Dissolution in Alkaline Solutions

More extensive research on Fe dissolution at alkaline pH has been reported than in the other pH ranges, due to its relevance to Fe-Ni batteries. One of their earliest notable mechanisms is by (Kabanov et al., 1947) in which two anodic Tafel slopes of 30 and 40 mV dec$^{-1}$ and $p_{OH}$ of 2 was observed.

$$Fe + OH^- \leftrightarrow FeOH_{ads} + e^- \quad (3.104)$$

$$FeOH_{ads} + OH^- \rightarrow FeO_{ads} + H_2O + e^- \quad (3.105)$$

$$FeO_{ads} + OH^- \leftrightarrow HFeO_2^- \quad (3.106)$$

$$HFeO_2^- + H_2O \leftrightarrow Fe(OH)_2 + OH^- \quad (3.107)$$

Whilst the existence of oxide or hydroxide films was accepted generally within this mechanism, initially there was a limited use of spectroscopic methods to interrogate the surfaces. However, (Kolotyrkin et al., 1987) employed modulated reflectance spectroscopy to examine presence of FeOH\textsubscript{ads} species in 0.1 M NaOH and Neugeberger et al employed internal reflection studies from which they proposed that HFeO$_2^-$ (adding water gives Fe(OH)$_3^-$?) is the reaction product and forms Fe(OH)$_2$ on hydrolysis.

(Drazic and Hao, 1982) also conducted an extensive study of activated ARMCO iron in alkaline solutions from which they obtained a reproducible Tafel line with a slope of about 65 mV dec$^{-1}$ and a reaction order of 1.1 with respect to [OH$^-$. With the presence of various concentrations of [HFeO$_2^-$] ions, they observed a negative reaction order of -0.45 with respect to these species. They proposed a mechanism involving:
\[ \text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}_{ads} + \text{H}^+ + e^- \quad (3.108) \]

\[ \text{FeOH}_{ads} + \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_{2ads} + \text{H}^+ + e^- \quad (3.109) \]

\[ \text{Fe(OH)}_{2ads} + \text{OH}^- \leftrightarrow \text{HFeO}_2^- + \text{H}_2\text{O} \quad (3.110) \]

\[ \text{HFeO}_2^- + \text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_2 + \text{OH}^- \quad (3.111) \]

If the second step (3.109) in the mechanism is assumed to be rate determining with a surface coverage of FeOH and FeOH$_2$ between 0.2-0.8 and the adsorption follows a Temkin adsorption isotherm, the predicted anodic Tafel slope $\beta_a$ is $2.3RT/F$ and the reaction orders with respect to [OH$^-$] and [HFeO$_2^-$] are equal to 1 and -0.5 respectively, in agreement with the experimental results. The negative reaction order with respect to HFeO$_2^-$ ions is in agreement with the effect of these species as inhibitors for the dissolution process.

(Kabanov et al., 1947) also suggested a similar mechanism to that of (Drazic and Hao, 1982). They obtained an experimental anodic slope $\beta_a$ of 40 mV dec$^{-1}$ which is also in accordance with the proposed mechanism if the surface coverage of the intermediate species, FeOH and FeOH$_2$ is less than 0.2 and the absorption follows a Langmuir-type isotherm.
3.11. The Mechanism of Hydrogen Evolution Reaction (HER) on Iron

A comprehensive understanding of the hydrogen evolution reaction mechanism was only achieved after 1950 through pioneering work by (Tafel, 1905; Heyrovsky, 1927; Volmer, 1930; Funmkin, 1967; Conway, 1965; and Kita, 1966). Mechanistically there are three well-known steps for the Hydrogen evolution reaction commonly referred to as the Volmer (1), Heyrovsky (2) and Tafel (3) steps.

Figure 3-13: General reaction scheme for iron dissolution (Drazic, 1989)
1. Volmer: \[ H^+ + e^- \rightarrow H_{ads} \]  \hspace{1cm} (3.112)

2. Heyrovsky: \[ H_{ads} + H^+ + e \rightarrow H_2(g) \]  \hspace{1cm} (3.113)

3. Tafel: \[ H_{ads} + H_{ads} \rightarrow H_2(g) \]  \hspace{1cm} (3.114)

The hydrogen evolution reaction is not a single step reaction; instead it proceeds in two steps with only one intermediary reaction (Weber and Peria, 1967; Eastman and Nathan, 1975; Park, 1975). There are two widely accepted pathways for the conversion of \( H^+ \) ions to molecular hydrogen. They are the discharge, chemical recombination (Volmer-Tafel mechanism) and the discharge, electrochemical desorption (Volmer-Heyrowsky) mechanism. (Weber and Peria, 1967; Eastman and Nathan, 1975; Park, 1975; Papp and Pritchard)

In the first pathway (1 and 3) as proposed by (Volmer, 1930) and (Tafel, 1905), protons are discharged onto the metal surface sites to form an adsorbed hydrogen atom by a single electron transfer (reaction (3.112)) (Weber and Peria, 1967; Eastman and Nathan, 1975; Park, 1975; Papp and Pritchard). This is followed by a chemical reaction in which the adsorbed hydrogen atoms (\( H_{ads} \)) diffuse to each other across the electrode surface and undergo a chemical recombination to form \( H_2(g) \), which accumulate to form bubbles (reaction (3.114)).

(Volmer, 1930) suggested the first reaction (3.112) was the rate determining step, so the surface coverage of adsorbed hydrogen \( \theta_H \) will tend to be small because, as the H atoms are adsorbed on the surface, they immediately react to form molecular \( H_2 \). On the other hand, (Tafel, 1905) considered reaction (3.114) to be rate determining and the reaction (3.112) to be in quasi-equilibrium such that \( \theta_H \) will be significantly higher than suggested by (Volmer, 1930).

In the second pathway (1 - 2), the first step is the same, but the electrochemical recombination mechanism (reaction (3.113)) consists of a second proton discharge reaction on the adsorbed \( H_{ads} \) produced by the first proton discharge. In this reaction mechanism (Volmer-Heyrovsky),
the first step, the proton discharge on empty sites was considered by (Kobosew and Nekrassow, 1972) to be the rate determining step. This is followed by a fast proton discharge onto the adsorbed hydrogen atoms to form H₂, so the surface coverage of adsorbed hydrogen θ_H will tend to be low. However, it is more likely that the desorption is slow and becomes the rate determining step and hence θ_H → 1.

Hydrogen permeation rates through Fe have been measured to elucidate the rate determining step for both the mechanism involving the chemical recombination and the electrochemical desorption. It is possible to demonstrate that if the discharge of protons is the rate determining step while the recombination is the fast reaction:

\[ \frac{\partial \ln P_H}{\partial \eta} = -\frac{F}{4RT} \]  

(3.115)

but if the electrochemical desorption at θ_H = 1 is rate determining then:

\[ \frac{\partial \ln P_H}{\partial \eta} \rightarrow 0 \]  

(3.116)

Based on experimental observations, from the equilibrium potential down to ca. -0.4 (SHE) discharge of the protons (the first solution) was the rate determining step whilst at more negative potentials, electrochemical desorption (the second solution) was the rate determining step. Similar results have been observed in alkaline solutions (Bockris and Koch, 1961; Conway and Bai, 1984).

3.12. Experimental work in CO₂-containing solutions

(de Waard et al., 1975) established a relationship between the corrosion rate of bare steel in carbonic acid solutions and the CO₂ partial pressure, as discussed in Section 3.4.12. Their work was based on determining the corrosion rates of cylindrical carbon steel samples in a stirred glass cell at 0.1 – 1 bar CO₂ and at different temperatures. They reported Tafel slopes β_a = 40
mV dec\(^{-1}\) and $\beta_c = 120$ mV dec\(^{-1}\). These were the only values for the Tafel slope that were reported by (de Waard et al., 1975) and the effect of pH and temperature were neglected.

(Wieckowski et al., 1983) studied the behaviour of iron electrodes in CO\(_2\) saturated sodium chloride solutions at 25°C, pH 3.25 with the use of cyclic voltammetry. The measurements were conducted with the use of stationary and rotating disk (99.8 % purity) iron electrodes. The effects of pH, CO\(_2\) partial pressure and temperature were not considered and Tafel slope measurements were not conducted.

(Eriksrud et al., 1984) conducted a series of experiments in 4% NaCl, various synthetic and real formation waters and in an oil/salt/water mixture at 20°C and 60°C. The experiments involved the use of a flow rig to investigate the effects of flow on CO\(_2\) corrosion and the CO\(_2\) partial pressure was varied from 1 to 2 bars. The recorded anodic current densities were similar in both quiescent and flowing conditions, whilst a limiting cathodic current was measured, which increased with increasing flowrate. For measurements conducted at pH 3.88 and 20°C, they reported an anodic slope, $\beta_a = 40$ mV dec\(^{-1}\) and $\beta_c \rightarrow \infty$. They reported that at low temperatures (20°C), the corrosion rates appeared to be independent of the solution flow rate whilst the corrosion rate is highly flow rate-dependent at higher temperatures (60°C), especially in the absence of protective layers. However, the effect of pH and temperature on the Tafel constants was not included in their studies.

(Valentini et al., 1985) studied the behaviour of polycrystalline iron electrodes in stagnant and stirred K\(_2\)CO\(_3\) and KHCO\(_3\) solutions in the 0-75°C temperature range with the use of cyclic voltammetry. The potentiostatic studies by (Arvia et al., 1985) showed three oxidation peaks in stagnant solutions and two in stirred solutions. The initial oxidation peak was attributed to the formation of a prepassive layer consisting of an oxide of iron, probably Fe(OH)\(_2\). The second anodic stage was ascribed to the electrodissolution of iron through the prepassive layer.
As the reaction proceeded, both the thickness of the prepassive layer and the concentrations of Fe\textsuperscript{II} and anions at the electrode−solution interface increase. Once the concentration of these ions exceeded the solubility limit for FeCO\textsubscript{3}, the latter was formed on the iron surface. Therefore, they assigned the potential range of peak II to the formation a complex layer structure of an inner hydrous Fe(OH)\textsubscript{2} layer and an outer FeCO\textsubscript{3} layer. (Castro et al., 1986) also obtained voltammograms over a wide range of scan rates, electrode rotation rates and ionic strengths. Their results showed that the dissolution and passivation of iron in the aqueous solutions containing carbonate and hydrogen carbonate ions in the 7.7–9.2 pH range strongly depended on the hydrodynamics and the electrolyte composition. (Castro et al., 1986) also found two distinct current maxima in the polarisation curves, which they assigned to formation of formation of a prepassive Fe(OH)\textsubscript{2} inner layer and the simultaneous electrodissolution of iron through the prepassive layer.

(Simard et al., 1997) investigated the voltammetric response of 1024 mild steel electrodes in the presence of 0.05−0.5 M NaCO\textsubscript{3} and NaHCO\textsubscript{3} at pH 8.9 and 25°C. The voltammograms displayed an oxidation peak followed by a region of passivity. They observed a linear increase in the peak height with the concentration of NaHCO\textsubscript{3}, which they proposed to be as a result of the formation of a Fe\textsuperscript{2+}-HCO\textsubscript{3}/CO\textsubscript{3}\textsuperscript{2−} complex most likely in the form of FeHCO\textsubscript{3}\textsuperscript{+}(aq). Thus anodic dissolution peak was ascribed to the electrodissolution of iron in the form of soluble FeHCO\textsubscript{3}\textsuperscript{+} and/or Fe\textsuperscript{II} with no significant amount of oxides accumulated on the surface.

(Grey et al., 1990) conducted polarization measurements to identify the active dissolution mechanisms for carbon steel specimens in aqueous CO\textsubscript{2} as a function of pH and temperature. Aqueous CO\textsubscript{2}-containing solutions at pH 2−6 were prepared by dissolving NaHCO\textsubscript{3} in 0.15 NaCl and purging with CO\textsubscript{2} and solutions at pH 8−11 were prepared with NaHCO\textsubscript{3} and Na\textsubscript{2}CO\textsubscript{3} purged with N\textsubscript{2}. They suggested that there was a change in the cathodic reaction mechanism with pH which was directly related to changes in the CO\textsubscript{2} speciation. Thus,
different reactions were assumed at different pH ranges and the recorded Tafel constants are shown in Table 3-9. (Grey et al., 1990) proposed that at pHs 2-4, the active dissolution of iron was enhanced by the chemically--controlled reduction of $\text{H}_2\text{CO}_3$. At higher pHs (6-10), the iron dissolution was enhanced by the charge-transfer controlled reduction of $\text{HCO}_3^-$. They also observed a rapid increase in the corrosion rate from 25°C to 90°C, however, little increases were observed from 90°C to 125°C, which was attributed to changes in the kinetics of the iron oxidation reaction.

Table 3-9: Electrochemical parameters derived for the redox reactions from modelling the polarisation curves, pH 2 -10, 25°C (Gray et al., 1990).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>pH</th>
<th>Tafel Constant/ mV/dec$^{-1}$</th>
<th>Exchange Current Density/ A cm$^{-2}$</th>
<th>Reversible Potential mV</th>
<th>Limiting Current µA cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/ Fe$^{2+}$</td>
<td>2.0</td>
<td>50</td>
<td>0.00002</td>
<td>-924</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>55</td>
<td>0.05</td>
<td>-924</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>70</td>
<td>0.046</td>
<td>-924</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>72</td>
<td>0.024</td>
<td>-924</td>
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</tr>
<tr>
<td></td>
<td>10.0</td>
<td>124</td>
<td>0.47</td>
<td>-924</td>
<td>N/A</td>
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<tr>
<td>$\text{H}_2\text{O}/\text{H}_2$</td>
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<tr>
<td></td>
<td>6.2</td>
<td>160</td>
<td>0.2</td>
<td>-478</td>
<td>N/A</td>
</tr>
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<td></td>
<td>8.1</td>
<td>125</td>
<td>0.16</td>
<td>-478</td>
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<tr>
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<td>10.0</td>
<td>78</td>
<td>0.25</td>
<td>-478</td>
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<tr>
<td>$\text{H}^+/\text{H}_2$</td>
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<td></td>
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<td>120</td>
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<td>3200 32</td>
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<td>144 55</td>
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<td>160</td>
<td>2.5</td>
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<td>144 55</td>
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</tr>
<tr>
<td></td>
<td>8.1</td>
<td>160</td>
<td>4.6</td>
<td>-608</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>133</td>
<td>2.0</td>
<td>-608</td>
<td>N/A</td>
</tr>
</tbody>
</table>
3.13. References


DeBerry, D. W., Clark, W. S. and Yost, A. 1979. Corrosion Due to the Use of Carbon Dioxide for Enhanced Oil Recovery. DOE Final report MC/ 08442, SumX Corporation. Austin, TX. 19, 342


Hoar, T. P. and Holliday, R. D. 1953. The Inhibition by Quinolines and Thioureas of the Acid Dissolution of Mild Steel. 3, 502-513.  


Nyborg, R., and Dugstad, A. 1998. Mesa Corrosion Attack in Carbon Steel and 0.5% Chromium Steel, *Corrosion 98*, Paper 29, NACE. Houston, TX.


4. Chapter 4

Experimental Methods and Materials

Kinetic studies were conducted to identify the effect of temperature, CO₂ loading, pH, amine type, amine concentration and oxygen concentration on iron corrosion in aqueous amine solutions. Based on the collected data, corrosion mechanisms and rates, in principle, may be determined for every set of experimental conditions. The experiments were conducted with the expectation that a trend in corrosion rates would be identified, which would enable future prediction as functions of these process conditions. In order to be able to deduce trends, it was deemed important to obtain a large body of data covering a wide range of conditions typical of amine scrubbing processes. Due to the substantial amount of experimental data required, the experimental techniques were selected based on their ability to acquire useful data in the most effective and efficient way. Hence, techniques such as weight loss measurement were excluded.

This chapter details the experimental methods and materials used to obtain micro-kinetic data for the following purposes:
i. To obtain the oxidation and reduction kinetics of iron in aqueous MEA-H$_2$O-CO$_2$ systems as functions of temperature (25-80°C), CO$_2$ loading (0-0.6 mol CO$_2$ (mol amine)$^{-1}$), pH (8.10-12.55), MEA concentration (5-60 wt%) and oxygen concentration.

ii. To determine and assign the oxidation and reduction reaction mechanisms of iron in aqueous MEA-H$_2$O- CO$_2$ systems.

iii. Determination of corrosion rates via the Tafel extrapolation method as functions of the experimental variables listed above.

iv. As inputs for the development of a mechanistic model for the uniform corrosion of iron in CO$_2$-loaded MEA systems

The mechanism for iron corrosion was characterized further with the use of a quartz crystal microbalance, the mass detection device discriminating between the dissolution reaction occurring in CO$_2$-loaded MEA solutions from the predominantly passivation reactions occurring in unloaded solutions.

This chapter also details the mechanical design, configuration and operation of an electrochemical reactor developed for the measurement of dissolved iron concentrations and electrode currents as functions of time, under typical CO$_2$ absorption conditions. During the constant potential measurements, samples were taken from the anolyte compartment at fixed time intervals to be analysed subsequently by Inductively Coupled Plasma Spectroscopy Optical Emission Spectroscopy (ICP-OES). The dissolved Fe$^{II}$ concentrations determined by ICP-OES enabled partial current densities leading to iron dissolution to be deconvoluted from measured current densities.
4.1. Materials

This section details the main chemicals and materials used within the course of this project, the purity and the suppliers from which they were obtained.

4.1.1. Chemicals

The CO$_2$ absorption solvents tested within this project include the benchmark amine monoethanolamine (MEA), methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP) and aminoethylpiperazine (AEP). A ferrous sulfate (FeSO$_4$) bath was used for iron plating in the Electrochemical Quartz Crystal Microbalance measurements described in Section 4.4.4 below. In the absence of CO$_2$, pH adjustments to the amine solution were made with 1 M sulphuric acid (H$_2$SO$_4$). A solution of 1 M Na$_2$SO$_4$ was used as the supporting electrolyte for all the electrochemical measurements. The reagent grade and sources of all the chemicals used are given in Table 4-1.

Table 4-1: Common reagents

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reagent Grade</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine</td>
<td>AnalAr, ≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methyl-diethanolamine</td>
<td>AnalAr, ≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2-Amino-2-methyl-1-propanol</td>
<td>AnalAr, ≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Aminoethylpiperazine</td>
<td>AnalAr, ≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Iron(II) Sulfate Heptahydrate</td>
<td>AnalAr, ≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>AnalAr, ≥ 99.0 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>AnalAr, ≥ 99.0 %</td>
<td>Fisher Scientific</td>
</tr>
</tbody>
</table>

4.1.2. Standard reagents

The standard reagents listed in Table 4-2 were used for calibration of the Inductively Coupled Plasma Spectroscopy Optical Emission Spectrometer (ICP-OES) prior to commencing analyses of dissolved metal concentrations.
Table 4-2: Standard reagents

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reagent Grade</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Standard solution for ICP</td>
<td>1000 mg dm(^{-3}) Fe in 2% HNO(_3)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Phosphorus, Potassium, Silica, Aluminum,</td>
<td>1000 mg dm(^{-3}) Fe in 5% HNO(_3) / Tartaric Acid / HF</td>
<td>SPEX CertiPrep</td>
</tr>
<tr>
<td>Antimony, Arsenic, Barium, Beryllium, Boron,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium, Chromium, Cobalt, Copper, Iron,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead, Lithium, Magnesium, Manganese,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molybdenum, Nickel, Selenium, Silver,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium, Strontium, Thallium, Tin, Vandium,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc Standard for ICP</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.3. Electrode Materials

Where required, the electrodes were cut into the desired size to suit the experimental procedure. Although carbon steel is the most commonly used material for pipe work and equipment in CO\(_2\) absorption plants, pure iron was used as the working electrode for most of the experiments reported in this thesis to elucidate its electrochemical behaviour in aqueous amine-CO\(_2\) solutions before considering the additional complexity of alloying elements. Iron cylindrical discs of diameter 6.4 mm (0.322 cm\(^2\)) and a 3.125 cm\(^2\) platinum flag was used as the working and counter electrodes for the rotating disc electrode experiments detailed in Section 4.4.2.1. The working electrode for the Electrochemical Quartz Crystal microbalance experiments described in Section 4.4.4 was made partially in-house by electroplating iron on Au-TiO\(_2\) coated Quartz Crystals supplied by Metrohm Autolab B.V., Utrecht (NL). For the flow reactor experiments in Section 4.5.1, three additional types of working electrode materials were tested in addition to pure Fe, namely carbon steel 1020 (Carbon Steel S355), Carbon Steel 1038.
(Carbon Steel EN8) and stainless steel AISI 304. The working electrodes used each had a surface area of 400 cm$^2$ and a thickness of 10 mm, whilst the platinised titanium electrode of equal surface area had a thickness of 1 mm. The electrode materials, their chemical composition and suppliers are listed in Table 4-3.

Table 4-3: Electrode Materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Material Grade</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Slug</td>
<td>≥ 99.95</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Platinum foil</td>
<td>99.85%</td>
<td>Goodfellow</td>
</tr>
<tr>
<td>Au coated, AT-Cut Quartz Crystals</td>
<td>Not specified</td>
<td>Metrohm</td>
</tr>
<tr>
<td>Iron Sheet</td>
<td>99.8%</td>
<td>Goodfellow</td>
</tr>
<tr>
<td>Carbon Steel S355</td>
<td>Iron ≥ 97.6%</td>
<td>West Yorkshire Steel</td>
</tr>
<tr>
<td></td>
<td>Carbon ≤ 0.20%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Manganese ≤ 1.60%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Silicon ≤ 0.55%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phosphorous ≤ 0.025%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfur ≤ 0.025%</td>
<td></td>
</tr>
<tr>
<td>Carbon Steel EN8</td>
<td>Iron ≥ 98.18%</td>
<td>West Yorkshire Steel</td>
</tr>
<tr>
<td></td>
<td>Carbon: 0.35 - 0.45%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Manganese: 0.60 - 1.00%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Silicon: 0.05 - 0.35%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phosphorous: 0.06%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfur: 0.06%</td>
<td></td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>Iron ≥ 66.35%</td>
<td>West Yorkshire Steel</td>
</tr>
<tr>
<td></td>
<td>Carbon: 0.08%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chromium ≤ 18 - 20%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Manganese ≤ 2%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Silicon ≤ 1.00%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phosphorous ≤ 0.045%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sulfur ≤ 0.030%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nickel ≤ 8 - 10.5%</td>
<td></td>
</tr>
<tr>
<td>Platinised Titanium Sheet</td>
<td>Not specified</td>
<td>Magneto Special Anodes B.V.</td>
</tr>
</tbody>
</table>
4.1.4. **Cation Exchange Membrane**

A Nafion membrane (Ion Power Inc., New Castle, DE, (USA)) was used in the electrochemical flow reactor described in Section 4.5. The chemically stable Nafion membrane is a perfluorosulfonic acid based polymer, which allows only the passage of cations due to the negative charge of the acid groups grafted onto the polymer backbone. The membranes were cut into the required size and conditioned by soaking in hot water at 80°C for 1 hour, to ensure maximum swelling. After the conditioning process, the membrane when not in use was soaked in solution to maintain the efficiency and performance.

Table 4-4: Cation exchange membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Membrane Type</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 424</td>
<td>Perfluorinated acid based</td>
<td>Ion Power</td>
</tr>
</tbody>
</table>

4.1.5. **Gases**

The gas supply set included 99.8% CO₂, compressed air (21.5% ± 0.5% O₂ and 78.5% Ni) and 99.998% N₂ (The BOC Group plc., London, UK).

4.2. **Electrode and Solution Preparation**

4.2.1. **Electrodes**

Prior to conducting the experiments, the exposed surface of the embedded iron disc in the rotating disc electrode described in section 4.4.2.1 was polished mechanically until it attained a mirror finish with the use of an Alpha 2-speed grinder-polisher polishing machine (Buehler Ltd., Lake Bluff, IL, (USA)). The Fe disk surface was polished on 600 grit CarbiMet® paper disks with 300 nm followed by 50 nm particle diameter aluminum oxide powder (Sigma Aldrich Co., Suffolk (UK)), wetted in semi-pure water. The electrode surface was then cleaned
by thoroughly rinsing in ultra pure water. The water was purified (PURELAB Ultra, ELGA LabWater Ltd., UK) by incorporating a series of water purification technologies namely reverse osmosis followed by ion exchange and adsorption on a bed of activated carbon particles.

Following the process of polishing and cleaning, the electrode was immersed in an ultrasonic bath (Thermo Scientific) for 5 minutes to remove any adhering aluminum oxide particles before commencing the electrochemical procedure.

The pure Fe, carbon steel 1020 (Carbon Steel S355), Carbon Steel 1038 (Carbon Steel EN8) and stainless steel AISI 304 electrodes used for the flow reactor in Section 4.5.2 were prepared by wet grinding on 600 grit CarbiMet® paper and degreasing with acetone as suggested by (Bockris et al., 2000).

4.2.2. Aqueous Amine Solutions

The aqueous amine solutions were classified into three different categories:

i. Unloaded amine solutions containing no CO$_2$.

ii. CO$_2$-loaded amine solutions containing desired amounts of CO$_2$.

iii. Fully saturated amine solutions containing the maximum amount of dissolved CO$_2$.

The unloaded amine solutions were prepared by simply diluting the pure amine solution with de-ionized water to the desired mass concentration. A 30 wt% solution of MEA was selected as the benchmark for the experiments as it represents the standard operating conditions for the CO$_2$ absorption process. For a loaded solution, the desired CO$_2$ loadings ($\alpha_{CO2}$) were achieved by varying the relative CO$_2$ / air or CO$_2$ / N$_2$ gas flow rates with the use of Platon NGX Glass Variable Area Flowmeters (Roxspur Measurement & Control Ltd, Sheffield, UK). The flow rates were set according to the CO$_2$ solubility data in 30 wt% MEA obtained by (Tong, Trusler et al. 2012) and (Jou, Mather et al. 1995), included in Appendix I. As an example, according
to Jou et al, a CO\textsubscript{2} partial pressure 8.96 Pa would be required to achieve a CO\textsubscript{2} loading of 0.203 mol CO\textsubscript{2} (mol MEA)\textsuperscript{-1} at 40\textdegree C. Fully saturated amine solutions were obtained by maintaining a constant CO\textsubscript{2} flow until the pH of the solution remained unchanged for a period of 30 minutes.

**4.3. Instrumentation for Electrochemical Measurements**

The electrochemical measurements reported in this thesis were carried out principally with Metrohm PGSTAT 30 Autolab potentiostat/galvanostat controlled using the Autolab NOVA software (Metrohm Autolab B.V., Utrecht (NL)). The chemicals were weighed for solution preparation with the use of a Mettler-Toledo AG245 balance supplied by Mettler-Toledo Ltd., Leicester, (UK). Following the weighing procedure, the solutions were prepared by diluting to the desired concentration with the use of de-ionised water. A solution of 1 M Na\textsubscript{2}SO\textsubscript{4} was used as the base electrolyte for all measurements. Silver / silver chloride (AgCl|Ag) electrodes supplied by Cole-Parmer Instrument Co., London (UK)) and Metrohm were used as reference electrodes for all experiments. All potentials reported in this work were measured against the AgCl|Ag electrode. Throughout the experiments, the pH of the amine solutions was monitored with a pH meter (Hanna Instruments Ltd., (UK)). To ensure accuracy in measurements, the pH meters were calibrated regularly by a three-point calibration with pH 4.0, 7.0 and 10.0 buffer solutions.

**4.4. Experimental Methods for Micro-kinetic studies on Iron**

**4.4.1. Cyclic Voltammetry**

Cyclic voltammetry is a commonly-used electrochemical technique with which useful information about the system can be obtained quickly and with a high level of precision. The technique entails measurement of the current response under potentiodynamic conditions
imposed by a potentiostat whereby the potential of the working electrode is cycled linearly with time at a scan rate (v / mVs⁻¹) expressed by equation (4. 1).

\[ E(t) = E(0) \pm vt \]  

(4. 1)

Whilst in linear voltammetry, the potential is swept in only one direction between two specified potential limits, in cyclic voltammetry it can be swept backwards and forwards between the two limits over an appropriate number of cycles, depending on the system being studied. The negative-going potential sweep induces the reduction of the species that may have been oxidized previously in the positive-going sweep. The scan limits were set based on thermodynamic predictions with the use of potential-pH diagrams for Fe-H₂O and Fe-H₂O-CO₂ systems. The potential cycling across the boundaries between different Fe species / phases results in cyclic voltammograms (CV) of current against potential which provides insight into the nature of the oxidation and reaction occurring at the electrode surface, the potentials at which they occur and the amount of charge and monolayers involved in such processes, and whether adsorbed products accumulated on successive cycling.

4.4.2. Kinetic Studies Using Rotating Disc Electrodes

Levich (Albery and Hitchman, 1971; White et al., 1984) solved the hydrodynamics of horizontal, downward-facing rotating discs rotating about a vertical axis in an ‘infinite’ liquid (i.e. no wall effects) behaves like a pump with axial flow to the centre of the disc and radial flow across it, resulting in mass transport rates to its surface that are independent of radial position. The requirement for zero liquid velocity at the disc/solution interface, gives rise to a hydrodynamic boundary layer and corresponding diffusion layer, with a thickness \( \delta_N \) remains stationary relative to the electrode. As electro-active species must be transported to the electrode | solution interface from the bulk solution, the maximum attainable current is limited by the rate of mass transport. As discussed in Chapter 2, if the electrode overpotential is
increased, surface concentrations of reacting species B decrease progressively to zero, at which a transport limited current \( i_L \) is reached:

\[
i_L = \frac{D_B F A[B]_{\text{bulk}}}{\delta_N} \tag{4.2}
\]

Where \( D_B \) is the diffusion coefficient of species B, and \( \delta_N \) is the Nernst diffusion layer thickness.

Figure 4-1: Schematic of the side and end view of the RDE and the flow pattern induced by rotation of an RDE system

A rotating disc electrode is constructed by embedding a small cylindrical rod of the desired electrode material centrally into an insulating sheath such as Teflon. The top of the sheath is attached to a rotator whilst the bottom in horizontal alignment with the disc surface is immersed into the electrochemical cell that contains the solution of interest. As the rotating disk electrode starts to rotate about the vertical axis, the rotation spins the solution out from the surface of the
cylinder in a radial direction, effectively drawing fresh material from the bulk towards the surface of the disk. The rotation creates a solution pattern as shown in Figure 4-1.

For the purposes of simplification, the experiments should be designed for laminar flow conditions only. During laminar flow conditions, the solution flow is characterized by smooth movement in layers along streamlines as described in Figure 4-2 unlike the random and chaotic motion in turbulent flow. Prediction of the nature of solution flow can be readily obtained with the dimensionless parameter, the Reynolds number, defined for the RDE system by:

$$Re = \frac{fr_c}{v}$$

(4.3)

Where $r_c$ is the radius of the cylinder, $f$ is the angular rotation speed (Hz) and $v$ is the solution viscosity. If Re does not exceed about $1 \times 10^5$, the solution flow induced by rotation is laminar (Fisher, 1996) and has the pattern shown schematically in Figure 4-1.

$$I_L = 1.555v_e FAD^{2/3}v^{-1/6}c f^{1/2}$$

(4.4)

Equation (4.4) is the Levich equation predicting the transport limiting current ($I_L$) generated with a rotating disc electrode, and is a function of the rotation frequency, $f$, the kinematic viscosity of the solution, $v$, the diffusion coefficient of the electrolyte species, $D$, and the electron stoichiometry, $v_e$ of the electrode reaction. Based on the Levich equation, for a mass transport controlled reaction, a plot of $I_L$ against the square root of the rotation rate should result in a straight line passing through the origin.

In order to understand the increase in limiting current density with rotation rate, it is important to recall that the velocity of the solution as it approaches the electrode surface increases with rotation speed leading to improved convective mass transport of the electro-active species and a simultaneous decrease in the diffusion layer thickness, as defined by equation (4.5):
\[ \delta_N = \frac{1}{1.554} D^{1/3} \nu^{1/6} f^{-1/2} \]  \hspace{1cm} (4.5)

i.e. increasing rotation rates \((f)\) decreases \(\delta_N\), so enabling higher diffusion limited currents.

In general, there are several advantages associated with the use of rotating disc electrodes such as the ease of fabrication and surface preparation. As discussed, the flow conditions are well defined and a laminar flow regime can be attained over an extensive range of rotation rates for small electrodes. In addition, the mass transport characteristics are established and can be easily varied by altering the rotation rate. However, there are also a few disadvantages associated with the use of rotating disc electrodes. The accumulation of bubbles at the electrode surface resulting from the hydrogen evolution reaction is principally relevant in acidic solutions. Bubbles are particularly adherent to certain insulating materials such as PTFE and produces a significant and detectable amount of noise in the measured currents, thus indicating disruption due to hydrogen bubble.

4.4.2.1. Experimental procedure

The rotating disc electrode was fabricated in-house by embedding a cylindrical, irremovable Fe disc of 99.95\% purity and 6.4 mm diameter in a cylindrical Teflon sheath. The rotating disc was connected to a modulated speed electrode rotator, Model E6 (Pine Instrument Company, Raleigh, NC, (USA)). The connection between the rotating disc electrode and the rotator was established via a conducting stainless steel cylindrical sheath.

The experiments were conducted in a standard three compartment glass cell fabricated by Cambridge Glassblowing Ltd (UK). A schematic of electrochemical cell and RDE system is shown in Figure 4-2.
The electrochemical cell was immersed in a temperature controlled water bath fitted with a temperature controller to maintain constant temperature within ± 0.1 °C throughout experiments. A silver-silver chloride electrode and a platinum flag, custom made by Cambridge Glassblowing Ltd, were used as reference and counter electrodes, respectively. For experiments conducted under anoxic conditions, the cell was bubbled with nitrogen gas for 20 minutes before each experiment to minimise dissolved oxygen concentrations. Before the start of each experiment, trapped bubbles within the Luggin probe were removed by tilting the cell until it appeared to be free of bubbles. Prior to conducting the experiments, the exposed surface of the embedded iron disk was prepared according to the procedure described in Section 4.2.

All kinetic measurements included were conducted at 6 different rotation rates i.e. 0 rpm, 60 rpm, 240 rpm, 540 rpm, 960 rpm and 1500 rpm, altering mass transport rates for studying diffusion-limited phenomena. The electrochemical measurements were conducted with the use of the computer controlled Metrohm PGSTAT 30 Autolab potentiostat/galvanostats described in section 4.3.
During the course of experiments, special precautionary measures were taken such as daily maintenance on the solution level in the AgCl|Ag reference electrodes and pH meter and adequate storage of the probes in their respective storage fluids to prevent crystallization.

Whilst cyclic voltammetry was the primary electrochemical technique of choice for characterizing the behaviour of iron in aqueous amine solutions with the use of rotating disk system, electrochemical parameters such as the scan rate, rotation rate and positive potential scan limit were used to probe the kinetics and mechanisms of iron in aqueous MEA as functions temperature (25-80°C), CO₂ loading (0-0.6 mol CO₂ (mol amine)⁻¹), pH (8.10-12.55), MEA concentration (5-60 wt%) and oxygen concentration. Electrode potential-pH and activity-pH diagrams of iron-water–CO₂ systems were used to assist with reaction assignments. Analysis of the resulting kinetic data via the Tafel slope extrapolation method described in section 4.4.3 enabled corrosion rates to be predicted as functions of the experimental variables.

4.4.2.2. Repeatability and Reproducibility

At the start of all the electrochemical measurements reported in this thesis, after the mechanical polishing and cleaning procedure, the iron electrode was also subjected to a potential pre-treatment at -1.4 V for 120 s to reduce any oxides that may have formed spontaneously in air. The polishing method and electrochemical cathodic reduction method chosen for the iron electrode resulted in very good repeatability and reproducibility of the experimental results obtained.

Due to the extensive number of experiments, each experiment was also repeated at least twice especially if the experimental data resulted in an outlier from a trend.

4.4.3. Tafel Slopes Extrapolation Method for Corrosion Rate Determination

The Tafel line extrapolation method, which involves plotting ln(current density) against potential is a method used for estimating the corrosion rate from experimental current-potential
data. At the corrosion potential ($E_{corr}$), the anodic and cathodic rates are exactly equal as such, the measured current density is zero. All the electrons released by the oxidation of the metal during the dissolution reaction are consumed by the reduction reaction. At significant overpotentials, in the potential region where the rate of a single partial corrosion reaction is predominant, the log current-potential plot for reactions under pure activation control result in straight lines called Tafel lines. A relation analogous to the Butler-Volmer equation describes the experimental current density potential curve.

$$j = j_{corr} \left[ \exp \left( \frac{a_F}{RT} \eta \right) - \exp \left( - \frac{a_F}{RT} \eta \right) \right]$$  \hspace{1cm} (4. 6)

Thus when $E \gg E_{corr}$, the Tafel equation is given by:

$$j_a = j_{corr} \exp \left( \frac{a_F}{RT} \eta \right)$$  \hspace{1cm} (4. 7)

Thus when $E \ll E_{corr}$, the Tafel equation is given by:

$$-j_c = j_{corr} \exp \left( - \frac{a_F}{RT} \eta \right)$$  \hspace{1cm} (4. 8)

According to the Tafel equation (4. 6), the value of the anodic and cathodic current intersection is the corrosion current density $j_{corr}$. Suggesting that $j_{corr}$ can be determined by extrapolating the linear segments of the anodic and cathodic Tafel region back to their intersection, at the corrosion potential ($E_{corr}$). The Tafel equation holds true for overpotentials within the range of ± 250 mV from the $E_{corr}$. At larger ‘corrosion overpotentials’ (over 250 mV) from $E_{corr}$, the measured current is a reflection of the kinetics for either the anodic or cathodic corrosion reactions. Figure 4-3 shows an example of a Tafel plot with extrapolation of the anodic and cathodic curves back to the corrosion potential $E_{corr}$.
By assuming uniform metal dissolution across the surface of the electrode, Faraday’s law can be used to calculate the corrosion rate from the current density with equations (4.9) and (4.10).

\[
r_{Fe} / \text{m s}^{-1} = \frac{j_{Fe} \cdot M_{Fe}}{v_e F \cdot \rho_{Fe}} \tag{4.9}
\]

\[
r_{Fe} / \text{m a}^{-1} = \frac{j_{Fe} \cdot M_{Fe}}{v_e F \cdot \rho_{Fe}} \times 3.154 \times 10^7 \text{ (s a}^{-1}) \tag{4.10}
\]

Where \(r_{Fe}\) is the corrosion rate in mm a\(^{-1}\), \(j_{Fe}\) is the corrosion current density in mA cm\(^{-2}\), \(M_{Fe}\) is the molar mass of iron and \(\rho\) is its density in g cm\(^{-3}\).

Figure 4-3: Tafel plot for the determination of corrosion current density and hence rate.

Whilst the Tafel extrapolation method has received general acceptance for the graphical determination of corrosion rates, the method can lead to various values (Badea et al., 2010), since inappropriate selection of the Tafel slopes can change corrosion rates by a factor of up to
10 (Badea et al., 2010). Thus, care was taken when applying the Tafel extrapolation, at least one of the branches if not both of the polarization curves exhibited Tafel behaviour, i.e. linearity on the semi-logarithmic scale over several decades of current density. In addition, the extrapolation was set to begin within 50-100 mV from the corrosion potential.

4.4.4. Electrochemical Quartz Crystal Microbalance

The Electrochemical Quartz Crystal Microbalance (EQCM) was developed to monitor frequency and hence mass changes in situ and effectively in real time; hence, it has found wide acceptance for the study of interfacial phenomena. The EQCM technique provides the capability to measure nanogram mass changes to the electrode, which can then be correlated to the amount of charge passed during electrochemical measurements. The EQCM consists of a thin piezoelectric quartz crystal sandwiched between two metal electrodes as schematically shown in Figure 4-4 (a). As the crystal is a piezoelectric material, it undergoes a slight vibrational deformation in the presence of an electric field. The application of an alternating electric field across the crystal through the two metal electrodes causes mechanical oscillation of the crystal at its resonant frequency, $f_0$, which is sensitive to changes in the mass on the surface of the crystal. One side of the crystal can then be used as the working electrode from which current transients and changes to the mass of the electrode may be measured as functions of potential (Buttry & Ward 1992) which makes this a suitable method for the verification of the dissolution and (or) passivation of iron.

For most Quartz Crystal Microbalance (QCM) applications, the AT-cut quartz crystals are the most commonly used. The quartz crystals are cut so that the thickness shear mode (TSM) of vibration dominates and is most responsive to changes in mass. The AT-cut means that the crystals, which are typically a few tenths of a mm in thickness are manufactured by slicing through a quartz rod at a 35°15’ angle from the crystalline axis. The AT-cut is also particularly
suitable as it provides stable oscillation with reproducible resonant frequencies, which are somewhat insensitive to temperature changes near room temperature. The vibrational motion of the quartz crystal produces an acoustic wave, which extends through the thickness of the crystal as shown schematically in Figure 4-4 (b).

Figure 4-4: Acoustic waves propagating through a quartz crystal, electrodes and deposit

The thickness of the crystal, \( W_q \), is half of the wavelength of the acoustic wave, \( \lambda \):

\[
W_q = \frac{\lambda}{2} \quad (4.11)
\]

The resonant frequency, \( f_o \), can be calculated equation (4.12) and is expressed as function of velocity of shear wave, \( v_{tr} \) and crystal thickness, \( W_q \) and the wavelength of the standing wave, \( \lambda \).

\[
f_o = \frac{v_{tr}}{\lambda} = \frac{v_{tr}}{2W_q} \quad (4.12)
\]

The velocity \( (v_u) \) of the wave is the speed of sound through a material expressed in equation (4.13), where \( \mu_q \) and \( \rho_q \) are the shear modulus and density of the quartz crystal:
\[
v_{tr} = \frac{\mu_{tr}}{\rho_{tr}} \quad (4.13)
\]

Thus,

\[
f_{o} = \frac{\mu_{tr}}{\rho_{tr}} \frac{1}{2W_q} \quad (4.14)
\]

In the thickness shear mode, both the underlying crystal and any mass adhering to the surface will oscillate at the same lateral displacement and frequency. Hence, an assumption is made for small changes (\(\leq 2\%\) of the quartz crystal mass), the addition of mass from external deposits can be treated as a mass change of the quartz crystal. If the crystal and the mass bound to the surface oscillate with no energy loss, then the process is said to be elastic. Thus, the expression for the \(f_{o}\) in equation (4.15) takes into account the increase in the thickness of the crystal.

\[
\frac{\Delta f}{f_{o}} = \frac{\Delta W}{W_q} = \frac{2f_{o}\Delta W}{\sqrt{\mu_q/\rho_q}} \quad (4.15)
\]

Thus,

\[
\Delta f = \frac{-2f_{o}^2\Delta W}{\sqrt{\mu_q/\rho_q}} \quad (4.16)
\]

The negative sign results from the fact that the acoustic wavelength increases with increasing thickness of the quartz, resulting in a decrease in the resonant frequency of the quartz crystal. The change in thickness can be related to the change in mass by taking into account the density of the deposited mass, \(\rho_q\), and the area of the electrode, \(A\).

\[
\Delta W = \frac{\Delta m}{\Delta \rho_q} \quad (4.17)
\]

Substituting equation (4.17) into equation (4.16) results in:
\[ \Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\mu q \rho q}} \] (4.18)

Thus,

\[ \Delta m = \frac{A \Delta f \sqrt{\mu q \rho q}}{2f_0^2} \] (4.19)

Equation (4.18), results in the well-established linear Sauerbray equation, which relates with nanogram sensitivity, the \( \Delta m \) to the shift in the resonant frequency of the quartz crystal.

\[ \Delta f = -\Delta m \frac{C_f}{A} \] (4.20)

Where \( C_f \) is the sensitivity constant and is expressed in units of ng cm\(^{-2}\) Hz\(^{-1}\).

\[ C_f = \frac{2f_0^2}{\sqrt{\mu q \rho q}} \] (4.21)

The sensitivity constant of the crystal is proportional to the square of \( f_0 \), so higher sensitivity can be achieved by selecting crystals with higher resonant frequencies. The resonant frequencies of crystals used within EQCM techniques are typically in the range of 5-20 MHz (Marx 2003). The typical values used for the electrode area of an AT-quartz, \( A \) is 0.196 cm\(^2\), density, \( \rho_q \) is 2.648 g cm\(^{-3}\) and the sheer modulus, \( \mu_q \) is \( 2.947 \times 10^{11} \) g cm\(^{-1}\) s\(^{-2}\) (Buttry and Ward 1992).

Whilst some QCM applications have been designed to measure \( \Delta m \) by incorporating a mass amplification feature into the signal to be transduced by the crystal, it is preferable that the measured quantity during experiments is the frequency change and not the mass change. Although a change in mass is the most obvious factor affecting the resonant frequency, it may be subject to other obscuring effects, which may result in misinterpretation of the results. For example, the frequency to mass relationship based on the Sauerbray equation (4.20) is valid only for mass changes of less than 2% of the original crystal mass, as the mass deposited on
the crystal moves synchronously with the resonance of the quartz crystal. Excessive mass loading may result in the outer region of the deposit exhibiting a phase delay with respect to the resonator, resulting in changes to the sensitivity of the crystal and thus inaccurate and incomprehensible frequency changes.

4.4.4.1. Experimental Procedure

The EQCM apparatus (Metrohm Autolab B.V., Utrecht (NL)) consisted of an EQCM cell fabricated from polypropylene, an EQCM oscillator, a spring-mounted Au/TiO$_2$ coated quartz crystal, an Au wire counter electrode and a AgCl|Ag reference electrode. The quartz crystal possessed a resonant frequency, $f_0$, of 6 MHz, the frequency resolution was 0.07 Hz, with a 1 Hz accuracy of frequency measurements. The sensitivity coefficient of $C_f$ was specified as 0.0815 Hz cm$^2$ ng$^{-1}$ and a maximum measurable frequency change was set as 80 kHz. The working electrode $A_{EQCM}$ was 0.35 cm$^2$ and the maximum volume of the EQCM cell was specified as 3 cm$^3$.

The EQCM cell was connected to a computer controlled Metrohm PGSTAT 30 Autolab potentiostat/ galvanostat in conjunction with a Metrohm - Autolab EQCM module. During the electrochemical measurements, one side of the AT-cut quartz crystal was exposed to the aqueous solution whilst the opposing side remained dry, in air.

The first step was to verify the stability of the frequency response with time and study the noise levels obtained on the Au electrode, by measuring the current and frequency response to the potential scan in the potential region $0 \ V \leq E \leq +0.3 \ V$ during which no significant frequency change was expected or detected.

As there are no commercially available Fe electrodes compatible with the EQCM cell supplied by Metrohm, the Fe electrodes were produced by electroplating the gold electrode in a 300 g dm$^{-3}$ ferrous sulphate solution at pH 3.2. This was achieved in two steps:
1) Firstly by conducting a potential scan in the potential region \(-1.4 \, V \leq E \leq 0.4 \, V\) to ascertain the values of the electrode potentials at which Fe electrodeposition occurred in the ferrous sulphate solution.

2) The Au electrode was electroplated with Fe by applying a potential of \(-1.0 \, V\) for 200 s, during which the frequency response was expected to decrease with time. The total mass of Fe deposited on the electrode surface was evaluated from the frequency response. The total charge passed calculated by integrating the area under the current-time graph, was used to evaluate the change in Fe mass that would have been detected with a charge yield of unity. The ratio between the detected mass and the expected mass (based on a charge yield of unity) was used to evaluate the experimental charge yield for iron electrodeposition.

On completion of the deposition process, the FeSO₄ solution in the EQCM cell was emptied and swiftly replaced with the aqueous amine solution used as the electrolyte solution. Cyclic voltammetry experiments were conducted on the Fe electroplated electrodes to determine the effects of CO₂ loading, pH and MEA concentration on the kinetics and mechanisms of iron. In conjunction with predictions from potential-pH diagrams, the change in the mass on the electrode was evaluated with the Sauerbray equation, allowing deconvolution of the Fe partial oxidation current densities leading to dissolution of iron and (or) the adsorption of products on the electrode surface.

Unfortunately, due to the high cost of the EQCM apparatus, incompatibility of the aqueous ethanolamine solution with polypropylene (the fabrication material for the EQCM cell) and the consumable nature of the crystals, this technique could be used only to obtain the kinetics of the iron dissolution and passivation reactions for a limited number of experiments. Furthermore, the design of the EQCM apparatus was suitable only for measurements under
quiescent conditions and could not be modified to investigate the effects of other operating parameters such as temperature.

4.4.4.2. Special precautionary measures

A Faraday cage was used to enclose the EQCM equipment in order to minimize the electrical noise from surrounding equipment. Each experiment was repeated at least three times to ensure reproducibility. Prior to the start of voltammetric measurements in amine solutions, the potential of the Fe electrode was held at -1.0 V for 50 s to reduce any oxides that may have formed spontaneously during the transfer of electrolyte solutions from FeSO$_4$ to MEA. Due to the small size of the EQCM cell, maintaining a constant flow of CO$_2$ to the solution throughout the experiment was not a procedure that could be conducted feasibly, so was not carried out. However, the pH of the test solution at the start and ending of the experiment were measured and found unchanged, so it can be assumed that there was no change in the CO$_2$ loading of the solution due to the short timescale of the experiment. Before the start of every experiment, about 15 minutes was given to allow the EQCM driving frequency to stabilize until the frequency shift per minute was less than 1 Hz. In order to reduce measurement errors, the crystals were kept clean and free of any extraneous materials by observing precautionary procedures such as using gloves and tweezers for handling, storing the crystals in the original packaging and the use of high purity water for cleaning.

4.5. Electrochemical Flow Reactor for Time-dependent Analysis of Iron Corrosion in Flow Reactor Mode

4.5.1. Reactor design, configuration and materials

In order to measure dissolved iron concentrations in the aqueous amine solution as functions of the operating parameters such as electrode potential, solution composition and flow rate,
temperature and CO$_2$ loading, a parallel plate flow reactor was designed and fabricated in-house principally from PTFE (PAR Group Ltd., Lancashire, UK). PTFE was selected to withstand the highly chemically aggressive and corrosive nature of MEA at pH 8.01 and the other amine solutions tested within this project.

Figure 4-5: Schematic diagram of membrane-divided electrochemical flow reactor.

Figure 4-5 shows a schematic diagram of the electrochemical flow reactor, consisting of a rectangular PTFE reactor body made of two separate compartments, each holding a rectangular plate electrode held in place by a set of G-clamps and sealed with custom made PTFE encapsulated Viton o-rings (PAR Group Ltd., Lancashire, UK). Unless otherwise specified, the anode was an iron plate with a purity of 99.8% (Goodfellow Cambridge Ltd., Huntingdon, UK), 400 mm in length, 100 mm in width with a thickness of 10 mm with a geometric surface area of 0.04 m$^2$ on each side. The cathode consisted of a 2.5 µm platinised titanium sheet (Magneto Chemie, Holland, The Netherlands) also with the same dimensions.
Once the reactor was assembled, the electrode area for both the anode and cathode exposed to the test solution was 0.01 m$^2$ and the inter-electrode gap was 50 mm. Both the anolyte and catholyte were both operated in batch recycle mode with separate reservoirs. The volume of the anode and cathode compartments of the reactor were identical at 0.25 dm$^3$ and the total volume of the anolyte and catholyte solutions was 4 dm$^3$. As shown schematically in Figure 4-6, 6.35 mm diameter tubular PTFE (Cole-Parmer Instrument Co., London, UK) were used to connect the reactor, reservoirs and a Masterflex Precision peristaltic pump (Cole-Parmer Instrument Co., London (UK)), to circulate the amine solutions from their reservoirs through the bottom of the anode and cathode chamber, out from the top and back into the reservoirs.
At the inlet (bottom) of the anolyte and catholyte compartments, flow distributors shown schematically in Figure 4-5 were utilised to enable an even distribution of the aqueous solution flow rate. The solution flow rate was set and varied by the pumps but still measured by a Titan 810-VOP-O-PTM micro-turbine flow meter (Titan Enterprises Ltd., Dorset, UK) integrated into the flow circuit and the data was logged by the data acquisition device NI DAQPad-6015 and the LabView software supplied by National Instruments. An AgCl|Ag reference electrode was placed in the reference electrode compartment with a hole of 1 mm drilled in the body of the anolyte compartment and emerging close to the surface of the iron electrode, to ensure liquid connection between the reference electrode and the electrolyte solution in the reactor.

4.5.2. Experiment Procedure

4.5.2.1. Electrochemical Technique - Chronoamperometry

The flow reactor shown schematically in Figure 4-7 was designed to characterize the kinetics of iron in aqueous amine solutions as functions of electrode potential, amine concentration, amine type, temperature, flow rate and CO₂ loading. The electrode potential in the flow reactor was controlled with respect to the AgCl|Ag reference electrode by the computer-controlled Metrohm PGSTAT 30 Autolab potentiostat/galvanostat (connected to a 10A current booster) and the current was recorded as a function of time. The series of constant potential measurements were conducted in the flow reactor, whilst recording the current with time, so that the charge passed could be determined by integration. Inductively Coupled Plasma Spectroscopy Optical Emission Spectroscopy (ICP-OES; Perkin Elmer Optima DV 2000, Perkin Elmer Waltham, MA, USA) was used to determine the concentrations of dissolved Fe^{II} in 1 cm³ samples taken from the reactor outlet enabling discrimination between partial current densities leading to dissolution from those resulting in adsorbed products.
In addition to pure Fe, measurements were also conducted on Carbon Steel 355 (carbon steel 1020), Carbon steel EN8 (carbon steel 1038) and stainless steel AISI 304 plates with the same dimensions as the Fe anode.

Throughout the entire duration of the experiment, the pH of anolyte and catholyte was monitored to ensure constant CO$_2$ loading. During the experiments, solution samples were taken from the top of the anolyte compartment and the samples were taken at 10 minute intervals for all the experiments conducted, with the exception of the longer term measurements during which samples were taken once day over a period of 28 days. Immediately after obtaining the samples, they were diluted in 1 M H$_2$SO$_4$ at a ratio of 1:10 before the dissolved metal concentration was analysed by ICP-OES.

Figure 4-7: (a) The assembled electrochemical flow reactor in action (b) The anolyte compartment (c) The catholyte compartment (d) A Fe plate (anode)

4.5.2.2. Charge Yield Determination

The charge yield $\Phi^e$ is the ratio of the theoretical charge that would be required for the amount of dissolved iron obtained ($Q_{FeII}$) to the actual total charge passed ($Q$) through the reactor during the time $t$. 
\[ \Phi^e = \frac{Q_{Fe^{II}}}{Q} \]  \\

\( Q_{Fe^{II}} \) for the amount of Fe\(^{II} \) dissolved in the amine solution was calculated from the stoichiometry of the half-cell reaction based on Faraday’s law:

\[
Q_{Fe^{II}} = \frac{m_{Fe^{II}}v_{Fe^{II}}}{v_{Fe^{II}}M} = \frac{n_{Fe^{II}}v_{e}}{v_{Fe^{II}}} \]  \\

where \( m_{Fe^{II}} \) is the mass and \( n_{Fe^{II}} \) is the number of mols of the Fe\(^{II} \) formed during the experiment, \( M \) is the Fe molar mass, \( F \) is the Faraday constant, \( v_{e} \) is the stoichiometric number (2) of electrons for the reaction producing Fe\(^{II} \).

The total amount of charged passed through the reactor was calculated from the current passed during the time \( (t) \) via equation (4.24).

\[ Q = \int I \, dt \]  \\

4.5.2.3. Analytical Technique - Inductively Coupled Plasma Spectroscopy

**Optical Emission Spectroscopy**

The ICP-OES used for this thesis was supplied from (Perkin Elmer Optima DV 2000, Perkin Elmer Waltham, MA, USA). The ICP-OES technique involves the application of a high frequency and highly energetic magnetic field to a stream of argon to excite the gas and create a plasma. A peristaltic pump is used to pump a liquid sample into the system, which was nebulised and sprayed into the plasma flame leading to the excitation of the sample. This resulted in an emission spectrum showing peaks at characteristic wavelengths indicative of the solution composition. The concentration of the dissolved metals in the solution samples at these wavelengths was determined by the calibration of emission intensity.

As discussed in 4.5.2.1, the aliquots obtained from the flow reactor outlet were diluted by a factor of 10 in 1 M H\(_2\)SO\(_4\) to prevent the dissolved Fe\(^{2+} \) ions from oxidising in air and forming
Fe(OH)$_3$ / Fe$_2$O$_3$ particles forming that otherwise may have blocked the nebuliser. Prior to commencing the sample measurement, a four-point calibration was carried out using diluted ICP standard solutions (Table 4-2) which represented concentrations below and above the expected dissolved metal ion concentrations in the samples. For repeatability purposes, each sample was measured three times and the arithmetic mean was calculated.

4.5.2.4. Reactor Characterization

The (mean) mass transport rate coefficient $k_m$ of the flow-through reactor was characterized using the transport controlled reduction of a known concentration of hexacyanoferrate(III) ions, a model fast reaction, as a function of solution flow rate and at a constant potential of -0.8 V (AgCl|Ag):

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-} \quad (4. 25)$$

For this purpose, 2 dm$^3$ of solution containing 50 mol m$^{-3}$ K$_3$Fe(CN)$_6$, 100 mol m$^{-3}$ K$_4$Fe(CN)$_6$ and a supporting electrolyte of Na$_2$CO$_3$ at pH 11.3 was circulated through the reactor at various solution linear velocities between 0.1 to 0.8 mm s$^{-1}$. The charge passed due to the reduction of hexacyanoferrate(III) to (II) was measured and subsequently used to evaluate $k_m$ via the equation (4. 26):

$$Q = t k_m A v_e F \quad (4. 26)$$
4.6. References


Chapter 5

Electrochemical Study of Iron Electrodes in MEA-H₂O-CO₂ Systems

The corrosion and passivation of iron and carbon steel in aqueous CO₂-containing environments has been researched for decades, resulting in numerous publications reporting a variety of corrosion rates and various mechanisms, as discussed in the Literature Review, Chapter 3. Despite the large amount of data reported from extensive investigations, the mechanistic interpretation of the processes involved in iron corrosion remains poorly understood.

Due to the use of alkanolamines for the post-combustion capture of dilute CO₂ from flue gas streams being heralded as one of the most promising CO₂ capture technologies currently being developed, there have been several recent attempts at establishing the corrosion mechanism of carbon steel in alkanolamine-H₂O-CO₂ systems, notably by (Veawab et al., 1999), (Kittel, 2010) and (Kladkaew et al., 2009a). These experimentally-based investigations aimed at establishing the impact of crucial operating parameters, such as amine concentration, temperature, CO₂ loading, and oxygen concentration. While there have been some systematic
trends governing the corrosion behaviour of these chemical solvents that have been identified, such as the detrimental effect of increasing CO₂ loading and temperature, the results of these studies have also resulted in conflicting and contradictory information, particularly about the effects of amine and oxygen concentrations. In addition, a consensus has yet to be reached on the actual mechanism of corrosion in these amine solutions. The models proposed depended on the amine type and absence/presence of oxygen. The previous studies on corrosion in amines have been based solely on electrode polarization measurements of carbon steel samples in quiescent solutions; the influence of the hydrodynamic conditions has been completely neglected.

In order to assign the corrosion mechanism(s), as well as firmly establish and quantify the effects of the critical operating conditions, the electrochemical behaviour of rotating iron disc electrodes in 5-60wt% MEA-H₂O-CO₂ aqueous solutions, in the pH range of 8.01 to 12.55 and from 18°C to 80°C, was investigated using cyclic and linear scan voltammetry, as described in Chapter 4. In addition, some measurements were made of iron electrodeposited on gold electrodes of an electrochemical quartz crystal microbalance (EQCM).

This section reports the experimental results obtained from a vast number of experiments over a wide range of amine concentrations, temperatures, CO₂ loadings, O₂ presence, as well as electrode rotation and potential scan rates and positive potential limits. The kinetic analysis of the resulting data was also conducted and reported in terms of corrosion rates as functions of the process parameters studied. The details of the electrochemical results such as the open circuit potential (OCP), corrosion potential (E_{corr}) and corrosion current (j_{corr}) for each of the experiments conducted are listed in Appendix (V).

This Chapter is dedicated entirely to establishing the corrosion behaviour of iron in (aqueous) MEA solutions, as it is the most extensively used alkanolamine and acts as the benchmark solvent for the CO₂ capture process. Comparisons with the corrosion behaviour in other
commercially-available solvents for the process will be discussed in Chapter 7. The majority of voltammetric experiments for which results are reported below were conducted in an aqueous solution of 30 wt% MEA at 25°C and full CO₂ saturation (pH 8.01); this particular MEA concentration was selected as it corresponds to the industry standard operating condition, above which corrosion rates are believed to increase dramatically.
5. Electrochemical Behaviour of Iron in MEA-H$_2$O-CO$_2$ Systems

5.1. Fe in MEA+ H$_2$O (absence of CO$_2$)

To understand the corrosion behaviour of iron in aqueous MEA solutions, firstly an aqueous solution of MEA was studied in the absence of CO$_2$. A stationary Fe rotating disc electrode immersed in 30wt% MEA solution of pH 12.55 attained an open circuit potential (OCP) of +0.43 V. The subsequent cyclic voltammogram for a potential scan rate (dE/dt) of 10 mV s$^{-1}$ is shown in Figure 5-1. On a positive-going potential scan from the negative potential limit of -1.4 V, current densities initially decreased exponentially, then at potentials > ca. -1.03 V (indicated by the red dashed line in Figure 5-1), net reduction reactions (resulting in negative current densities by convention) changed to net oxidation reactions (positive current densities). This region of oxidation reaction also marked the start of passivation extending over 1.6 V (from -1.03 V to +0.6 V at the end of which is demarcated by a blue dashed line in Figure 5-1). The potential-pH diagram for Fe-H$_2$O systems (Figure 5-5) was used to assign reactions to the main features of Figure 5-1 by approximating equilibrium potentials with potentials of (partial) current onsets, a discussion of which follows.

At pH 12.55, the equilibrium potential of water reduction $E_{H_2O/H_2}$ is -0.92 V, so reduction current densities at more negative potentials (region A) were assigned to the evolution of hydrogen by the direct reduction of water via reaction (5. 1).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$  \hspace{0.5cm} (5. 1)

For electrode potentials more negative than ca. -1.03 V, net reduction occurred, after which there was an onset of net oxidation (region B) due to the oxidation of elemental Fe by reaction (5. 2). For a very small electrode potential window, it is possible that this was the only reaction operating.
\[ Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^- \]  \hspace{1cm} (5.2)

Figure 5-1: Cyclic voltammogram of a stationary iron RDE in 30 wt% MEA, at 10 mV s\(^{-1}\) (T = 25°C, pH 12.55).

However, starting at potentials less negative than -1.01 V, a secondary reaction (5.3) also occurred, predicted according to Figure 5-5, to result in the formation of magnetite (Fe\(_3\)O\(_4\)).

\[ 3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + 2H^+ + 2e^- \] \hspace{1cm} (5.3)

As the positive-going potential scan continued, the formation of hematite (Fe\(_2\)O\(_3\)) and ferric hydroxide (Fe(OH)\(_3\)) also became thermodynamically favourable reactions. Under these circumstances, there was a very slow increase in current density, but because of the slow potential scan rate, there was no distinctive current density peak due to the formation of the thermodynamically stable III phase hematite (Fe\(_2\)O\(_3\)) and metastable ferric hydroxide (Fe(OH)\(_3\)). On increasing the electrode potential to values positive of the equilibrium potential for the formation of Fe(OH)\(_3\), ca. -0.70 V, passivation of the iron electrode continued with
anodic current densities remaining essentially constant at 3.2 A m$^{-2}$. At electrode potentials $>\text{ca. } +0.60$ V, current densities started to increase exponentially (region C) due to evolution of oxygen from water, for which the equilibrium potential, $E_{H_2O/O_2}$ is $+0.29$ V at pH 12.22. After reversing the potential scan from the positive potential limit of +1.0 V, no reduction current density peak was evident at slow potential scan rates.

$$2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + 2H^+ + 2e^- \quad (5.4)$$

$$Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e^- \quad (5.5)$$

Oxidation and reduction charge densities passed within the potential range of -1.0V and +0.6V in the voltammogram were respectively 418 C m$^{-2}$ for oxidation ($Q_{ox}$), corresponding to ca. 38.5 monolayers of Fe assuming a perfectly planar Fe | solution interface, and 114 C m$^{-2}$ for reduction ($Q_{red}$). The $Q_{ox} / Q_{red}$ ratio of ca. 4 reflected the irreversibility of the reactions involved. In particular, this highlights the charge transfer controlled nature of this redox process, i.e. it reveals the extent to which the species oxidised on the positive-going scan were reduced in the subsequent negative-going scan. The initial investigation demonstrated the result for a stationary electrode at a single temperature. The roles of rotation speed and effect of temperature were studied subsequently.

Passivation current densities appeared to be independent of the rotation rate, implying that the passivation process is not controlled by diffusion but by the underlying charge transfer process. The dependence of current densities on rotation rate was evident only in the hydrogen evolution region at highly negative potentials ($E \leq -1.0$ V) and the oxygen evolution region at highly positive potentials ($E \geq +0.6$ V). In both cases, current densities increased with rotation speed (Figure 5-2 - 5-4), which also shifted the onset of oxidation to more positive potentials, as evident in Figure 5-2 (25 °C) in which oxidation current densities occurred at $\geq$ -0.32 V for 1500 rpm as opposed to -1.03 V at 0 rpm.
At low temperatures (25 °C) for a rotating disc electrode in 30 wt% MEA solution, there was no evidence of a current density peak during the positive-going potential scan for all rotation rates used in this work (0-1500 rpm). This demonstrated that aqueous MEA solutions are not inherently corrosive in the absence of CO₂. However, for solution temperatures of 40 °C and 60 °C, there were suggestions of active–passive behaviour with a slightly visible current density peak at ca. -0.10 V for higher rotation rates (>240 rpm). Increasing temperature had no notable effect on the magnitudes of passive current densities.

Figure 5-2: Influence of electrode rotation rate on voltammogram of iron RDE in 30 wt% MEA, at 10 mV s⁻¹ (T = 25 °C, pH 12.55)
Figure 5-3: Influence of rotation rate on the voltammogram obtained on an iron RDE in 30 wt% MEA, at 10 mV s\(^{-1}\) (T = 40 °C, pH 12.27)

Figure 5-4: Influence of electrode rotation rate on voltammograms of iron RDE in 30 wt% MEA, at 10 mV s\(^{-1}\) (T = 60°C, pH 12.10)
Figure 5-5: Stable (black) and meta-stable (red) potential-pH diagrams for Fe-H_2O system for dissolved iron activity of 10^6, 298 K and 0.1 MPa (Kelsall 2011); red lines correspond to meta-stable behaviour of iron hydroxides rather than the more stable oxides.
5.2.  Fe in MEA + H₂O + CO₂

Iron in an aqueous solution of MEA at pH 12.55 showed predominantly passive behaviour, whereas addition of CO₂ decreased the pH to 8.01 at which active iron (II) dissolution and hence spontaneous corrosion is thermodynamically favourable, as predicted by Figure 5-5. This change in pH can be explained by considering the main reactions of CO₂ absorption in alkanolamines. MEA (RNH₂) reacts with water to form protonated amine and hydroxide ions evidenced by the high pH measured in the absence of CO₂. CO₂ is absorbed by MEA and reacts to form carbamate ions (RNHCOO⁻), protonated amine (RNH₃⁺) and hydrogen carbonate ions (HCO₃⁻). The RNH₃⁺ and HCO₃⁻ ions in turn may dissociate and produce hydrogen ions (H⁺), resulting in the observed pH decrease in aqueous MEA solutions on addition of CO₂.

Reaction of MEA with water:

\[ RNH₂ + H₂O \leftrightarrow RNH₃⁺ + OH⁻ \]  \hspace{1cm} (5.6)

Reaction of MEA with water and CO₂:

- Formation of carbamate

\[ 2RNH₂ + H₂O + CO₂ \leftrightarrow RNHCOO⁻ + RNH₃⁺ + H₂O \]  \hspace{1cm} (5.7)

- Hydrolysis of carbamate

\[ RNHCOO⁻ + H₂O \leftrightarrow RNH₂ + HCO₃⁻ \]  \hspace{1cm} (5.8)

- Dissociation of protonated amine ions

\[ RNH₃⁺ \leftrightarrow RNH₂ + H⁺ \]  \hspace{1cm} (5.9)

- Dissociation of hydrogen carbonate ions
\[ HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \]  \hspace{1cm} (5.10)

Figure 5-6: Liquid-phase composition of 30wt% MEA solution loaded with CO\(_2\) at 25°C. Compositions were calculated with the Kent-Eisenberg Model (Kent and Eisenberg, 1976).

The cyclic voltammogram recorded for a stationary iron electrode in 30 wt% MEA at 25°C where the solution is fully saturated with CO\(_2\) and has a pH 8.01 is reported in Figure 5-7 and Figure 5-8. The iron electrode attained an OCP of -0.71 V after being cleaned cathodically at -1.4 V for 120 s to reduce any oxides that may have formed spontaneously in air. The electrode potential was scanned under the same constraints as for those solutions not containing CO\(_2\) to provide a direct comparison (-1.4 V to +1.0 V, dE/dt = 10 mV s\(^{-1}\)). The potential-pH diagram for Fe-H\(_2\)O-CO\(_2\) systems (Figure 5-9) was used to assign reactions to the main features of Figure 5-8.
Figure 5-7: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA + H₂O + CO₂; 10 mV s⁻¹ (T = 25 °C, pH 8.01).

Figure 5-8: Cyclic voltammogram of a stationary iron RDE in 30 wt% MEA + H₂O + CO₂, at 10 mV s⁻¹ (T = 25 °C, pH 8.01) with reactions assigned.
Large cathodic current densities resulted from potentials between the negative potential limit and -0.75 V (AgCl|Ag) (region A), due to hydrogen evolution, firstly from the reduction of water \( \left( E_{\text{H}_2/\text{H}_2\text{O}} = -0.68 \text{ V} \right) \) (5.15) and secondly from protons resulting from the reaction of CO\(_2\) in the aqueous MEA solution. The dissociation of protonated amine \( (\text{RNH}_3^+ \text{)} (5.9) \) and HCO\(_3^-\) formed from the reaction of CO\(_2\) in aqueous MEA (5.10) and CO\(_2\) in water (5.13) serve as an additional source of H\(^+\) which are consequently reduced via equation (5.14).

*Hydration of CO\(_2\):*

\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \quad (5.11)
\]

*Hydrolytic Ionisation of CO\(_2\) (aq):*

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad (5.12)
\]

\[
\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (5.13)
\]

*Hydrogen Evolution reduction reactions:*

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (5.14)
\]

\[
2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (5.15)
\]

With increasing potentials, oxidation current densities resulted at potentials ≥ -0.78 V (region B); predictions from the potential-pH diagram (Figure 5-8) for Fe-H\(_2\)O-CO\(_2\) systems at pH 8.01, suggested that this is due to the active dissolution of iron to Fe\(^{II}\)\(_{aq}\) species \( (E_{\text{Fe}^{2+}/\text{Fe}^{3+}} = -0.79 \text{ V}) \) via reaction (5.16).
Dissolution of Fe:

\[ \text{Fe} \leftrightarrow \text{Fe}^{2+} + 2e^- \] (5.16)

The cyclic voltammogram was characterised by three oxidation peaks at ca. -0.72 V (peak I) and a maximum current density of 16.2 A m\(^{-2}\) at ca. -0.49 V (peak II), followed by another broad peak at ca. -0.31 V. Similar behaviour has been reported (Castro et al., 1986) for iron in stagnant and stirred KHCO\(_3\)/K\(_2\)CO\(_3\) at pH 8.9, whereas others (Clerbois and Massart, 1962), (Thomas et al., 1970), (Simard et al., 1998) reported only two distinct current maxima.

The \(j\)-\(E\) data in Figure 5-7 exhibited an active-passive transition, indicated by the blue dashed line; The active region was followed by sharp decrease in anodic current to 3.2 A m\(^{-2}\) at potentials > -0.3 V and a passive region extending over 1.1 V. Passivation became evident at potentials at potentials more positive of those corresponding to peak (III) at which oxidation to a Fe(III) phase was thermodynamically favourable. In the passive region, current densities remained relatively constant until the scan was reversed at the positive potential limit. From the Fe-H\(_2\)O-CO\(_2\) potential-pH diagram in Figure 5-9, passivation can be ascribed to formation of an adsorbed film of Fe\(_2\)O\(_3\) \(\left( E_{\text{Fe}_2\text{O}_3/\text{Fe}_2\text{O}_3} = -0.48 \text{ V} \right) \) and Fe(OH)\(_3\) \(\left( E_{\text{Fe(OH)}_3/\text{Fe(OH)}_3} = -0.43 \text{ V} \right) \). This potential-independent passive region ensued even on the negative-going potential scan until low cathodic current densities occurred at ca. -0.52 V < \(- E < -0.02 \text{ V} \). Unexpectedly, on the negative-going potential scan to potentials < -0.52 V, the oxidation process was suddenly reactivated, leading to net oxidation current densities, causing an anodic peak (IV) at ca. -0.59 V. After this abrupt change, anodic current densities decreased and changed to a net reduction process (region A, indicated by the red dashed line). There was a reduction peak (V) at ca -0.80 V before hydrogen evolution current densities were detected at the most negative potentials.
Successive potential cycling resulted in very little change in both anodic and cathodic current densities and the voltammograms were invariant with cycle number, suggesting that at this chosen scan rate of 10 mV s\(^{-1}\), the adsorbed species from the anodic scan were completely reduced at the set negative potential limit of -1.4 V.

The total oxidation charge density was significantly higher than that corresponding to the reduction reactions (\(Q_{\text{ox}}/Q_{\text{red}} = 12\), in the potential range of -0.78 V to 1.00 V) resulting most probably due to active dissolution of Fe to Fe\(^{II}\)\text{aq} within the active region.

At the end of each experiment, it was evident to the naked eye that the electrode surface had been etched strongly, with evidence of pitting and a general change in surface roughness.

**Figure 5-9**: Potential-pH diagram for Fe-CO\(_2\)-H\(_2\)O System, showing the lines for dissolved iron activity of 10\(^{-4}\) and (0.1 MPa CO\(_2\), 298 K).
5.3. Effect of electrochemical parameters

On establishing the typical behaviour of a stationary Fe electrode in CO₂-loaded MEA solutions, the effects are described below of potential scan rate, rotation rate and positive potential limit to elucidate the mechanisms of the various electrode processes of iron in MEA-H₂O-CO₂ systems.

5.3.1. Effect of electrode rotation rate

As discussed previously in the Experimental Methods section of Chapter 4, a rotating disc electrodes (RDE) system offers the benefit compared to the use of a stationary electrode of an easily changeable and predictable mass transport regime and hence mass transport limited current densities \( j_L \), for which Levich published an analytical solution for steady-state laminar flow conditions:

\[
j_L = 1.554 v_o F C D^{2/3} v^{-1/6} f^{1/2}
\]  

Hence, for mass transfer controlled reactions, current densities are proportional to the square root of the rotation rate \( f \).

Figure 5-10 shows the effects of rotation rate on the cyclic voltammetric behaviour of a Fe RDE in 30wt% MEA saturated in CO₂ at pH 8.01. Within the active dissolution region (region B), both the peak current densities and charges associated with peaks II and IV increased significantly with increasing rotation rate, while there was no effect on peak I or on passive current densities at potentials > ca. -0.3 V (AgCl|Ag) and peak (III) disappeared completely.
Figure 5-10: Effect of rotation rate on cyclic voltammograms of an iron RDE in 30wt% MEA + H₂O + CO₂, at 10 mV s⁻¹ (T = 25°C, pH 8.01).

Figure 5-10 shows the effects of rotation rate on the peak current densities (jₚ). Current densities of Peak (II) and Peak (IV) increased linearly with f^{1/2}. At constant potential scan rate, temperature and pH, jₚ vs f^{1/2} was linear for the whole range of experimental conditions used. This increase in current densities with electrode rotation rate suggested that the diffusion of Fe⁺ from the electrode into the solution controlled the magnitudes of Peak (II) and Peak (IV), confirming that anodic dissolution was mass transport controlled. The absence of an obvious reduction current density peak due to:

\[ Fe_{2}O_{3} + 6H^{+} + 2e^- \rightarrow 2Fe^{2+} + 3H_{2}O \]  \hspace{1cm} (5.18)

\[ Fe(OH)_{3} + 3H^{+} + e^- \rightarrow Fe^{2+} + 3H_{2}O \]  \hspace{1cm} (5.19)

In Figure 5-10 suggested that it was masked by a larger oxidation current density:
leading to a measured net positive current density in the potential range $E_{FeCO_3/Fe} > E > E_{Fe_2O_3/FeCO_3}$, as removal of (hydr-)oxide by reactions (5.18) and (5.19) reactivated reaction (5.20), giving rise to peak IV. While there was a linear relationship between the $j_{\text{PL}}$ and $j^{1/2}$, the lines did not intercept the origin, as current densities due to the process corresponding to peak II were still finite in quiescent solutions ($j_{\text{PL}} \neq 0$ for $j^{1/2} = 0$). This suggested that the diffusion-limited dissolution process occurred in parallel with a kinetically-limited oxidation process. In the whole range of solution composition studied, the value of $j_{\text{PL}}$ increased linearly with $j^{1/2}$, but the gradients of the lines and their intercepts to the origin of coordinate increased with temperature, reflecting the temperature dependence of the Fe$^{II}$ diffusion coefficient:

$$D_{Fe^{II}} = \frac{k_B T}{6 \pi \eta R}$$  \hspace{1cm} (5.21)

![Figure 5-11: Effect of rotation rate on $j_P$ for Fe RDE in 30wt% MEA + H$_2$O + CO$_2$, at 10 mV s$^{-1}$ (T = 25 °C, pH 8.01) in the a) positive-going and b) negative-going potential scan.](image)
5.3.2. Effect of positive potential limit

To further establish the oxidation mechanisms for iron in aqueous MEA solutions, the participation and stability of adsorbed or passive film-forming species was studied, by varying the electrode potential perturbation applied to the iron electrode. Figure 5-12 shows the current density response to varying the positive potential limit $E_{s,a}$ on the subsequent negative-going potential excursion for a Fe electrode rotated at 1500 rpm ($dE/dt = 10$ mV s$^{-1}$) in 30 wt% MEA + H$_2$O + CO$_2$. As the positive potential limit $E_{s,a}$ was decreased, the apparent magnitude of the re-activation current peak (IV) increased on the subsequent negative-going scan. When $E_{s,a}$ was set to a potential (-0.4 V) just beyond the potential of peak II, an anodic current peak was detected with no prior cathodic current. At more positive limit potentials (-0.2 V < $E_{s,a}$ < 1.0 V), there was a broad reduction current (III) before the oxidation current peak (IV). The charge density of the anodic current peak IV decreased while the charge of the cathodic current peak III increased with more positive values of $E_{s,a}$.

The magnitudes of peaks I and V did not change on varying $E_{s,a}$, suggesting that they were conjugated in nature and can be assigned to the oxidation and subsequent reduction of an inner surface layer. Peak I was assigned to the oxidation of iron to form the first layers of a pre-passive insoluble phase such as Fe(OH)$_2$ as predicted by the potential-pH diagram of the Fe-H$_2$O-CO$_2$ system (Figure 5-9):
$Fe \rightarrow Fe^{2+} + 2e^{-}$ \hspace{1cm} (5.22)

$Fe + HCO_3^- \rightarrow FeCO_3 + H^+ + 2e^-$ \hspace{1cm} (5.23)

$E_{FeCO_3/Fe} (SHE) / V = -0.413 - 0.0296pH - 0.0296\log(HCO_3^-)$ \hspace{1cm} (5.24)

$3Fe_2O_3 + 2H^+ + 2e^- \rightarrow 2Fe_3O_4 + H_2O$ \hspace{1cm} (5.25)

$Fe_3O_4 + 5H^+ + 3HCO_3^- + 2e^- \rightarrow 3FeCO_3 + 4H_2O$ \hspace{1cm} (5.26)

And or: $Fe_2O_3 + 4H^+ + 2HCO_3^- + 2e^- \rightarrow 2FeCO_3 + 3H_2O$ \hspace{1cm} (5.27)

$E_{FeCO_3/Fe} (SHE) / V = 0.659 - 0.118pH + 0.0592\log(HCO_3^-)$ \hspace{1cm} (5.28)

Where $V_{Fe_2O_3} = 30.274 \text{ cm}^3 \text{ mol}^{-1}$; $V_{Fe_3O_4} = 44.524 \text{ cm}^3 \text{ mol}^{-1}$; $V_{FeCO_3} = 29.378 \text{ cm}^3 \text{ mol}^{-1}$ (Haynes and Lide, 2011).

(Castro et al., 1991) reported a similar peak (I), attributed to the formation of a monolayer of Fe(OH)$_2$, in voltammograms of Fe in hydrogen carbonate / carbonate solutions at pH 8.9; this inner passive layer of Fe(OH)$_2$ formation was believed to occur simultaneously with the active dissolution of Fe to Fe$^{II}$, while the potential region of peak (II) and above could be associated with the growth of the outer passive layer.
Figure 5-12: Cyclic voltammograms for Fe | 30wt% MEA + H₂O + CO₂, at 10 mV s⁻¹ ($T = 25^\circ C$, pH 8.01) with positive potential limits: (a) -0.40 V, (b) -0.20 V, (C) +0.20 V (d) +0.60 V (e) +1.0 V.

In general, the electrochemical response during the negative-going potential scan to changes in $E_{s,a}$ could be attributed to changes in the stabilisation of the oxidation products formed during the prior positive-going potential scan. The increase in the magnitude of the reactivation peak (IV) with decreasing positive potential limits $E_{s,a}$ was due to the decreasing amount of passivating film formed and so less charge was required subsequently for its reductive removal by reaction (5. 18) and (5. 19), thereby reactivating the oxidation reaction (5. 20) anodic peak (IV) was shown clearly to result from cathodic reduction of the passive film with the anodic dissolution of the Fe to soluble Fe$^{II}_{(aq)}$. 
5.3.3. Effect of potential scan rate

The potentiodynamic behaviour of Fe in 30 wt% MEA at pH 8.01 also varied with the potential scan rate, but the anodic part of the voltammograms generally exhibited the same form and the onset of oxidation occurred at the same potential for all scan rates (Figure 5-13).

At constant rotation rate, the magnitude of peak I depended linearly on the scan rate and the potentials corresponding to the peaks also shifted with changes in scan rate which is indicative of a process that is not diffusion limited but rather controlled by the charge-transfer process (Figure 5-14). The negative-going potential scan at 100 mV s\(^{-1}\) exhibited cathodic current densities independent of rotation rate with a current density peak at -0.39 V, the associated charge of which decreased at 50 mV s\(^{-1}\). Current densities detected during the negative-going potential scan due to re-activation of the oxidation process occurred only at lower scan rates (1-50 mV s\(^{-1}\)), with oxidation charge densities increasing and reduction charge densities decreasing with decreasing scan rate. The current density of peak (II) appeared to be independent of potential scan rate between 10 – 100 mV s\(^{-1}\), but increased with scan rate at lower scan rates. The current densities of peak II did not increase linearly with either the potential scan rate or its square root, as it was likely to result from diffusion controlled dissolution occurring simultaneously with passivation of the iron surface by (hydr-)oxides. The potential corresponding to the current peak II became more positive with increasing scan rate, due to the latter process; hence for near steady-state measurements, a potential scan rate of 10 mV s\(^{-1}\) was maintained for all other experiments. The magnitude of peak II increased linearly with \(\nu\) for the range of potential scan rates used (Figure 5-15 and Figure 5-16) and the variation in peak II with scan rate at each rotation rate used is also reported in Appendix (II). The total anodic charge density \((Q_{ox})\) also increased with decreasing scan rate and is tabulated below:
Table 5-1: Effects of rotation and potential scan rates on anodic charge / C m\(^{-2}\) passed with Fe RDE in 30 wt% MEA + H\(_2\)O + CO\(_2\) (T = 25°C, pH 8.01).

<table>
<thead>
<tr>
<th>Potential scan rate / mV s(^{-1})</th>
<th>100</th>
<th>50</th>
<th>10</th>
<th>5</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation rate / s(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>2.00</td>
<td>3.23</td>
<td>11.53</td>
<td>15.35</td>
<td>62.35</td>
</tr>
<tr>
<td>16</td>
<td>1.82</td>
<td>2.85</td>
<td>11.12</td>
<td>13.79</td>
<td>54.31</td>
</tr>
<tr>
<td>9</td>
<td>2.00</td>
<td>2.78</td>
<td>10.22</td>
<td>13.05</td>
<td>44.14</td>
</tr>
<tr>
<td>4</td>
<td>1.92</td>
<td>2.59</td>
<td>8.70</td>
<td>10.76</td>
<td>29.91</td>
</tr>
<tr>
<td>1</td>
<td>1.67</td>
<td>2.56</td>
<td>7.86</td>
<td>8.77</td>
<td>27.07</td>
</tr>
<tr>
<td>0</td>
<td>1.98</td>
<td>2.46</td>
<td>7.44</td>
<td>8.47</td>
<td>20.12</td>
</tr>
</tbody>
</table>
Figure 5-13: Effect of potential scan rate on voltammograms for a Fe RDE in 30wt% MEA + \( \text{H}_2\text{O} + \text{CO}_2 \) (\( T = 25^\circ\text{C} \), pH 8.01, \( f = 1500 \) rpm,) (a) \( 100 \leq \nu \leq 10 \text{ mV s}^{-1} \) (b) \( 10 \leq \nu \leq 1 \text{ mV s}^{-1} \).

Figure 5-14: Effect of potential scan rate on current density for peak I of stationary Fe electrode in 30wt% MEA + \( \text{H}_2\text{O} + \text{CO}_2 \) (\( T = 25^\circ\text{C} \), pH 8.01).
Figure 5-15: Effects of rotation and potential scan rates on current density of peak(II), \( j_{\text{pII}} \), on Fe in 30wt% MEA + H\(_2\)O + CO\(_2\), at scan rates \( 100 \leq v \leq 10 \text{ mV s}^{-1} \)

Figure 5-16: Effects of rotation and potential scan rates on peak (II) current density \( j_{\text{pII}} \) of Fe in 30wt% MEA + H\(_2\)O + CO\(_2\), at various scan rates \( 10 \leq v \leq 1 \text{ mV s}^{-1} \)
5.4. Effect of Process Parameters

Results are reported below for the effects of CO₂ loading, amine concentration, solution temperature and oxygen presence on the electrochemical behaviour of iron in MEA-H₂O- CO₂ system using 30wt% MEA at full CO₂ saturation 25°C as the reference point.

5.4.1. Effect of temperature

A variation in solution temperature has a significant effect on the electrochemical behaviour of iron in aqueous MEA-CO₂ systems. Figure 5-17 shows the effect of temperature in the range 25°C ≤ T ≤ 80°C on cyclic voltammograms for an iron electrode rotated at 1500 rpm in 30 wt% MEA fully saturated with CO₂ at a pH 8.01, as previously over the same potential range -1.4 V ≤ E ≤ +1.0 V; similar results were obtained for other rotation rates (see Appendix II).

![Figure 5-17: Effect of aqueous solution temperature on cyclic voltammograms for iron RDE in 30 wt% MEA + H₂O + CO₂ at pH ~8.01; 10 mV s⁻¹, f = 1500 rpm.](image)

The following observations were made from the experimental results:
(i) The onset of oxidation occurred at essentially the same potential (−0.75 ± 0.1 V) for the temperature range studied.

(ii) Increasing temperatures resulted in peak (I), peak (II) and peak (IV) being displaced towards less positive potentials. Peak (I) also became less pronounced with increasing temperature and eventually disappeared at 80°C. This displacement of the peak potentials could be explained by the change in the standard potential of the AgCl/Ag reference electrode with temperature. The standard potential (the potential at which the chloride activity is 1 mol kg\(^{-1}\)) of the AgCl/Ag electrode is a function of temperature. The correlation for the standard potential of the AgCl/Ag electrode as a function of temperature, for \(0 \leq T \leq 95\) °C is given by (Bard, 1985):

\[
E^0(V) = 0.23695 - 4.8564 \times 10^{-4}T - 3.4205 \times 10^{-6}T^2 - 5.869 \times 10^{-9}T^3
\]

(5.29)

This correlation was used to produce the data in the table below:

Table 5-2: Effect of temperature on the peak (II) electrode potential after taking into account the shift in electrode potential of AgCl/Ag with respect to standard hydrogen electrode (SHE)

<table>
<thead>
<tr>
<th>Temperature, (T/°C)</th>
<th>AgCl/Ag vs. SHE /V</th>
<th>(E_p(II)) vs. Ag/AgCl /V</th>
<th>(E_p(II)) vs. SHE at (T/)V</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.2224</td>
<td>-0.453</td>
<td>-0.675</td>
</tr>
<tr>
<td>40</td>
<td>0.2120</td>
<td>-0.463</td>
<td>-0.675</td>
</tr>
<tr>
<td>50</td>
<td>0.2045</td>
<td>-0.471</td>
<td>-0.676</td>
</tr>
<tr>
<td>60</td>
<td>0.1965</td>
<td>-0.481</td>
<td>-0.678</td>
</tr>
<tr>
<td>70</td>
<td>0.1881</td>
<td>-0.490</td>
<td>-0.678</td>
</tr>
<tr>
<td>80</td>
<td>0.1791</td>
<td>-0.499</td>
<td>-0.678</td>
</tr>
</tbody>
</table>

(iii) As expected, current densities increased with temperature in the active region, peak (1), peak (III) and the anodic reactivation peak (IV), whereas passive current densities were independent of the temperature. At elevated temperatures, hydrogen
evolution current densities were increased, while oxygen evolution current densities were detected only at $T \geq 50$ °C and increased with temperature.

(iv) In the 25-80°C range studied, there was a linear increase in the magnitude of peak II with $j^{1/2}$ and gradients of the lines and intercepts increased with temperature.

(v) The number and distribution of peaks in the voltammograms remained the same in the 25-80°C range studied, and the relationship between the current density for peak II and $T^{-1}$ was found to be linear, as shown in the Arrhenius plot for various rotation rates in Figure 5-19. The apparent activation energy, $E_a$ related to each peak was calculated from the gradients of the Arrhenius plots and listed in Table 5-2.

![Graph showing the effect of rotation rate and temperature on peak current density](image)

**Figure 5-18:** Effect of rotation rate and temperature (18 °C ≤ T ≤ 80 °C) on $j_{II}$ for Fe RDE in 30 wt% MEA + H$_2$O + CO$_2$, at 10 mV s$^{-1}$ (pH 8.01).
Figure 5-19: Arrhenius plot for $j_{\text{pII}}$ 30 wt% MEA + H$_2$O + CO$_2$, at 10 mV s$^{-1}$ (pH 8.01) for varying aqueous solution temperatures ($18 \, ^{\circ}\text{C} \leq T \leq 80 \, ^{\circ}\text{C}$) and rotation speeds (60 rpm $\leq f \leq$ 1500 rpm).

Table 5-3: Activation energy associated with $j_{\text{pII}}$ for Fe RDE in 30 wt% MEA + H$_2$O + CO$_2$, at 10 mV s$^{-1}$ (pH 8.01) for varying aqueous solution temperatures ($18 \, ^{\circ}\text{C} \leq T \leq 80 \, ^{\circ}\text{C}$) and rotation speeds (60 rpm $\leq f \leq$ 1500 rpm)

<table>
<thead>
<tr>
<th>Rotation rate / rpm</th>
<th>Activation Energy (Peak II) / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>20.4</td>
</tr>
<tr>
<td>960</td>
<td>18.4</td>
</tr>
<tr>
<td>540</td>
<td>17.9</td>
</tr>
<tr>
<td>240</td>
<td>11.6</td>
</tr>
<tr>
<td>60</td>
<td>0.9</td>
</tr>
</tbody>
</table>

$E_{\text{act}} < 30 \, \text{kJ mol}^{-1}$, implies process was controlled by diffusional process(es) rather than chemical reaction control, i.e. breaking of chemical bonds, which normally requires $> 60 \, \text{kJ mol}^{-1}$. 
5.4.2. Effects of CO₂ loading and pH

From the voltammetric behaviour of iron in 30 wt% MEA, it was inferred that the decrease in pH due to absorption of CO₂ facilitated oxidative dissolution, whereas alkanolamines alone are not intrinsically corrosive. In order to further validate this behaviour, an Electrochemical Quartz Crystal Microbalance (EQCM) was used to measure the resulting mass loss and discriminate between passivation and dissolution processes with a resolution on the nanogram (ng cm⁻²) scale. It has been employed effectively in the study of FeCO₃ passive film formation by (Fajardo et al.) and the growth and dissolution of passive Fe-Cr alloys by (Hamm et al., 2002) & (Schmutz and Landolt, 1999)

As there are no commercially available Fe quartz crystal electrodes compatible with the EQCM cell utilized for this research, iron electrodes were produced by electroplating the gold electrode at a potential of -1.0 V in a 300 g dm⁻³ ferrous sulfate solution at pH 3.2 and 25 °C. Figure 5-20 shows the polarisation behaviour and the accompanying mass change of the gold quartz crystal in that solution.

On the positive-going potential scan starting from the negative potential limit (-1.4 V), reduction current densities were detected initially with a corresponding increase in mass due to the reduction of the Fe²⁺ₐq species to Fe, which was deposited on the surface of the gold crystal via reaction (5.30):

\[ \text{Fe}^{2+} + 2e^- \leftrightarrow \text{Fe} \]  

(5.30)

On scanning the potential to values positive of the equilibrium potential for iron dissolution to Fe⁺ₐq \( (E_{Fe^{2+}/Fe} = -0.79 \text{ V}) \), oxidation current densities were recorded accompanied by an expected mass loss, until the electrode reached the set positive potential limit. On the subsequent negative-going potential excursion, current densities and the resulting mass change
remained essentially constant until the potential reached the equilibrium potential $E_{\text{Fe}^{2+}/\text{Fe}}$, after which reduction of the dissolved $\text{Fe}^{II}_{\text{aq}}$ species to $\text{Fe}$ occurred with an increase in mass.

Figure 5-20: Cyclic voltammogram and corresponding massogram for Au quartz crystal in 300 g dm$^{-3}$ aqueous FeSO$_4$ at pH 3.2; at 10 mV s$^{-1}$, $T = 25$ °C).

From the voltammogram, it was deduced that the reduction of $\text{Fe}^{II}$ from a solution of FeSO$_4$ would occur at potentials negative of the equilibrium potential. Hence, a potential of -1.0 V was selected for iron deposition; the resulting current density-time and $\Delta m$-time data are shown in Figure 5-21. $\Delta m$ increased linearly with time and a total mass of 5838 mg m$^{-2}$ was deposited in 200 s. The total mass increase detected by the EQCM corresponded to 89.3% of the total charge passed ($2.26 \times 10^4$ C m$^{-2}$) in the current-time data.
Figure 5-21: Potentiostatic deposition of Fe on Au quartz crystal in 300 g dm\(^{-3}\) FeSO\(_4\) at pH 3.2, -1.0 V (AgCl|Ag) and \(T = 25 \, ^\circ\mathrm{C}\).

After the deposition process was completed, the FeSO\(_4\) solution in the quartz crystal cell was emptied and swiftly replaced with unloaded 30wt\% MEA at pH 12.55. Figure 5-22 shows the resulting cyclic voltammogram of the electroplated Fe crystal swept at a rate 100 mV s\(^{-1}\) from -1.0 V to a positive limit of +0.1 V and negative limit of -1.2 V. Figure 5-23 shows the mass change corresponding to the voltammogram in Figure 5-22. Prior to the voltammetric procedure, the electrode was reduced at -1.0 V for 60 s to reduce any oxides that may have formed spontaneously on the surface. At the starting potential of -1.0 V, the voltammogram showed oxidation current densities due to the oxidation of Fe to Fe(OH)\(_2\) \((E_{\text{Fe(0H)2/Fe}} = -1.03 \, \text{V})\) and the subsequent oxidation to Fe\(_3\)O\(_4\) \((E_{\text{Fe3O4/Fe(0H)2}} = -1.01 \, \text{V})\). The first cycle produced 3 anodic peaks, while on the second cycle, the first and third peak became less evident and only the second peak was prominent. This broadening effect of the peaks, as well as decreasing current densities, was due to the accumulation of passivating species on the surface which were not completely reduced on the subsequent negative-going potential scan. In
accordance with the results from the cyclic voltammogram, on the positive-going cycle, there was a net increase in mass due to the adsorption of oxides/hydroxides on the surface, and a loss in mass on the negative-going cycle as these oxides/hydroxides were reduced back to elemental Fe (Figure 5-23). On closer inspection of the voltammogram and the resulting $\Delta m$, it can be seen that between the starting potential of -1.0 V and -0.6 V (peak II), increasing current density resulted in an increase in mass and at -0.6 V $\leq E \leq$+0.1 V, both current densities and $\Delta m$ remained essentially constant due to passivation of the electrode surface. On the subsequent negative-going potential scan, passivation current densities and $\Delta m$ were initially constant until reaching a potential of ca. -0.56 V, below which current densities and $\Delta m$ started to decrease due to reduction of the species that had been oxidised during the previous positive-going scan. In general, there was a net accumulation of mass from cycle to cycle.

![Cyclic voltammogram](image)

Figure 5-22: Cyclic voltammogram obtained on the deposited Fe quartz crystal in 30 wt% MEA + H$_2$O, at 100 mV s$^{-1}$ (T = 25 °C, pH 12.55) with equilibrium reaction potentials assigned.
Figure 5-23: Mass change corresponding to voltammogram (Figure 5-22) of electrodeposited Fe quartz crystal in 30 wt% MEA + H₂O, at 100 mV s⁻¹ (T = 25 °C, pH 12.55) with reactions assigned.

The voltammetric / Δm-E behaviour was completely different in CO₂ loaded 30 wt% MEA solutions at pH 8.01 (Figure 5-24 and Figure 5-25). The voltammogram (dE/dt = 100 mV s⁻¹) exhibited 3 oxidation peaks at ca. -0.67 V, -0.51 V and -0.28 V and two reduction peaks at ca. -0.44 V and -0.91 V, as in the voltammogram recorded with the RDE under the same conditions (f=0) and scan rate. However, unlike the voltammogram recorded in the absence of CO₂, there was a net loss in mass during the positive-going potential scan corresponding to the oxidative dissolution of Fe as aqueous FeII. From the potential at which oxidation current densities resulted from ca. -0.88 V to -0.38 V just after the appearance of peak II, there was a mass loss of 9.28 mg m⁻² which corresponded to about 52 % of the total anodic charge passed (60.84 C m⁻²). In the passive region extending from -0.4 V to the positive potential limit of +0.5 V, both current densities and Δm remained essentially constant, even on the negative-going scan until reaching a potential of -0.4 V. At more negative potentials, reduction current densities resulted and Δm continued to decrease due to a reduction of the species formed back to elemental iron. Suddenly, at ca. -0.85V there is an increase in Δm even with increasing reduction current. This
was due to the deposition of Fe from dissolved Fe$^{II}_{aq}$ in the solution ($E_{Fe^{2+}/Fe} = -0.79$ V).

From cycle to cycle, there was a slight increase in current densities and a significant mass loss.

![Cyclic voltammogram](image)

Figure 5-24: Cyclic voltammogram of electrodeposited Fe quartz crystal in 30 wt% MEA + H$_2$O + CO$_2$ at pH 8.01, 100 mV s$^{-1}$, $T = 25$ °C; equilibrium reaction potentials assigned.

![Mass change](image)

Figure 5-25: Mass change corresponding to voltammogram (Figure 5-24) of electrodeposited Fe quartz crystal in 30 wt% MEA + H$_2$O + CO$_2$, at 100 mV s$^{-1}$ ($T=25$ °C, pH 8.01).
The effects of CO\textsubscript{2} loading / pH was studied further with the RDE by varying the CO\textsubscript{2}-air mixture to achieve the desired CO\textsubscript{2} loading. The reported pH values were recorded at 25 °C. As mentioned previously, in the absence of CO\textsubscript{2} at pH 12.55, the oxidation part of voltammogram displayed only a passive region; the same was found for low CO\textsubscript{2} loading at pH 11.00 (Figure 5-27).

The characteristic active-passive behaviour of Fe electrodes in MEA solutions loaded with CO\textsubscript{2} became evident only at pH 10.01 (Figure 5-28), at which a barely visible and broad current density peak at ca. -0.67 V appeared due to the active oxidative dissolution of Fe to Fe\textsuperscript{II}. The current density and charge resulting from the active current peak continued to increase with CO\textsubscript{2} loading (decreasing pH), with the highest value for the active current peak being recorded at the lowest pH, when the solution was fully saturated with CO\textsubscript{2} at pH 8.01 (Figure 5-34). The same was found for the re-activation current density peak on the negative-going scan which became evident only at pH ≤ 8.43 and increased with CO\textsubscript{2} loading. It is also worth noting that increasing the CO\textsubscript{2} loading and reducing the pH led to a positive potential shift in the onset of oxidation, the active current density peak and re-activation peak.

![Figure 5-27: Voltammogram at pH 12.55](image-url)

- \( E_{\text{Fe(OH)}_2/\text{Fe(OH)}_3} = -0.70 \text{V} \)
- \( E_{\text{Fe}_{204}/\text{Fe}_{203}} = -0.75 \text{V} \)
- \( E_{\text{Fe(OH)}_2/\text{Fe}_{304}} = -1.01 \text{V} \)
- \( E_{\text{Fe}/\text{Fe(OH)}_2} = -1.03 \text{V} \)
- \( E_{\text{H}_2\text{O}/\text{H}_2} = -0.94 \text{V} \)
- \( E_{\text{H}_2\text{O}/\text{O}_2} = +0.29 \text{V} \)
Figure 5-26: Effect of rotation rate on cyclic voltammograms of iron RDE in 30 wt% MEA at pH 12.55 and $T = 25 ^\circ$C; 10 mV s$^{-1}$, with equilibrium potentials of reactions assigned.

![Figure 5-26](image1)

$pH$ 11.00

![Figure 5-26](image2)

Figure 5-27: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA+ CO$_2$ at pH 11.00 and $T = 25 ^\circ$C; 10 mV s$^{-1}$, with equilibrium potentials of reactions assigned.

![Figure 5-27](image3)

$pH$ 10.01

![Figure 5-27](image4)

Figure 5-28: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA+ CO$_2$ at pH 10.01 and $T = 25 ^\circ$C; 10 mV s$^{-1}$, with equilibrium potentials of reactions assigned.

![Figure 5-28](image5)
Figure 5-29: Cyclic voltammogram of stationary iron RDE in 30wt% MEA + CO\textsubscript{2} at pH 9.54 and \( T = 25 \, ^\circ\text{C} \); 10 mV s\textsuperscript{-1}, with equilibrium potentials of reactions assigned.

Figure 5-30: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA + CO\textsubscript{2} at pH 9.06 and \( T = 25 \, ^\circ\text{C} \); 10 mV s\textsuperscript{-1}, with equilibrium potentials of reactions assigned.
Figure 5-31: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA + CO$_2$ at pH 8.78 and $T = 25$ °C; 10mVs$^{-1}$, with equilibrium potentials of reactions assigned.

Figure 5-32: Cyclic voltammogram of stationary iron RDE in 30 wt% MEA + CO$_2$ at pH 8.43 and $T = 25$ °C; 10 mV s$^{-1}$, with equilibrium potentials of reactions assigned.
Figure 5-33: Cyclic Voltammogram obtained on a stationary iron RDE in 30 wt% MEA + CO$_2$ at pH 8.17 and $T = 25$ °C; 10 mV s$^{-1}$, with equilibrium potentials of reactions assigned.

Figure 5-34: Cyclic Voltammogram obtained on a stationary iron RDE in 30wt% MEA + CO$_2$ at pH 8.01 and $T = 25$ °C; 10 mV s$^{-1}$, with equilibrium potentials of reactions assigned.
Figure 5-35: Effect of pH on voltammograms of a stationary iron RDE in 30wt% MEA + CO₂ at $T = 25 \, ^\circ\text{C}$; 10 mV s⁻¹, $f = 1500$ rpm.

Figure 5-36: Effects of rotation rate and pH on peak current density $j_{\text{pII}}$ of Fe in 30 wt% MEA + H₂O + CO₂; potential scan rate: 10 mV s⁻¹.
Whilst it was established that MEA solutions became corrosive only on absorption of CO$_2$, it was yet to be determined if this is due primarily to the shift in pH of the system or as a result of the aqueous C$^{IV}$ species (HCO$_3^-$, CO$_3^{2-}$) and amine species (RNH$_3^+$) resulting from the chemical reactions of MEA, CO$_2$ and H$_2$O (Reactions 5.6 – 5.15). For this purpose, the effect of pH on the voltammetric behaviour of iron in MEA was also studied in the absence of CO$_2$ using both the RDE (Figure 5-38) and the EQCM (Figure 5-39 & Figure 5-40). The pH of the unloaded 30 wt% MEA solution was adjusted to the desired pH of 8.01 by addition of aliquots of 1.0 M H$_2$SO$_4$ solution at 25°C. The MEA solution with H$_2$SO$_4$ resulted in a radically different voltammogram from that of the solutions loaded with CO$_2$ at the same pH. The onset of oxidation occurred at the same potential for both solutions and current densities continued to increase due to the dissolution of Fe to Fe$^{II}_{aq}$ ($E_{Fe^{2+/Fe}} = -0.79$ V) until it reached a plateau at ca. -0.56 V, possibly limited by a dissolution-precipitation process due to the formation of (hydr-)oxides. As predicted by the potential-pH diagram for the Fe-H$_2$O system (Figure 5-5), this was due to the formation of Fe(OH)$_3$, which was also observed during the experiments as
a green rust on the surface of the electrode and in the solutions. Unlike the previous voltammogram in CO$_2$, in MEA + H$_2$SO$_4$ solutions, after scanning past the potential range for the active dissolution of Fe to Fe$^{II}$, current densities started to increase and there was a second active peak ca. +0.30 V at high rotation rates (540-1500 rpm). At lower rotation rates (0-240 rpm), the second peak broadened. This was also evidenced in the $\Delta m$ response of the EQCM (Figure 5-40) where it can be seen that there was a continued mass loss during the positive-going potential scan even at potentials up to +0.15 V, unlike the case of MEA-CO$_2$ systems in which mass loss ceased at potentials $\geq$ -0.4 V. In total, the mass lost during the anodic scan in MEA + H$_2$SO$_4$ solution was about 16.5 times that of the MEA + CO$_2$ systems.

Further positive-going potential scan resulted in a short passive region from potentials greater ca. +0.4 V for the RDE and +0.15 V in the case of the EQCM. It is important to note that the current densities and charge of the peak associated with Fe$\rightarrow$Fe$^{II}$ were much higher in the presence of CO$_2$. The contrary was the case for the rest of the positive-going potential scan, for which higher current densities were recorded in sulfuric acid due to active dissolution as opposed to passivation in the CO$_2$ system. The negative-going potential scan was also characterised by a reduction current peak at ca. -0.41 V and not a re-activation peak as evident in solutions loaded with CO$_2$. 
Figure 5-38: Effects of CO$_2$: – Comparisons between cyclic voltammogram for iron RDE in 30 wt% MEA+ CO$_2$ and 30 wt% MEA+ 1 M H$_2$SO$_4$; 10 mV s$^{-1}$ (T = 25 °C, $f = 0$- 1500 rpm).
Figure 5-39: Cyclic voltammogram of electrodeposited Fe quartz crystal in 30 wt% MEA + H$_2$SO$_4$ at pH 8.01 and $T = 25^\circ$C; 100 mV s$^{-1}$, with equilibrium potentials of reactions assigned.

$E_{\text{Fe}^{2+}/\text{Fe}^{3+}} = -0.66$ V
$E_{\text{Fe}/\text{Fe(OH)}_2} = -0.76$ V
$E_{\text{Fe}/\text{Fe}^{2+}} = -0.79$ V

Figure 5-40: Mass change corresponding to voltammograms (Figure 5-39) of electrodeposited Fe quartz crystal in 30 wt% MEA + H$_2$O + CO$_2$ at pH 8.01 and $T = 25$ C; 100 mV s$^{-1}$. 
5.4.3. Effect of MEA concentration

The MEA concentration in the aqueous solution also appeared to have important effects on the electrochemical behaviour of iron. Figure 5-41 & Figure 5-42 are voltammograms for an iron RDE rotated at 1500 rpm in 5-30 wt% and 30-60 wt% MEA consecutively (25 °C) that had been fully saturated with CO₂. As shown in Appendix (III), similar results were obtained for other rotation rates.

The anodic and cathodic sections of the voltammograms generally exhibited the same form, with the same number of peaks occurring at essentially the same potentials \((E_p)\) as for 30 wt% MEA and the onset of oxidation occurred at the same potential for each of the MEA concentrations. However, MEA concentrations had a significant effect on anodic current densities (Region B) associated with the Fe-Fe\(^{II}\)\(_{aq}\) dissolution process. Contrary to expectations reported in the literature (Kittel, 2010, Veawab et al., 1999, Kladkaew et al., 2009a) of anodic current densities increasing with MEA concentration, there were two distinct effects:

(i) Firstly, at lower concentrations (5-30 wt %), the anodic current densities increased with increasing MEA concentration. The peak potential also shifted slightly to lower potentials at higher MEA concentrations for 25-60 °C, but at 80°C, the maximum current density occurred in 40 wt% solution and was verified with the EQCM. The voltammograms (Figure 5-54) obtained from the EQCM were similar to those obtained from the RDE at 0 rpm. With increasing MEA concentration, the \(\Delta m\)-potential plot (Figure 5-45 and Figure 5-46) showed a net loss of mass during the positive-going potential scan.

(ii) At higher concentrations (30-60 wt% for 25-60°C, and 40-60 wt% for 80°C), anodic current densities decreased and peaked at higher potentials with increasing amine concentrations.
The linear relationship between the magnitude of the peak current density \( (j_{\text{PII}}) \) and the square root of RDE rotation rate \( (f^{1/2}) \) was maintained for the entire range of experiments, regardless of the amine concentration and temperature.

While the anodic current densities ascribed to the dissolution process (region B) were affected considerably, the passivation process (region C) appeared to be completely independent of MEA concentration.

![Diagram](image)

Figure 5-41: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at \( f = 1500 \) rpm in MEA+ CO\(_2\) at pH\( \approx 8.01\) and \( T = 25 \) °C; 10 mV s\(^{-1}\).
Figure 5-42: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at $f = 1500$ rpm in MEA+ CO$_2$ at pH-8.01 and $T = 25^\circ$C; 10 mV s$^{-1}$. 
Figure 5-43: Effects on $j_{\text{pH}}$ of rotation rate, temperature (25-80 °C) and aqueous MEA concentration (10-60 wt%) for Fe RDE in MEA + H$_2$O + CO$_2$ at pH~8.01; 10 mV s$^{-1}$. 
Figure 5-44: Cyclic voltammograms and corresponding mass change of electrodeposited Fe quartz crystal in (5-30 wt%) MEA + H₂O + CO₂ at pH 8.01 and T = 25°C, 100 mV s⁻¹.
Figure 5-45: Cyclic voltammogram of electrodeposited Fe on quartz crystal in (5-30) wt% MEA + H$_2$O at pH = 8.01 and $T = 25 \, ^\circ C$; 100 mV s$^{-1}$.

Figure 5-46: Mass changes corresponding to voltammograms (Figure 5-45) of electrodeposited Fe quartz crystal in (5-30 wt%) MEA + H$_2$O + CO$_2$ at pH 8.01 and $T = 25 \, ^\circ C$; 100 mV s$^{-1}$.
5.4.4. Effect of Oxygen

To clarify the effect of oxygen, cyclic voltammetry experiments for iron in 30 wt% MEA solutions fully loaded with CO\textsubscript{2} (25-80 °C) were repeated in the absence of O\textsubscript{2} by purging solutions with N\textsubscript{2} prior to loading with CO\textsubscript{2}. During experiments, the cell was covered with cling film and a nitrogen blanket was maintained to minimise oxygen ingress.

Cyclic voltammograms (Figure 5-47) obtained in the absence of oxygen generally exhibited the same form and the onset of oxidation occurred at the same potential as those obtained in the presence of oxygen; similar results were obtained for other rotation rates. However, the magnitudes of current densities of peaks (I) & (II) in the active region were lower in the absence of oxygen, the difference being more distinct at elevated temperatures (60-80°C). In the passive region, the magnitudes of potential-independent current densities were also marginally lower in the absence of dissolved oxygen.
Figure 5-47: Effect of oxygen concentration and temperature on cyclic voltammograms of iron RDE rotating at $f = 1500$ rpm in 30 wt% MEA+ CO$_2$ at pH (7.24-8.01) ; 10 mV s$^{-1}$. 
5.5. Interpretation and Discussion

Cyclic voltammograms obtained over a wide range of potential scan rates, RDE rotation rates positive potential limits, CO₂ loadings, MEA concentrations and temperatures showed that the active to passive transition of iron was strongly dependent on both the local hydrodynamic conditions and the composition of the MEA solutions.

Iron in aqueous MEA solutions in the absence of CO₂ exhibited passive behaviour, implying minimal corrosion of the underlying metal. However, CO₂ absorption in aqueous MEA reaction resulted in the formation of protonated amine (RNH₃⁺) and hydrogen carbonate ions (HCO₃⁻) that dissociate producing hydrogen ions (H⁺). The resulting decrease in pH from 12.55 in unloaded solutions to 8.1 in fully saturated solutions, as well as the increased equilibrium concentrations of oxidising species (H⁺ and HCO₃⁻) shifted the system from a passive to an active state, in which corrosion was thermodynamically and kinetically favourable.

**Anodic dissolution region**

Voltammograms of iron in MEA solutions at full saturation of CO₂ exhibited at least two anodic current peaks within the potential range of the active-passive transition, suggesting that the dissolution and passivation of metal involves a minimum of two stages.

The first anodic stage occurred in the potential range of peak I, at which only Fe²⁺ species are likely as oxidation products, according to predictions from the potential-pH diagram of iron in H₂O-CO₂ (Figure 5-8). The charge and magnitude of current density peak (I) in voltammograms of iron in MEA solutions were essentially independent of RDE rotation rate and pH, but increased linearly with potential scan rate, as expected for a surface transformation. However, the current density of peak (I) was temperature dependent and the corresponding charge increased with temperature. These results agree with those reported by (Castro et al.,

Based on these observations, as well as thermodynamic predictions, the first stage of oxidation of Fe (Peak I) can be assigned to a surface transformation reaction: the formation of a pre-passive layer of Fe(OH)$_2$ by the overall reaction:

$$\text{Fe} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + 2\text{e}^- \quad (5.31)$$

As the iron surface was covered by the Fe(OH$_2$) layer, the current decreased once the potential of peak I was exceeded.

The second oxidation stage, linked to the higher anodic peak (II) occurred in the potential range of -0.48 V to -0.52 V, at which only Fe$^{II}$ species can be formed according on thermodynamically predictions. There was a linear relationship between the current density at peak II ($j_{\text{pII}}$) with rotation rate ($f^{1/2}$) and $j_p \neq 0$ at $f^{1/2} = 0$, suggesting that diffusion of ionic species at the iron surface plays a role in limiting the rate of the oxidation process. The resulting mass loss from EQCM results (Figure 5-24) clearly showed that reaction 5.19 occurred simultaneously with the oxidative dissolution of Fe via reaction (5.32):

$$\text{Fe} \leftrightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (5.32)$$

Therefore, peak II can be attributed to the dissolution of iron through the pre-passive layer most likely in the form of soluble Fe$^{II}_{\text{aq}}$ species. As the reaction proceeded, both the thickness of the Fe(OH)$_2$ pre-passive layer and the concentration of Fe$^{II}$ at the electrode-solution interface increased. The dependence of $j_{\text{pII}}$ on rotation rate suggested that the latter reaction was the major contributor to current densities in this potential range. The same was also found for the anodic re-activation reaction that occurred during the negative-going potential sweep (peak IV).
At the outer layer, dissolved Fe\textsuperscript{II} can be precipitated as FeCO\textsubscript{3} if the concentration of the former at the iron | solution interface exceeds the saturation value of the latter. On close inspection of the $\Delta m$ data from the EQCM study of iron under stationary conditions, (Figure 5-24) there was a mass gain in the region of peak 3 due to the precipitation reaction (5.33).

$$Fe^{2+} + HCO_3^- + OH^- \rightarrow FeCO_3 + H_2O$$  \hspace{1cm} (5.33)

The formation of FeCO\textsubscript{3} was predicted by the potential-pH diagram in Figure 5-8. FeCO\textsubscript{3} precipitation was induced only by high local concentration of both the ferrous ions and carbonate / hydrogen carbonate ions. As the rotation rate was increased, the local concentrations of the soluble species near the electrode surface were decreased, deferring or even preventing precipitation, so explaining the disappearance of peak III (Figure 5-10) on rotating the RDE. The Fe\textsuperscript{II} activity-pH diagram for FeCO\textsubscript{3} and Fe(OH)\textsubscript{2} precipitation in H\textsubscript{2}O-CO\textsubscript{2} systems is shown in Figure 5-48.

Figure 5-48: Activity-pH diagram of Fe-H\textsubscript{2}O-CO\textsubscript{2} at 0.1 MPa CO\textsubscript{2}; 298 K (Kelsall, 2015).

In addition to FeCO\textsubscript{3}, another likely corrosion product of iron in CO\textsubscript{2}-containing systems is iron hydroxycarbonate Fe\textsubscript{2}(OH)\textsubscript{2}CO\textsubscript{3}, for which the International Mineralogy Association (IMA) approved the name ‘chukanovite’. The formation of Fe\textsubscript{2}(OH)\textsubscript{2}CO\textsubscript{3} according to
reactions (5.34) or (5.35) was also predicted by the potential-pH diagram in (Figure 5-8) for Fe-H₂O-CO₂ systems, from pH = 7-8 to pH 11.5-12, depending on the CO₂ partial pressure. However, the precipitation of chukanovite occurs preferentially to siderite at higher Fe\textsuperscript{II} activities.

\[
Fe₂(OH)_2CO₃ + 2H^+ \leftrightarrow Fe^{2+} + FeCO₃ + 2H₂O \quad (5.34)
\]

\[
Fe^{2+} + FeCO₃ + 2OH^- \leftrightarrow Fe₂(OH)_2CO₃ \quad (5.35)
\]

At equilibrium: \[
\log(Fe^{2+}) = 10.70 - 2pH \quad (5.36)
\]

so higher Fe\textsuperscript{II} activities / concentrations are predicted to favour chukanovite rather than siderite. The reactions that occurred within the active region were affected significantly by temperature; the charge density of peak II more than doubled at 80°C compared to at 25°C.

In order to establish the effect that CO₂ had on the corrosion behaviour of iron in MEA systems, it was important to distinguish between the effects of pH and the effect oxidising species resulting from the absorption of CO₂ (HCO₃⁻, CO₃²⁻, RNH₃⁺). Hence, the behaviour was studied of iron in CO₂-free solutions of MEA that had been adjusted by the addition of H₂SO₄ to the same pH as that of fully CO₂ loaded solutions. The results clearly showed that in the absence of CO₂, even at the same pH, the electrochemical behaviour was radically different. As observed in MEA-CO₂-H₂O systems, there was also an anodic current peak in the potential range associated with dissolution of Fe to Fe\textsuperscript{II}ₐq, but current densities were significantly less in the absence of CO₂; the differences were more evident at higher rotation rates (Figure 5-38). The presence of CO₂ increased the Fe oxidation rate predominantly by increasing the rate of the hydrogen evolution reaction (HER):
\[
2H^+ + 2e^- \rightarrow \text{H}_2 \tag{5.37}
\]

The rate of the dissolution reaction was limited by the mass transport of H\(^+\) ions from the bulk solution to the surface of the iron electrode. In solutions of pH > 4, this limiting flux of H\(^+\) ions is usually quite small. In the case of MEA-H\(_2\)O-CO\(_2\), the flux of H\(^+\) ions was increased by the presence of RNH\(_3^+\) and HCO\(_3^-\) resulting from the absorption of CO\(_2\) in MEA (5.7 – 5.8) and from the reaction of H\(_2\)O and CO\(_2\) (5.12). This explains the increased dissolution current densities in the presence of CO\(_2\), as compared to the same MEA solution pH-adjusted with sulfuric acid to the same pH.

The presence of HCO\(_3^-\) and RNH\(_3^+\) in the solution can increase Fe dissolution rates through dissociation via reactions (5.9) – (5.10) which serve as additional sources of H\(^+\) ions and were consequently reduced via reaction (5.37). Thus, it was unsurprising when the dissolution current increased with increasing CO\(_2\) loading and decreasing pH (Figure 5-26 and Figure 5-35).

The dependence of the iron dissolution kinetics on ionic composition was also studied using cyclic voltammetry in sodium hydrogen carbonate-carbonate solutions at pH 8.1 (Appendix IV). The voltammograms obtained were similar to those of iron in MEA+CO\(_2\)+H\(_2\)O systems. There was also a large anodic peak (II) at the same potential which corresponded to the dissolution of Fe to Fe\(^{II}\)\(_{\text{aq}}\). In addition to the observed dependence of peak (II) on rotation rate, its magnitude and associated charge increased linearly with HCO\(_3^-\) ion concentration. As this set of results was obtained over a range of HCO\(_3^-\)/CO\(_3^{2-}\) concentration ratio at a practically constant pH, it can be concluded that the change in the kinetics of the dissolution reaction was related principally to a process under HCO\(_3^-\) ion transport control.
It has also been suggested that the charge and current density of the peak increasing with hydrogen carbonate concentration could be due to the removal of the pre-passive Fe(OH)₂ layer according to the following dissolution reaction (Castro et al., 1986):

\[ \text{Fe(OH)}_2 + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{OH}^- + \text{Fe}^{2+} + \text{H}_2\text{O} \quad (5.38) \]

The presence of carbonate and hydrogen carbonate ions also contributed, by precipitating the Fe²⁺ resulting from the dissolution of the underlying metal and enhancing the transport of ions through the complex passive layer consisting of an Fe(OH)₂ inner layer and an outer layer of FeCO₃.

In summary, it can be said that reactions (5.18), (5.19) and (5.38) coupled with reaction (5.32) result in the corrosion of the metal, as evident from Figure 5-24 and Figure 5-25, showing EQCM data of mass loss in the potential range of peak II. Within this region, there was competition between the dissolution of iron and the protective passive layer formation.

**Passivation region**

In the MEA solution, Fe dissolution was inhibited by the formation of a passive film, characterized by the presence of peak III, which was evident only when the RDE was stationary and disappeared when it was rotated. The magnitudes of the current densities detected within the passive region were proportional to the scan rate and were practically independent of the rotation rate, solution pH and the CO₂ loading. This implied that the rate-determining step in the passive region of peak III was indeed a surface transformation reaction. This implied that the passive layer was an oxide or hydroxide film and HCO₃⁻ / CO₃^{2-} played no part in the passivation process.

The potential-pH diagram for the relevant pH region predicts that passivation of iron / mild steel at sufficiently anodic potentials, can be assigned to the formation of a Fe₂O₃ / Fe₃O₄ film. At low potentials, the presence of Fe₃O₄ is thermodynamically favourable (at potentials ≥ -
0.66 V, pH 8.1) while Fe₂O₃ is more stable at higher potentials (≥ -0.48 V). The formation of (metastable) Fe³⁺ hydroxide (Fe(OH)₃) was also possible at potentials > -0.43 V. The total charge density involved in passive film formation corresponded to ca. 5 monolayers.

On negative-going potential sweeps to potentials below the passive region, the j-E response was dependent on the anodic potential limit; a reactivation of the anodic process (peak IV) occurred at about the same potential range in which the dissolution reaction occurred on the positive-going potential scan. This sudden and unexpected anodic current was probably due to reductive dissolution of the passive film, exposing the underlying metal, which then oxidised producing net current densities that decayed with decreasing potential. That decay could also have resulted from Fe²⁺ surface concentrations inhibiting further dissolution because of e.g. FeCO₃ formation. In summary, the passive film becomes increasingly stable as the positive potential limit was increased (Figure 5-12).

5.6. Kinetic analysis

From the potentiodynamic study of iron in MEA solutions, it was apparent that operating parameters such as temperature, CO₂ loading, amine concentration and oxygen content significantly altered the electrochemical response. The changes in the electrochemical behaviour could be directly related to the impact that the operating conditions had on the chemistry and the ionic composition of the aqueous solution. A Kent-Eisenberg type model, explained in detail in Chapter 6, was employed to estimate the concentrations of these chemical species in the bulk solution at each operating condition. Each ionic species has a different effect on the corrosion of iron, with a strong dependence on the operating conditions especially the amine concentration, pH (CO₂ loading) and temperature. Results reported in this section aimed to relate the Fe oxidation kinetics to the operating conditions. Details of the experimental results are summarised in Appendix (V). The results were analysed and corrosion rate
measurements were conducted using Tafel plots, as described previously in the experimental methods Chapter 4.

5.6.1. Effect of CO₂ loading

CO₂ loading is an important parameter affecting iron / steel oxidation rates in alkanolamines; most of those commonly used in CO₂ absorption plants are not intrinsically corrosive, but become so on absorption of CO₂, as found for MEA. Figure 5-49 shows the effect of CO₂ loading on the voltammetric behaviour of iron in MEA+ H₂O systems, demonstrating that higher CO₂ loading resulted in higher cathodic and anodic current densities, implying higher corrosion rates. In short, increases in CO₂ loading led to a significant rise in the corrosion rates. As shown in (Figure 5-50), the corrosion rate of an iron electrode rotated at 1500 rpm (dE/dt = 10 mV s⁻¹) in 30 wt% MEA + H₂O (25 °C) in the absence of CO₂ had a comparably negligible corrosion rate of 0.278 mm y⁻¹ which, increased to 6.189 mm y⁻¹ at full CO₂ saturation under the same conditions. The impact of CO₂ on the corrosion of iron in the MEA-H₂O-CO₂ system can be explained by the absorption reaction of CO₂ in MEA via reaction schemes (5. 7) – (5. 10) and the reaction of CO₂ in water (5. 11) – (5. 13). As the CO₂ loading increases, there are higher amounts of hydrogen carbonate ion (HCO₃⁻) and protonated amine (RNH₃⁺) which then subsequently dissociate to form the hydrogen ion H⁺. Enhancement in the hydrogen evolution reaction (5. 14) with increasing concentrations of HCO₃⁻ and RNH₃⁺ results in expediting the kinetics of the anodic reactions, which in the active region primarily consists of the dissolution of iron.
The influence of CO$_2$ loading was evaluated further by calculating the equilibrium concentrations of the ionic species using the Kent Eisenberg model. It can be seen from (Figure 5-6) that increases in CO$_2$ loading yields higher amounts of hydrogen carbonate ion and protonated amine and thus hydrogen ions (Figure 5-51). This increase in H$^+$ ions at higher CO$_2$ loadings is also evidenced experimentally as the pH decreases with CO$_2$ loading. Unloaded 30 wt% MEA+ H$_2$O (25°C) solutions have a pH of 12.55 but the pH gradually lowers with increasing CO$_2$ loading, reaching a minimum of pH 8.01 at full saturation. This change in pH shifts the MEA + H$_2$O+ CO$_2$ aqueous system from the ‘passive’ region in which corrosion is thermodynamically unfavourable to the ‘active region’ where corrosion is predicted.
5.6.2. Temperature effect

The experimental results showed, as expected, that over the range 25 and 80 °C, temperature had a very significant role on the oxidation rate of iron in MEA-H₂O-CO₂ systems. On a typical CO₂ absorption plant, the absorber operates at ca. 40 °C and the heat exchanger at 80 °C.
The voltammograms (Figure 5-52 & Figure 5-55) for various concentrations of MEA showed that increasing the temperature had a substantial effect on both the anodic and cathodic reaction rates with increases in current densities at higher temperatures. For example, the corrosion rate of an iron electrode rotated at 1500rpm \((dE/dt = 10 \text{ mVs}^{-1})\) in 30 wt\% MEA + H\(_2\)O + CO\(_2\) at full saturation of CO\(_2\) increased from 6.189 mm y\(^{-1}\) at 25°C to 17.675 mm y\(^{-1}\) at 80°C. Similar results were obtained at all rotation rates and MEA concentrations studied within this work (Appendix V).

The increase in corrosion rate with temperature can be explained by the role of temperature in the reaction kinetics as temperature generally expedites the rate of any reaction (Levenspiel, 1999). Elevated temperatures increase the rate of all processes involved in the corrosion processes including the mass transport of the species, chemical reactions in the bulk solution and the electrochemical reactions at the iron surface. In this particular case, reactions (5. 7) and (5. 8) are accelerated with increasing temperature which in turn increases the amounts of protonated amine (RNH\(_3^+\)) and hydrogen carbonate ion (HCO\(_3^-\)) in solution. The effect of temperature on the equilibrium H\(^+\) concentration in solution, calculated by the Kent-Eisenberg model is also shown in Figure 5-56. The increased amounts of RNH\(_3^+\) and HCO\(_3^-\) ions result in a shift in order to maintain the equilibrium of reactions (5. 9) and (5. 10), therefore producing more H\(^+\) ions in the system. This increase in hydrogen ion concentration was also evidenced experimentally by the reduction of solution pH with increasing temperature at full CO\(_2\) saturation (Table 5-4).
Figure 5-52: Effect of solution temperature on polarisation curves of iron RDE in 30 wt% MEA + H₂O + CO₂ at pH 7.24 - 8.01; 10 mV s⁻¹, f = 1500 rpm.

Figure 5-53: Effect of solution temperature on the corrosion rate obtained on iron RDE in 5-60 wt% MEA + H₂O + CO₂ at pH 7.24 - 8.01; 10 mV s⁻¹, f = 1500 rpm.
Figure 5-54: Effect of temperature on hydrogen ion concentration \([\text{H}^+]\) based on the Kent-Eisenberg model for 30 wt% MEA solution and 25°C.

Table 5-4: Effect of solution temperature on the pH for 30 wt% MEA at full CO\(_2\) saturation.

<table>
<thead>
<tr>
<th>Temperature/ °C</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>8.01</td>
</tr>
<tr>
<td>40</td>
<td>7.83</td>
</tr>
<tr>
<td>60</td>
<td>7.49</td>
</tr>
<tr>
<td>80</td>
<td>7.24</td>
</tr>
</tbody>
</table>
Figure 5-55: Effect of solution temperature on polarisation curves of iron RDE in 5-60wt% MEA + H₂O + CO₂ at pH 7.24-8.01; 10 mV s⁻¹, f = 1500 rpm.
5.6.1. Effect of MEA Concentration

The effects of amine concentration on iron / steel corrosion rates have been the subject of a few report (Kohl and Riesenfeld, 1985), (Kohl and Nielsen, 1997), (Veawab et al., 1999), (Kladkaew et al., 2009a) and (Kittel, 2010). While (Kladkaew et al., 2009b) & (Kittel, 2010) used MEA alone, (Veawab et al., 1999) & (Nainar and Veawab, 2009) also conducted studies on other commercially-available amines, such as AMP, DEA and MDEA. Based on the previously conducted studies on MEA, 20-30 wt% has been considered to be the maximum concentration range, above which the corrosion rate was thought to increase drastically. In order to verify this, seven experiments were conducted in 5-60 wt% MEA, fully saturated in CO₂ at varying temperatures and rotation rates (25-80 °C, 0-1500 rpm). The resulting polarization curves are presented in Figure 5-56 – Figure 5-59. For all the experiments conducted, the open circuit potential measured at the start of each experiment was very close (± 0.03 V) to the observed corrosion potential obtained from the polarization curves. Based on the Tafel plots, it was evident that MEA concentration had a significant effect on anodic current densities. According to Figure 5-60, MEA concentrations affected corrosion rates in two distinctive ways:

i) At lower concentrations, corrosion rates increased with increasing amine concentration, for concentrations < 30 wt%, for all temperatures and mass transport rates studied. This initial increase in corrosion rate with amine concentration was also evident from the polarisation curves (Figure 5-56 and Figure 5-59). As the MEA concentration was increased from 5 wt% to 30 wt%, anodic current densities increased in the active region of the polarisation curve. The increase in corrosion rate with MEA concentration can be explained by taking into account the vapour-liquid equilibrium of the MEA-H₂O-CO₂ system. Based on simple stoichiometry of reactions (5. 7) – (5. 10) and the equilibrium concentrations of the chemical species in solution calculated by the Kent-Eisenberg
Model, there was a corresponding increase in the total amount of CO$_2$ absorbed with increasing amine concentration, i.e. increased CO$_2$ loading with MEA concentration. This increased CO$_2$ loading directly affected the predicted concentrations of protonated amine (RNH$_3^+$) and hydrogen carbonate ion (HCO$_3^-$), and H$^+$ ions (Figure 5-61).

ii) As shown by Figure 5-60, corrosion rates increased dramatically between 20-30 wt% and reached a peak at 30 wt%, above which it decreased gradually with increasing MEA concentration. This type of behaviour was also reported by (Veawab et al., 1999) with AMP at concentrations $> 3$ kmol m$^{-3}$ (ca. 18.2 wt%), but not for MEA systems. Veawab et al studied the corrosion behaviour in MEA only at concentrations between 1-5 kmol m$^{-3}$ (ca. 6-30 wt%) and also reported increasing corrosion rates with concentration, as in Figure 5-60 for concentrations $\leq$ 30 wt%.

This result is in complete contradiction with recommendations from the literature Kohl and Nielsen, 1997 that 20 to 30 % should be the maximum MEA concentration, due to concerns about corrosion. Veawab et al attributed the decreasing corrosion rates in AMP solutions at concentrations $\geq$ 18.2 wt% to the decreasing amount of water available. The decrease in corrosion rates at the maximum corrosion rates could result from two separate causes. Firstly, H$_2$O acts as an additional oxidising agent in the system via (5.39):

$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$$  \hspace{1cm} (5.39)

Secondly, this retardation in corrosion rates at high amine concentrations could also be due to mass transport limitations as the solutions become viscous with increasing concentration. This will be discussed in further detail in Chapter 6 & 7.

Depending on the amine concentration, some differences were evident in the passive region at electrode potentials $> -0.40V$. At potentials ca. $> -0.40$ V, measured current densities from secondary oxidation reactions resulted in accumulation of a passivating layer. At lower
temperatures (25-40 °C), it was difficult to identify the effect of MEA concentration on passive layers, while at higher temperatures (60-80 °C), current densities in the passive region followed the same trend as in the active region; i.e. increasing passivating current densities with increasing concentration for ≤ 30 wt% MEA and decreasing passivating current densities with increasing concentration for ≥ 30 wt% MEA. Kittel et al reported the effect of MEA concentration (20, 30 & 40 wt% at a temperature of 80°C) on steel corrosion rates and on passive layer formation but were unable to do so due to low reproducibility of their experimental results.
Figure 5-56: Effect of MEA concentration on the polarisation curves obtained on iron RDE in MEA + H₂O + CO₂ at pH 8.01 and \( T = 25^\circ C \); 10 mVs⁻¹, \( f = 1500 \) rpm.

Figure 5-57: Effect of MEA concentration on polarisation curves of iron RDE in MEA + H₂O + CO₂ at pH 7.83 and \( T = 40^\circ C \); 10 mVs⁻¹, \( f = 1500 \) rpm.
Figure 5-58: Effect of MEA concentration on polarisation curves of iron RDE in MEA + H$_2$O + CO$_2$, at 10 mV s$^{-1}$; pH 7.49, $f = 1500$ rpm, $T = 60^\circ$C.

Figure 5-59: Effect of MEA concentration on polarisation curves of iron RDE in MEA + H$_2$O + CO$_2$ at pH 7.24 and $T = 80^\circ$C; 10 mV s$^{-1}$, $f = 1500$ rpm.
Figure 5-60: Effect of MEA concentration on the corrosion rate obtained on iron RDE in MEA + H₂O + CO₂ at pH 7.24 – 8.01 and T = 25-80°C; 10 mV s⁻¹, f = 0-1500 rpm.
Figure 5-61: Effect of MEA concentration on the species concentrations of the aqueous bulk solution at chosen CO₂ loading of 0.6 CO₂ loading / mol CO₂ (mol amine)⁻¹, T = 25 °C, calculated by the Kent-Eisenberg Model (Kent and Eisenberg, 1976).
5.6.2. Effect of Mass Transport

Surprisingly, the effects of mass transport conditions on the corrosion of Fe in aqueous alkanolamine-CO$_2$ systems, does not appear to have been reported. However, the polarisation curves in Figure 5-62 show that increasing RDE rotation rates / mass transport rates affected both cathodic and anodic current densities and hence accelerated corrosion rates significantly. For example, the corrosion rate of a stationary Fe electrode in 30wt% MEA + H$_2$O + CO$_2$ at full saturation of CO$_2$ and 25 °C was 4.345 mm y$^{-1}$ and increased to 6.189 mm y$^{-1}$ when the RDE rotated at 1500 rpm. Similar results were obtained at all rotation rates, temperatures and MEA concentrations studied in this project.

The increase in corrosion rates can be attributed partly to the increased mass transport of the oxidising species, resulting from chemical reactions in the bulk solution, to the surface of the iron. This is due to the rate of the dissolution reaction being limited by mass transport rates of H$^+$ and HCO$_3^-$ ions from the bulk solution to the surface of the iron electrode.

The introduction of rotation also increased corrosion rates by preventing or decreasing the rate of FeCO$_3$ precipitation, which is predicted thermodynamically to occur when the local concentrations of Fe$^{2+}$ and CO$_3^{2-}$ ions exceed the solubility product of FeCO$_3$. As the rotation rate increases, this local concentrations of the soluble species near the electrode surface decreases, ultimately preventing the formation of the protective FeCO$_3$ film.
Figure 5-62: Effect of rotation rate on polarisation curves of iron RDE in 30 wt% MEA + H₂O + CO₂, at 10 mV s⁻¹, pH 8.01, f = 0-1500 rpm, T = 25 °C.

Figure 5-63: Effect of rotation rate on corrosion rates of iron RDE in 5-30 wt% MEA + H₂O + CO₂ at pH 8.01; 10 mV s⁻¹, f = 0-1500 rpm, T = 25 °C.
5.6.3. Effect of Oxygen

The effect of oxygen on corrosion rates of iron / steel in alkanolamine solvents used for CO₂ capture has been much debated. Initially and surprisingly, it was assumed that oxygen did not participate in the corrosion process (Kohl and Nielsen, 1997). However, several publications (e.g. Veawab et al., 1999) & (Kittel, 2010) reported that, as expected, the presence of oxygen increased corrosion rates in amine solutions.

Figure 5-64 shows the effects of dissolved oxygen on the polarisation curves as functions of temperature. It can be seen that at 25 °C, there was a significant increase in both anodic and cathodic current densities in the presence of oxygen. However, at higher temperatures ≥ 40 °C, there was no obvious effect of oxygen on cathodic current densities, while anodic current densities were slightly higher with aqueous MEA solutions in which oxygen was present. In the passive region, current densities were generally higher when oxygen was present.

From the analysis of corrosion rates, it was evident that the presence of oxygen induced higher corrosion rates. For example, the corrosion rate of iron in an anoxic 30 wt% MEA system at 25 °C had a corrosion rate of 5.761 mm y⁻¹, which increased to 6.189 mm y⁻¹ in the presence of oxygen. Veawab et al attributed the corrosion rate increase they measured at higher concentrations of O₂ to the formation of Fe(OH)₂ and Fe(OH)₃ via reactions (5. 40) and (5. 41):

\[
2Fe + 2H₂O + O₂ → 2Fe(OH)₂ \quad (5. 40)
\]

\[
2Fe(OH)₂ + 2H₂O + 1/2O₂ → 2Fe(OH)₃ \quad (5. 41)
\]

Whereas additional oxidant would be expected to increase cathodic currents, apparent anodic (net) currents would be expected to decrease, rather than increase, as measured. One possible reason could be that the soluble H₂O₂ intermediate of oxygen reduction ultimately to water,
reacts homogeneously with Fe\(^{2+}\) species, precipitating ‘Fe(OH)_3’ in a less compact form than Fe$_2$O$_3$, so enabling slightly higher net oxidation current densities:

\[
2H_2O + O_2 + 2e^- \rightarrow H_2O_2 + 2OH^- \quad (5.42)
\]

\[
Fe \rightarrow Fe^{2+} + 2e^- \quad (5.43)
\]

\[
2Fe^{2+} + H_2O_2 + 4OH^- \rightarrow 2Fe(OH)_3 \quad (5.44)
\]

\[
H_2O_2 + 2e^- \rightarrow 2OH^- \quad (5.45)
\]

The electrons for reduction of the hydrogen peroxide intermediate by the reaction (5.45) could also be provided by oxidation reactions of the alkanolamine, with its own intermediates being oxidised and so contributing to the net increase in iron oxidation current densities:

\[
R - CH_2NH_2 \xrightarrow{-e^-} R - CH_2N^+H_2 \xrightarrow{-H^+} R - CH = NH_2 \quad (5.46)
\]

\[
R - CH = NH_2 \xrightarrow{-e^-} R - CH = N^+H_2 + H_2O \xrightarrow{-H^+} RCH = O + NH_3 \quad (5.47)
\]

\[
RCH = O + H_2O \rightarrow RCOO^- + 3H^+ + 2e^- \quad (5.48)
\]
Although MEA itself was not oxidised on iron for the range of potentials used, partial reduction of oxygen to peroxide that diffused away from the electrode, reacting homogeneously with MEA and producing intermediates, such as from reactions (5. 46 – 5. 48) above, would have caused the diffusion of those intermediates to the electrode. Their further oxidation, could have resulted in the measured net increase in current densities in the presence of oxygen.

While this may be the case for the passive region, the increase in corrosion rates at active dissolution potentials was most likely due to oxygen acting as an additional oxidant, by reaction (5. 49):

\[ 2H_2O + O_2 + 4e^- \rightarrow 4OH^- \]  

(5. 49)
Figure 5-64: Effect of oxygen on the polarisation curves obtained on iron RDE in 30wt% MEA + H$_2$O + CO$_2$ at pH 7.24-8.01 and T = 25-80°C; 10 mV s$^{-1}$, f = 1500 rpm.
5.7. Summary & Conclusions

The electrochemical behaviour of Fe was investigated using a rotating Fe disc electrode (RDE) in aqueous MEA-CO\textsubscript{2} solutions using voltammetry, as functions of potential sweep rate \((dE/dt)\), rotation rate \((f)\), positive potential limit \((E_a)\), solution temperature, CO\textsubscript{2} loading, MEA concentration and oxygen content. In the absence of CO\textsubscript{2}, aqueous MEA had a pH of 12.55, so Fe oxidation resulted in passivation, probably due to Fe\textsubscript{2}O\textsubscript{3} / Fe(OH)\textsubscript{3} formation. However, when CO\textsubscript{2} was absorbed, the pH decreased to ca. 8, causing iron to dissolve at potentials in the range ca. -0.8 to -0.5 V (AgCl|Ag), above which it passivated, as predicted thermodynamically from potential-pH diagrams. Cyclic voltammograms exhibited an anodic peak on negative-going potential sweeps from potentials corresponding to the passivation; this probably resulted in net currents due to reductive dissolution of the iron (III) (hydro-)oxide, followed by oxidative dissolution of the Fe substrate.

Kinetic analysis of the experimental results showed that temperature and CO\textsubscript{2} loading were the most significant parameters affecting the corrosion of iron or steel in MEA-CO\textsubscript{2}-H\textsubscript{2}O. For example, corrosion rates of iron in fully CO\textsubscript{2}-saturated MEA solutions increased from 6.19 mm y\textsuperscript{-1} at 25\textdegree C to 17.68 mm y\textsuperscript{-1} at 80\textdegree C. Whilst, the corrosion rate in unloaded MEA solutions at 25\textdegree C had a comparably negligible corrosion rate of 0.28 mm y\textsuperscript{-1}. Corrosion rates increased with increasing CO\textsubscript{2} loading, due to the accompanying decrease in pH and increased concentration of species such as RNH\textsubscript{3}\textsuperscript{+}, HCO\textsubscript{3}\textsuperscript{-} and H\textsuperscript{+}. As an additional oxidant, dissolved oxygen enhanced Fe corrosion rate.

At amine concentrations < 30 wt\%, corrosion rates increased with increasing concentration, while at concentrations > 30 wt\%, corrosion rate decreased gradually, implying more complex behaviour than for Fe in CO\textsubscript{2}-H\textsubscript{2}O alone. As solution viscosities \((\mu)\) increased at MEA concentrations > 30 wt\%, mass transport rates of HCO\textsubscript{3}\textsuperscript{-} and H\textsuperscript{+} ions and O\textsubscript{2} to the Fe surface...
and Fe\textsuperscript{II} away from it, would have decreased, as predicted by the Stokes-Einstein equation: 
\[ D = \frac{k_B T}{6\pi \eta r} \]. Such high concentrations would also have affected dissolved reactant activities, including that of H\textsubscript{2}O which also acts as an oxidant for Fe.

As expected for a system exhibiting dissolution-precipitation-passivation behaviour, current densities due to oxidative dissolution increased with increasing mass transport rate coefficients, which decreased Fe\textsuperscript{II} concentrations at the Fe|solution interface, minimising or even preventing precipitation of FeCO\textsubscript{3}.

To discriminate between partial current densities resulting in Fe\textsuperscript{II} dissolution from those leading to adsorbed products, a flow reactor was used in batch recycle mode with a stirred tank reservoir, from which solution samples were taken for subsequent analysis by ICP-OES to determine dissolved Fe\textsuperscript{II} concentrations in the amine solution after constant potential electrolyses as functions of the process parameter. This enabled the charge yield for dissolution to be determined by relating the amount of charge passed to the amount of iron dissolved, enabling more accurate estimates of corrosion rates.
5.8. References


6. Chapter 6

Mechanistic Model for the Prediction of Corrosion of Iron in MEA +H₂O+ CO₂ solutions

As discussed in the literature review (Chapter 3), the corrosion of Fe in MEA-CO₂-H₂O systems has been studied by a few researchers, but the underlying mechanism is not very well understood. This has led to electrochemical reactions being assigned without appropriate verification methods being carried out. The arbitrary and sometimes uninformed assignment of chemical species as principal oxidising agents can be detrimental to the implementation of corrosion control techniques. Therefore, it was also important to identify the oxidising agents which participate in the corrosion reaction, the influence that operating parameters have on the concentration of such species and the resulting impact on the corrosion rate.

A mechanistic model for the uniform corrosion of Fe in aqueous MEA-CO₂ solutions was developed, describing the electrochemical reactions at the metal surface and the chemical reactions occurring in the bulk solution, aiming to predict corrosion rates as well as the concentrations of the solution species at various operating conditions and hence corrosion rates.
6.1. Integrated Model for Fe corrosion in MEA+ H₂O+CO₂

During corrosion of iron in aqueous MEA loaded with CO₂, chemical, electrochemical and transport processes occur simultaneously at the Fe | solution interface.

**Chemical Reactions in the Bulk Solution**

During the absorption reaction of CO₂ in MEA, the following chemical reactions occur:

- **Dissolution of carbon dioxide**
  \[ CO_{2(g)} \leftrightarrow CO_{2} \]  
  \[ (6.1) \]

- **Formation of carbamate**
  \[ 2RNH_2 + H_2O + CO_2 \leftrightarrow RNHCOO^- + RNH_3^+ + H_2O \]  
  \[ (6.2) \]

- **Dissociation of protonated amine ion**
  \[ RNH_3^+ \leftrightarrow RNH_2 + H^+ \]  
  \[ (6.3) \]

- **Hydrolysis of carbamate**
  \[ RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^- \]  
  \[ (6.4) \]

- **Hydrolytic ionization of CO₂(aq)**
  \[ CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^- \]  
  \[ (6.5) \]

- **Water dissociation**
  \[ H_2O \leftrightarrow H^+ + OH^- \]  
  \[ (6.6) \]

- **Dissociation of bicarbonate ion**
  \[ HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \]  
  \[ (6.7) \]
When the chemical reactions are very fast compared to the other processes which are occurring simultaneously, the chemical equilibrium of the system is maintained. However, when the chemical reactions progress relatively slowly, the faster processes such as the mass transport or electrochemical reactions can lead to a local offset in equilibrium. The rate of the chemical reactions occurring can also change the rate of the electrochemical reactions occurring on the surface of the iron. An example of this is when there is a high local concentration of species such as Fe$^{2+}$ and CO$_3^{2-}$ ions and the solubility limit is exceeded, leading to the precipitation of FeCO$_3$. The model took into account the homogeneous chemical reactions (6.1)-(6.7) occurring in the solution, but it excluded heterogeneous chemical reactions such as the precipitation of FeCO$_3$. The model also made an assumption that all the dissolved CO$_2$ within the system are present as Carbon (IV) species.

**Electrochemical Reactions at the Iron Surface**

The model assumed that corrosion rates were spatially uniform across the iron surface, which oxidised, driven primarily by the hydrogen evolution reactions:

\[ 2H^+ + 2e^- \rightarrow H_2 \quad (6.8) \]

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (6.9) \]

There are three well known steps for the hydrogen evolution reaction commonly known as the Volmer (1), Heyrovsky (2) and Tafel (3) steps.

1. Volmer: \( H^+ + e^- \rightarrow H_{ads} \) \quad (6.10)

2. Heyrovsky: \( H_{ads} + H^+ + e^- \rightarrow H_2(g) \) \quad (6.11)

3. Tafel: \( H_{ads} + H_{ads} \rightarrow H_2(g) \) \quad (6.12)
As discussed in the Literature Review there are two widely accepted pathways for the hydrogen evolution process. They are the discharge, chemical recombination (Volmer-Tafel mechanism) and the discharge, electrochemical desorption (Volmer-Heyrowsky) mechanism. (Weber and Peria, 1967; Park, 1975). Whilst the hydrogen evolution reaction proceeds in two steps with one intermediary reaction (Weber and Peria, 1967; Eastman and Nathan, 1975; Park, 1975), the mechanistic model makes an assumption that it occurs via a single step two-electron process (reaction 6.8).

The concentration of H⁺ ions was increased by the dissociation reactions of RNH₃⁺ (6. 3) and HCO₃⁻ (6. 7) resulting from the reactions of CO₂ in MEA and H₂O.

It was also clear from the cyclic voltammetric results in Chapter 5 that the reduction of oxygen, if present, also played a significant role in the corrosion of iron in MEA-H₂O-CO₂ systems, so it also was included in the model:

\[ 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^- \]  \hspace{1cm} (6. 13)

The results obtained from the combined use of the RDE and EQCM (Chapter 5) and electrode potential-pH diagrams indicated that the dissolution of iron occurs primarily within the potential range where only Fe^{II} is predicted thermodynamically. Therefore, it was assumed in the model that the electrochemical dissolution of iron in MEA- CO₂-H₂O systems according to equation (6. 14) is the dominant anodic reaction:

\[ \text{Fe} \leftrightarrow \text{Fe}^{2+} + 2e^- \]  \hspace{1cm} (6. 14)

The model was focused on the anodic dissolution region of the cyclic voltammetry experiments and did not take into account the passive region resulting from adsorption of products such as iron(III) (hydr-)oxide at higher potentials.
6.1.1. Model scheme

The model scheme, shown schematically in Figure 6-1 below, illustrates how both chemical and electrochemical reactions occur simultaneously at the iron metal | amine solution interface. It includes five chemical reactions typical of the MEA-H₂O-CO₂ absorption process (Table 6-1): i) dissociation of the protonated amine (RNH₃⁺), ii) hydrolysis of carbamate (RNHCOO⁻), iii) hydrolysis of CO₂, iv) dissociation of water, v) dissociation of bicarbonate ions. 11 chemical species were considered in the solution, namely MEA (RNH₂), carbamate (RNHCOO⁻), protonated amine (RNH₃⁺), un-dissociated water (H₂O), dissolved CO₂ (CO₂(aq)), bicarbonate ion (HCO₃⁻), carbonate ions (CO₃²⁻), hydrogen ions (H⁺), hydroxyl ions (OH⁻), dissolved oxygen (O₂) and ferrous ions (Fe²⁺).

At the iron | solution interface, electrons produced by the oxidation of iron to ferrous ions by reaction (6.14) were consumed at the corrosion potential at an exactly equal and opposite rate by reduction of: hydrogen ions (H⁺), water and dissolved oxygen.
Figure 6-1: Schematic representation of the corrosion process in aqueous MEA-CO₂ solutions, including the chemical reactions occurring at the iron surface.
Table 6-1: Chemical and electrochemical reactions represented in the mechanistic corrosion model

<table>
<thead>
<tr>
<th>Type of reaction</th>
<th>Reaction Description</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Reactions</td>
<td>Dissociation of protonated amine.</td>
<td>( RNH_3^+ \leftrightarrow RNH_2 + H^+ )</td>
</tr>
<tr>
<td></td>
<td>2. Hydrolysis of carbamate.</td>
<td>( RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^- )</td>
</tr>
<tr>
<td></td>
<td>3. Hydrolysis of carbon dioxide.</td>
<td>( CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^- )</td>
</tr>
<tr>
<td></td>
<td>4. Water dissociation</td>
<td>( H_2O \leftrightarrow H^+ + OH^- )</td>
</tr>
<tr>
<td></td>
<td>5. Dissociation of hydrogen carbonate ions</td>
<td>( HCO_3^- \leftrightarrow CO_3^{2-} + H^+ )</td>
</tr>
<tr>
<td>Electrochemical Reactions</td>
<td>1. Dissolution of iron</td>
<td>( Fe \leftrightarrow Fe^{2+} + 2e^- )</td>
</tr>
<tr>
<td></td>
<td>2. Reduction of hydrogen ions</td>
<td>( 2H^+ + 2e^- \rightarrow H_2 )</td>
</tr>
<tr>
<td></td>
<td>3. Reduction of water</td>
<td>( 2H_2O + 2e^- \rightarrow H_2 + 2OH^- )</td>
</tr>
<tr>
<td></td>
<td>4. Reduction of oxygen</td>
<td>( 2H_2O + O_2 + 4e^- \rightarrow 4OH^- )</td>
</tr>
</tbody>
</table>
6.1.2. Model Structure and Development

The model was structured with three main components: inputs, the thermodynamic and electrochemical models followed by the outputs, as demonstrated in Figure 6-2. The inputs included information on the operating conditions of the aqueous MEA-CO\textsubscript{2} solution such as temperature, CO\textsubscript{2} loading and pH, MEA concentration, mass transport conditions (electrode rotation rate) and oxygen content.

Firstly, concentrations of species at the iron | solution interface were established using thermodynamic vapour-liquid equilibrium (VLE) principles of a Kent-Eisenberg based model, assuming ideal behaviour, so implying that the activity coefficients of all the chemical species were unity. The thermodynamic model integrated VLE data from literature, mass balances for MEA and carbon (IV) species, as well as the principle of electro-neutrality for charged species in solution.

Once the concentrations for each of the species had been determined, based on the parameters from the ‘input’, the electrochemical model for corrosion of iron in the aqueous environment could then be established, incorporating the oxidation of iron coupled to reduction of the oxidising agents at the iron surface. Standard equilibrium potentials ($E^\theta_{O/R}$) for all electrochemical reactions considered were calculated from Gibbs energies of formation (Allen Bard, 1985). Concentrations of species involved in electrode reactions enabled equilibrium potentials ($E_{O/R}$) to be calculated using Nernst equations, so overpotentials ($\eta$) could be defined for each reaction as a function of applied potential ($E$). Where available for relevant compositional conditions, values for exchange current densities ($j_0$) and anodic ($\alpha_a$) and cathodic ($\alpha_c$) transfer coefficients were taken from the literature. The mass transport contributions to the corrosion behaviour were established by using the Levich equation for a rotating disc electrode or the experimentally-derived laminar flow mass transport correlation...
for the flow-through reactor. The model output included the speciation of the amine solution and current density – electrode potential data defined by Butler-Volmer equations (6.15) for each of the electrochemical reactions \((i)\), so enabling corrosion rates to be predicted.

\[
j_i = j_{0,i} \left[ \exp \left\{ \frac{\alpha_{i,j} F}{RT} \eta_i \right\} - \exp \left\{ -\frac{\alpha_{e,j} F}{RT} \eta_i \right\} \right]
\]  \hspace{1cm} (6.15)
Figure 6-2: Flow diagram showing the model structure
6.1.3. Thermodynamic Modelling of Aqueous MEA-CO$_2$ system

Thermodynamic modelling of the MEA-CO$_2$-H$_2$O system enabled the speciation and redox behaviour to be predicted as functions of process parameters. There are a few experimental techniques that could be employed to measure the vapour-liquid (VLE) data for the absorption of CO$_2$ in amine systems (Tong, 2012), however they are tedious and time-consuming. In addition, experimental techniques do not provide accurate data under certain conditions, such as low CO$_2$ loading, high system temperatures and very high amine concentrations, due to analytical constraints (Chakma and Meisen, 1990). Therefore, a few mathematical models have been developed to obtain accurate information on the solubility of CO$_2$ in aqueous MEA solutions over the full range of operating conditions required for the design of the equipment used in alkanolamine plants.

Different approaches to thermodynamic modelling have been proposed by researchers to correlate experimental VLE data, the most popular of which include: i) Kent-Eisenberg model (Kent and Eisenberg, 1976), ii) model of (Edwards et al., 1978), iii) Deshmukh-Mather model (Deshmukh and Mather, 1981) iv) Electrolyte-NRTL (e-NRTL) model (Austgen et al., 1989), v) SAFT-VR model (MacDowell, 2010).

The Kent and Eisenberg model, the first VLE model for alkanolamine absorption of CO$_2$, was adopted because of its computational simplicity. It is a solubility model, which follows a regression-based approach, based on equilibria of the ionic species in the liquid phase. The equilibrium constants were fitted to available CO$_2$ partial pressure and vapour-liquid equilibrium data for the absorption of CO$_2$ in alkanolamines. The model could then be used to predict the solubility of CO$_2$ in amine solutions even at operating conditions outside of the range of existing data.
Table 6-2: Equilibrium expressions for chemical reactions

<table>
<thead>
<tr>
<th>Reaction Description</th>
<th>Equilibrium Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dissociation of protonated amine</td>
<td>( K_1 = \frac{[RNH_2][H^+]}{[RNH_3^+]}) )</td>
</tr>
<tr>
<td>2. Hydrolysis of Carbamate</td>
<td>( K_2 = \frac{[RNH_2][HCO_3^-]}{[RNHCOO^-]} )</td>
</tr>
<tr>
<td>3. Hydrolysis of carbon dioxide</td>
<td>( K_3 = \frac{[H^+][HCO_3^-]}{[CO_2]} )</td>
</tr>
<tr>
<td>4. Water dissociation</td>
<td>( K_4 = [H^+][OH^-] )</td>
</tr>
<tr>
<td>5. Dissociation of bicarbonate ion</td>
<td>( K_5 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} )</td>
</tr>
<tr>
<td>6. Amine mass balance</td>
<td>([MEA] = [RNH_2] + [RNH_3^+] + [RNHCOO^-])</td>
</tr>
<tr>
<td>7. CO(_2) mass balance</td>
<td>([MEA]a_{CO_2} = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RNHCOO^-])</td>
</tr>
<tr>
<td>8. Charge Balance</td>
<td>([RNH_3^+] + [H^+] )</td>
</tr>
</tbody>
</table>

The equilibrium between the solution species is governed by the reactions (1-5) in Table 6-1 and the corresponding equilibrium constants (\( K_i \)) are expressed in Table 6-2. (Austgen et al., 1989) noted that other side reactions such as degradation reactions may also take place.
simultaneously; however, rates of these side reactions are negligible on a laboratory scale so they were ignored within this model.

Kent and Eisenberg assumed that the MEA-H$_2$O-CO$_2$ system behaves ideally (activity coefficient of unity) and the equilibrium constants ($K_i$) are dependent only on the temperature of the system. The equilibrium constants used within this model were represented by the empirical equation:

$$\ln K_i = a_i T^{-1} + b_i \log T + c_i T + d_i$$  \hspace{1cm} (6.16)

Where $a_i$ - $d_i$ are constants and the temperature unit is Kelvin. Values of the constants were taken from literature and are listed in Table 6-3. Mass balances of the MEA species (reaction 7) and the carbon (IV) species (reaction 8) were included, as well as a charge balance (Equation 9) in order to maintain the system’s electroneutrality.

Table 6-3: Temperature dependent equilibrium constants for chemical reactions 1-5

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$c_i$</th>
<th>$d_i$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>-17.3</td>
<td>0</td>
<td>0.05764</td>
<td>-38.846</td>
<td>(Hamborg and Versteeg, 2009)</td>
</tr>
<tr>
<td>$K_2$</td>
<td>-1545.3</td>
<td>0</td>
<td>0</td>
<td>2.151</td>
<td>(Haji-Sulaiman and Aroua, 1995)</td>
</tr>
<tr>
<td>$K_3$</td>
<td>-12092.1</td>
<td>-36.7816</td>
<td>0</td>
<td>235.482</td>
<td>(Edwards et al., 1978)</td>
</tr>
<tr>
<td>$K_4$</td>
<td>-13445.9</td>
<td>-22.4773</td>
<td>0</td>
<td>140.932</td>
<td>(Edwards et al., 1978)</td>
</tr>
<tr>
<td>$K_5$</td>
<td>-12431.7</td>
<td>-35.4819</td>
<td>0</td>
<td>220.067</td>
<td>(Edwards et al., 1978)</td>
</tr>
</tbody>
</table>

6.1.4. Electrochemical model for Iron in MEA-CO$_2$-H$_2$O

As discussed previously, the electrochemical reactions occurring at the iron surface are the dissolution of iron and the reduction of the oxidising agents such as H$^+$, H$_2$O and O$_2$. The oxidising agents were identified from the results of the cyclic voltammetry experiments in chapter 5 which clearly indicated that the rate of the electrochemical reactions at the iron
surface depend on the applied electrode potential, the concentrations of the species at the interface, as well as the operating conditions such as temperature and pH.

The mechanistic model was tested by simulating anodic and cathodic polarisation curves based on the pre-calculated concentrations of the species involved in the corrosion reactions. This was achieved by varying the electrode potential from the equilibrium potentials \((E_{O/R})\) and hence the overpotentials \((\eta)\) for the reactions considered, and predicting the resulting current densities \((j)\) from the Butler-Volmer equations for mixed charge transfer-mass transfer control by equation (6.17):

\[
j = \frac{j_0 \left( \exp \frac{\alpha_c \eta}{RT} - \exp -\frac{\alpha_c \eta}{RT} \right)}{1 + \frac{j_0}{j_{LH}} \exp \frac{\alpha_c \eta}{RT} - \frac{j_0}{j_{LO}} \exp -\frac{\alpha_c \eta}{RT}} \tag{6.17}
\]

Where

\[
\eta = E - E_{O/R} \tag{6.18}
\]

The Butler-Volmer equation (6.17) was expressed for each of the electrochemical reactions occurring at the iron surface; e.g. for the anodic iron dissolution reaction:

\[
j_{Fe^{2+}} = \frac{j_{0Fe^{2+}} \exp \left[ \alpha_{Fe^{2+}} \eta_{Fe^{2+}} \right] - \exp \left[ \alpha_{Fe^{2+}} \eta_{Fe^{2+}} \right]}{1 - \frac{j_{0Fe^{2+}}}{j_{LOFe^{2+}}} \exp \left[ -\alpha_{Fe^{2+}} \eta_{Fe^{2+}} \right]} \tag{6.19}
\]

and for the cathodic reactions (6.8), (6.9) & (6.13) respectively:

\[
j_{H_2} = \frac{j_{0H_2} \exp \left[ \alpha_{H_2} \eta_{H_2} \right] - \exp \left[ -\alpha_{H_2} \eta_{H_2} \right]}{1 + \frac{j_{0H_2}}{j_{LRH_2}} \exp \left[ \alpha_{H_2} \eta_{H_2} \right] - \frac{j_{0H_2}}{j_{LOH_2}} \exp \left[ -\alpha_{H_2} \eta_{H_2} \right]} \tag{6.20}
\]

\[
j_{O_2} = \frac{j_{0O_2} \exp \left[ \alpha_{O_2} \eta_{O_2} \right] - \exp \left[ -\alpha_{O_2} \eta_{O_2} \right]}{1 - \frac{j_{0O_2}}{j_{LOO_2}} \exp \left[ -\alpha_{O_2} \eta_{O_2} \right]} \tag{6.21}
\]
Where the limiting diffusion current density \( j_L \) for a RDE system was defined by the Levich equation as:

\[
   j_L = \pm 1.554\nu_e F A D^{2/3} v^{-1/6} f^{1/2} C
\]  

(6.22)

The diffusion coefficients for the solution species in listed in Table 6-4 were obtained from the literature. The kinematic viscosities of the MEA solutions were derived from the dynamic viscosity and density measurements reported by (Amundsen et al., 2009) which have been listed in Table 6-6 to Table 6-9. In the absence of available data for the diffusion coefficient, density and dynamic viscosity at elevated temperatures, the equations displayed in Table 6-5 were used to obtain the approximate values.

**Table 6-4: Diffusion Coefficients for species in water at 25°C**

<table>
<thead>
<tr>
<th>Species</th>
<th>Diffusion coefficient / m² s⁻¹</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺</td>
<td>0.72 × 10⁻⁹</td>
<td>(Newman and Thomas-Alyea, 2004)</td>
</tr>
<tr>
<td>O₂</td>
<td>1.92 × 10⁻⁹</td>
<td>(Han and Bartels, 1996)</td>
</tr>
<tr>
<td>CO₂ (aq)</td>
<td>1.94 × 10⁻⁹</td>
<td>(Tamimi et al., 1994)</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>2.00 × 10⁻⁹</td>
<td>(Kvarekval, 1997)</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1.11 × 10⁻⁹</td>
<td>(Newman and Thomas-Alyea, 2004)</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>0.92 × 10⁻⁹</td>
<td>(Kvarekval, 1997)</td>
</tr>
</tbody>
</table>

**Table 6-5: Liquid properties as a function of temperature (Haynes and Lide, 2011)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic Viscosity/ kg m⁻¹ s⁻¹</td>
<td>( \mu = 0.001002 \cdot 10^{1.3277(293.15−T)−0.001053(298.15−T)^2} ) ( T=188.15 )</td>
</tr>
<tr>
<td>Density/ kg m⁻³</td>
<td>( \rho = (753.596 + 1.877487 − 0.003564T^2) )</td>
</tr>
<tr>
<td>Diffusion coefficient / m² s⁻¹</td>
<td>( D_T = D_{298.15} \cdot \frac{T}{298.15} \cdot \frac{\mu_{298.15}}{\mu} )</td>
</tr>
</tbody>
</table>
Table 6-6: Density $\rho$ / kg m$^3$ for MEA +H$_2$O from (T= 25- 80°C) as a function of MEA mass fraction $w$ (Amundsen et al., 2009).

<table>
<thead>
<tr>
<th>T/ °C</th>
<th>$w$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 wt%</td>
</tr>
<tr>
<td>25</td>
<td>1005.3</td>
</tr>
<tr>
<td>40</td>
<td>999.1</td>
</tr>
<tr>
<td>50</td>
<td>994.3</td>
</tr>
<tr>
<td>70</td>
<td>983.0</td>
</tr>
<tr>
<td>80</td>
<td>976.6</td>
</tr>
</tbody>
</table>

Table 6-7: Density $\rho$ / kg m$^3$ for 30 wt% MEA +H$_2$O from (T= 25- 80°C) as a function of temperature and CO$_2$ loading ($\alpha$ =0.1 - 0.5) (Amundsen et al., 2009).

<table>
<thead>
<tr>
<th>T/ °C</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>25</td>
<td>1028.0</td>
</tr>
<tr>
<td>40</td>
<td>1021.0</td>
</tr>
<tr>
<td>50</td>
<td>1016.0</td>
</tr>
<tr>
<td>70</td>
<td>1004.0</td>
</tr>
<tr>
<td>80</td>
<td>997.0</td>
</tr>
</tbody>
</table>

Table 6-8: Dynamic viscosity $\mu$ / mPa s$^{-1}$ for MEA +H$_2$O from (T= 25- 80°C) as a function of MEA mass fraction $w$ (Amundsen et al., 2009).

<table>
<thead>
<tr>
<th>T/ °C</th>
<th>$w$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 wt%</td>
</tr>
<tr>
<td>25</td>
<td>1.70</td>
</tr>
<tr>
<td>40</td>
<td>1.18</td>
</tr>
<tr>
<td>50</td>
<td>0.95</td>
</tr>
<tr>
<td>70</td>
<td>0.67</td>
</tr>
<tr>
<td>80</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Table 6-9: Dynamic viscosity $\mu / \text{mPa s}^{-1}$ for 30 wt% MEA +H$_2$O from (T= 25- 80$^\circ$C) as a function of temperature and CO$_2$ loading ($\alpha$=0.1 - 0.5) (Amundsen et al., 2009).

<table>
<thead>
<tr>
<th>T / °C</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>25</td>
<td>2.6</td>
</tr>
<tr>
<td>40</td>
<td>1.7</td>
</tr>
<tr>
<td>50</td>
<td>1.4</td>
</tr>
<tr>
<td>70</td>
<td>0.9</td>
</tr>
<tr>
<td>80</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The electrochemical parameters $E_{O/R}, j_0$ and $\alpha$ are contingent upon the electrochemical reaction and are dependent on the temperature and the concentration of the species at the surface of the metal.

$E_{O/R}$ was calculated from the Nernst equations in equation (6. 23) to (6. 25), assuming that activities could be approximated by concentrations:

$$E_{Fe^{2+/Fe^0}} = E_{Fe^{2+/Fe^0}}^\theta + \frac{RT}{2F} \ln [Fe^{2+}]$$  \hspace{1cm} (6. 23)

$$E_{H^{+}/H_2} = E_{H^{+}/H_2}^\theta - \frac{RT}{2F} \ln \left( \frac{P_{H_2}}{[H^+]^2} \right)$$ \hspace{1cm} (6. 24)

$$E_{O_2/H_2O} = E_{O_2/H_2O}^\theta + \frac{RT}{4F} \ln \left( \frac{P_{O_2} * [H^+]^4}{\gamma_{e^0}} \right)$$ \hspace{1cm} (6. 25)

Where $E^{\theta}$ is the standard electrode potential for each of the reactions under standard conditions (298.15 K, 0.1 MPa) calculated from standard Gibbs energies for formation.

$$E^{\theta} = \frac{-\Delta G^{\theta}}{v_eF}$$ \hspace{1cm} (6. 26)

At elevated temperature conditions, the Gibbs energy change ($\Delta G_t^{\theta}$) was calculated by determining the heat capacity at constant pressure from the equation:
\[ C_p = A + B(10^{-3})T + \frac{C(10^5)}{T^2} + D(10^{-6})T^2 \]  \hspace{1cm} (6.27)

The heat capacity values were obtained from the HSC software database and have been listed in the Appendix VI. In addition to the following equations for entropy (S), enthalpy (H) and Gibbs energy of formation (\(\Delta G\)):

\[ S = S_{298.15} + \int_{298.15}^{T} \frac{C_p}{T} dT \]  \hspace{1cm} (6.28)

\[ H = \Delta H_{298.15} + \int_{298.15}^{T} \frac{C_p}{T} dT \]  \hspace{1cm} (6.29)

\[ \Delta G = \Delta H - T\Delta S \]  \hspace{1cm} (6.30)

The anodic and cathodic transfer coefficients are defined by equations (6.31) and (6.32) (Guidelli et al., 2014).

\[ \alpha_a = \left(\frac{RT}{F}\right)\left(d\ln j_a/dE\right) \]  \hspace{1cm} (6.31)

\[ \alpha_c = -\left(\frac{RT}{F}\right)\left(d\ln j_c/dE\right) \]  \hspace{1cm} (6.32)

According to (Bockris et al., 1961) \(\alpha\), the transfer coefficient is 0.5 for cathodic reactions and 2 for anodic reactions. The values expressions for \(j_0\) were obtained from (Nordsveen et al., 2003) and are listed in Table 6-10.

At the (open circuit) corrosion potential, the rate of production of electrons by oxidation must be equal and opposite to their rate of consumption by reduction:

\[ \Sigma j_a = \Sigma |j_c| \]  \hspace{1cm} (6.33)

As iron dissolution is the main oxidation reaction in the active region:

\[ j_{Fe} = \Sigma |i_c| \]  \hspace{1cm} (6.34)
As $\text{H}^+$, $\text{H}_2\text{O}$ and $\text{O}_2$ all participate as oxidising agents the total reduction rate will be:

$$\Sigma |j_c| = |j_{\text{H}^+}| + |j_{\text{H}_2\text{O}}| + |j_{\text{O}_2}|$$  \hspace{1cm} (6.35)

The values of $j_{\text{corr}}$ and corrosion potential ($E_{\text{corr}}$) were determined from the intersection point of the simulated anodic and cathodic polarization curves.
Table 6-10: Kinetic parameters of the electrochemical reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( j_0 / \text{A m}^2 )</th>
<th>( J_{0,\text{ref}} / \text{A m}^2 )</th>
<th>( c_{\text{H}^+, \text{ref}} )</th>
<th>( c_{\text{HCO}_3^-, \text{ref}} )</th>
<th>( T_{\text{ref}} / ^\circ\text{C} )</th>
<th>( k_a / \text{s}^{-1} )</th>
<th>( -E_a / \text{kJ mol}^{-1} )</th>
<th>( \Delta H / \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe oxidation</td>
<td>( j_{0,\text{Fe}^{2+}} = j_{0,\text{Fe}^{2+}, \text{ref}} \left( \frac{c_{\text{HCO}<em>3^-}}{c</em>{\text{HCO}<em>3^- \text{,ref}}} \right)^2 \left( \frac{c</em>{\text{H}^+}}{c_{\text{H}^+, \text{ref}}} \right)^{-0.5} \exp \left[ -\frac{\Delta H}{R} \left( \frac{1}{T} \right) \right] )</td>
<td>0.53</td>
<td>10^{-9.1}</td>
<td>1</td>
<td>50</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(^+) reduction</td>
<td>( j_{0,\text{H}^+} = j_{0,\text{H}^+, \text{ref}} \left( \frac{c_{\text{H}^+}}{c_{\text{H}^+, \text{ref}}} \right)^{0.5} \exp \left[ -\frac{\Delta H}{R} \left( \frac{1}{T} \right) \right] )</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>-</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>H(_2)O reduction</td>
<td>( j_{0,\text{H}_2\text{O}} = 3 \times 10^{-5} \text{ A m}^{-2} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(_2) reduction</td>
<td>( j_{0,\text{O}<em>2} = k_0 c</em>{\text{O}_2} \exp \left( -\frac{E_a}{RT} \right) )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.69 \times 10^3, 2.00 \times 10^4</td>
<td></td>
</tr>
<tr>
<td>HCO(_3^-) reduction</td>
<td>( j_{0,\text{H}^+} = j_{0,\text{H}^+, \text{ref}} \left( \frac{c_{\text{H}^+}}{c_{\text{H}^+, \text{ref}}} \right)^{0.5} \exp \left[ -\frac{\Delta H}{R} \left( \frac{1}{T} \right) \right] )</td>
<td>0.15</td>
<td>-</td>
<td>0.5</td>
<td>50</td>
<td>-</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>
6.2. Model Verification by Comparison with Experiments

The validity of the corrosion model was tested by comparing the model predictions with the experimental results. The voltammetric data simulated for Fe in 30 wt% MEA+H\textsubscript{2}O solution by the electrochemical model showed good agreement with the experimental data, specifically within cathodic potentials and at active dissolution potentials. However, the model did not take into account the precipitation of FeCO\textsubscript{3} / Fe(OH)\textsubscript{2} or passivation by adsorbed species at higher potentials. Details of the model results are summarised in Appendix VII.

Figure 6-3: Comparison between predicted and measured voltammetric sweep for iron RDE in 30 wt% MEA+ CO\textsubscript{2}, at pH=8.1 and $T = 25 \, ^\circ\text{C}$; 10 mV s\textsuperscript{-1}, $f = 1500$ rpm. Black dotted lines represent the Tafel extrapolation of the anodic and cathodic linear sections to find the intersection at $E_{\text{corr}}$ and $i_{\text{corr}}$.

The model-predicted voltammetric data indicated slightly higher corrosion rates, within +25.2\% of the corrosion rates calculated from experimental data. However, due to the complexity of the process(es) and the precipitation of FeCO\textsubscript{3} and Fe(OH)\textsubscript{2} which had been neglected within the model, this result was acceptable.
As observed experimentally, the mass transport conditions had a considerable effect on the anodic and cathodic current densities which increased with increasing mass transport rate (Figure 6-4). Thus the corrosion rates (Figure 6-5) also increased with mass transport rates due to the increased transport of the oxidising species resulting from the reactions in the bulk solution to the surface of the iron.

Figure 6-4: Comparison between predicted and measured voltammetric sweep for iron RDE in 30 wt% MEA+ CO₂, at pH=8.1 and T = 25 °C; 10 mV s⁻¹, f = 960 rpm, 540 rpm and 240 rpm.

Figure 6-5: Comparisons of experimental and model-predicted corrosion rates as a function of rotation rate for iron RDE in 30 wt% MEA+ CO₂, at pH=8.1 and T = 25 °C; 10 mV s⁻¹.
6.3. Effect of CO₂ loading

As described in Chapter 5, the chemical composition of the MEA solution changes depending on the CO₂ loading; the speciation of 30 wt% MEA with CO₂ loading at 25°C is shown in Figure 6-6 and listed in Table 6-11.

![Figure 6-6: Predicted effect of CO₂ loading on liquid phase compositions of 30 wt% aqueous MEA solution at 25 °C, as predicted by the Kent-Eisenberg Model (Kent and Eisenberg, 1976).](image)

Figure 6-8 shows the model-predicted effect of CO₂ loading on corrosion rates, which increased mainly because of increased rates of hydrogen evolution. As shown in Table 6-11, increased CO₂ loading was predicted to cause higher equilibrium concentrations of H⁺, RNH₃⁺ and HCO₃⁻; the last two species were produced by reactions of CO₂ and MEA-H₂O and acted as proton sources by the dissociation reactions (6. 3) and (6. 7), leading to higher rates of hydrogen evolution.
Figure 6-7: Comparison between predicted and measured voltammetric sweep for iron RDE in 30 wt% MEA+ CO$_2$, at $T = 25 \, ^\circ C$; 10 mV s$^{-1}$, $f = 1500$ rpm as a function of CO$_2$ loading($\alpha$).

Figure 6-8: Comparisons of experimental and model-predicted corrosion rates for iron RDE in 30 wt% MEA+ CO$_2$, at $T = 25 \, ^\circ C$; 10 mV s$^{-1}$, $f = 1500$ rpm as a function of CO$_2$ loading($\alpha$).
(Waard and Milliams, 1975), (Nordsveen et al., 2003) suggested that the presence of hydrogen bicarbonate can also increase the hydrogen evolution rate by undergoing direct reduction via reaction:

$$2\text{HCO}_3^- + 2e^- \rightarrow \text{H}_2 + 2\text{CO}_3^{2-}$$  \hspace{1cm} (6.36)

However, hydrogen evolution from weak acids in general involves fast chemical pre-equilibria, prior to the reduction of the resulting protons. Nonetheless, the direct reduction of HCO$_3^-$ was implemented in the model by including the cathodic current density and reversible electrode potential for HCO$_3^-$ reduction.

$$j_{\text{HCO}_3^-} = \frac{j_{o\text{HCO}_3^-}\left[\exp\left(a_{\text{HCO}_3^-}\eta_{\text{HCO}_3^-}\right) - \exp\left(-a_{\text{HCO}_3^-}\eta_{\text{HCO}_3^-}\right)\right]}{1 + \left(j_{o\text{HCO}_3^-}\right)^{\frac{a_{\text{HCO}_3^-}}{2F}}} \exp\left(-a_{\text{HCO}_3^-}\eta_{\text{HCO}_3^-}\right)$$ \hspace{1cm} (6.37)

$$E_{\text{HCO}_3^-/H_2} = E_{\text{HCO}_3^-/H_2}^a - \frac{RT}{2F} \ln \left(\frac{P_{\text{H}_2}[^\text{CO}_3^2^-]^2}{[^\text{HCO}_3^-]^2}\right)$$ \hspace{1cm} (6.38)
This resulted in current density-electrode potential data that agreed less well with experimental data than model predictions excluding HCO$_3^-$ reduction and a slightly higher corrosion rate of 19.06 mm y$^{-1}$ in comparison to 7.75 mm y$^{-1}$ in the absence of HCO$_3^-$ reduction.

**6.4. Effect of Temperature**

As expected, increasing the temperature increased model-predicted corrosion rates, as shown in Figure 6-11. The effect of temperature on the equilibrium H$^+$ ion concentration as a function of CO$_2$ loading, calculated by the Kent-Eisenberg Model is also shown in Figure 6-12. However, it is important to note that the model showed a closer agreement to the experimental results at low temperatures (25 - 40 °C) than at higher temperatures. This discrepancy at higher temperatures is probably as a result of the shortcomings of the Kent-Eisenberg model to predict the solution species concentrations at higher temperatures.

![Figure 6-10](image-url)  
**Figure 6-10:** Comparison between predicted and measured voltammetric sweep for iron RDE in 30 wt% MEA+ CO$_2$, at pH=8.1 10 mV s$^{-1}$, $f=1500$ rpm as a function of temperature.
Figure 6-11: Comparison of experimental and model-predicted Fe corrosion rates in 30 wt% MEA solution at different temperatures.

Figure 6-12: Effect of temperature and CO₂ loading on hydrogen ion concentration [H⁺] predicted by Kent-Eisenberg model for 30 wt% aqueous MEA solution.
Table 6-11: Predicted species concentration / kmol m$^{-3}$ for 30 wt% MEA-H$_2$O-CO$_2$ systems at 25°C

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<tr>
<td>RNH$_3^+$</td>
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<tr>
<td>RNHCOO$^-$</td>
<td>2.72E-01</td>
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<tr>
<td>HCO$_3^-$</td>
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<tr>
<td>CO$_3^{2-}$</td>
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<td>H$^+$</td>
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<tr>
<td>OH$^-$</td>
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Table 6-12: Predicted species concentration / kmol m$^{-3}$ for 30 wt% MEA-H$_2$O-CO$_2$ systems at 40°C

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<td>RNHCOO$^-$</td>
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<td>HCO$_3^-$</td>
<td>1.17E-01</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>1.02E-01</td>
</tr>
<tr>
<td>CO$_2$</td>
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<tr>
<td>OH$^-$</td>
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Table 6-13: Predicted species concentration / kmol m$^{-3}$ for 30 wt% MEA-H$_2$O-CO$_2$ systems at 60°C

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<td>1.63E+00</td>
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<td>1.86E-08</td>
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<td>7.17E-06</td>
<td>2.86E-06</td>
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<td>5.37E-07</td>
<td>3.62E-07</td>
<td>2.10E-07</td>
<td>1.27E-07</td>
<td>6.31E-08</td>
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Table 6-14: Predicted species concentration / kmol m$^{-3}$ for 30 wt% MEA-H$_2$O-CO$_2$ systems at 80°C

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<td>3.56E+00</td>
<td>3.02E+00</td>
<td>2.48E+00</td>
<td>2.01E+00</td>
<td>1.61E+00</td>
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<td>1.07E+00</td>
<td>8.93E-01</td>
<td>8.49E-01</td>
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<tr>
<td>R NH$_3$</td>
<td>6.72E-01</td>
<td>1.19E+00</td>
<td>1.64E+00</td>
<td>2.13E+00</td>
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<td>3.22E+00</td>
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<td>5.93E-01</td>
<td>8.71E-01</td>
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<td>H$^+$</td>
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<td>2.23E-08</td>
<td>4.15E-08</td>
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<td>4.00E-08</td>
<td>2.33E-08</td>
</tr>
</tbody>
</table>
6.5. Effect of MEA Concentration

According to the model predictions, corrosion rates decreased with increasing amine concentration. Due to limitations on the available data for the dynamic viscosity and density measurements of MEA solutions loaded with CO$_2$, the model was tested for (20-50) wt% MEA concentration and compared to the experimental results in Figure 6-13. In spite of the increase in the equilibrium concentration of H$^+$ ions predicted at higher MEA concentrations, there was a decrease in the corrosion rate which can be attributed to the change in viscosity with MEA concentration (Figure 6-14). This model-predicted decrease in corrosion rates with increasing MEA concentration provides direct evidence for the experimental observation at higher MEA concentrations resulting from the change in viscosity of the solution. Increased viscosity of the solution resulted in the dissolution reaction being limited by the decreased mass transport of the oxidising species H$^+$, H$_2$O and O$_2$ to the iron electrode.

![Graph](image-url)

**Figure 6-13:** Comparison of experimental and model-predicted corrosion rates at different MEA concentrations, $T = 25^\circ$C, CO$_2$ loading = 0.5 mol CO$_2$ (mol amine)$^{-1}$. 
Figure 6-14: Dynamic viscosity of 30 wt% MEA at 25 °C and CO$_2$ loading ($\alpha =0.5$), as a function of mass fraction (Amundsen et al., 2009).
Table 6-15: Predicted species concentration / M for 20 wt% MEA-H₂O-CO₂ systems at 25°C

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<td>1.88E+00</td>
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<td>8.24E-01</td>
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<td>1.63E+00</td>
<td>1.87E+00</td>
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<tr>
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<td>3.97E-01</td>
<td>8.65E-01</td>
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Table 6-16: Predicted species concentration / M for 40 wt% MEA-H₂O-CO₂ systems at 25°C

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<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
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<td>4.48E+00</td>
<td>3.66E+00</td>
<td>2.92E+00</td>
<td>2.43E+00</td>
<td>1.94E+00</td>
<td>1.59E+00</td>
<td>1.32E+00</td>
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<td>1.66E+00</td>
<td>2.49E+00</td>
<td>3.74E+00</td>
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<td>4.94E+00</td>
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<td>3.92E-01</td>
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Table 6-17: Predicted species concentration / M for 50 wt% MEA-H2O-CO2 systems at 25°C

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6.6. Discussion and Conclusions

A mechanistic model for the prediction of corrosion of iron in MEA-CO$_2$-H$_2$O was developed by taking into account the following cathodic reactions: hydrogen evolution, direct water reduction, oxygen reduction and hydrogen carbonate ion reduction. Iron dissolution was the only anodic reaction considered within the model. The data obtained from the model was used for:

- Prediction of corrosion rates;
- Elucidating the governing corrosion mechanism and identify the primary oxidising species;
- Determination of the electrochemical kinetics as a function of operating parameters: CO$_2$ loading, temperature, electrode rotation rate and MEA concentration.

The mechanistic model incorporated mathematical equations for the chemical and electrochemical reaction rates and mass transport processes governing the rates of iron corrosion in MEA-CO$_2$ systems. The equilibrium concentrations of the aqueous species in solution calculated using the Kent-Eisenberg method showed good agreement with experimental data for the pH and CO$_2$ loading. Concentrations of MEA, the protonated amine (RNH$_3^+$) and hydrogen bicarbonate ions (HCO$_3^-$) and thus hydrogen ions (H$^+$) were predicted to increase with CO$_2$ loading and temperature.

Based on the results of the speciation model, a simplified electrochemical model was developed for the ‘uniform’ corrosion of iron in aqueous MEA-CO$_2$ solutions. Model-predicted steady state current density - electrode potential data were compared with corresponding experimental data, as functions of MEA concentration, temperature, CO$_2$ loading and electrode rotation rate.
Values of exchange current densities and transfer coefficients for iron oxidation and reduction of protons, water and oxygen were obtained from the literature.

Model predictions were in modest to fairly good agreement with experimental data, with the model generally predicting higher corrosion rates than those determined experimentally, especially at higher temperatures and low MEA concentrations. The discrepancy was attributed to the model omitting the effects of FeCO$_3$ precipitation, which would have partially passivated the dissolution of Fe to Fe$^{II}$. In addition, the diffusion coefficients used with the model were obtained at low temperatures and a theoretical relationship was used to extend their validity to higher temperatures.

In addition to predicting corrosion rates, the mechanistic model was useful in elucidating the effects of CO$_2$ and of MEA concentrations on the iron corrosion rates and mechanism.

Contrary to suggestions by (Waard and Milliams, 1975) and (Veawab et al., 1999) that the direct reduction of HCO$_3^-$ participates in the corrosion reaction and acts as the primary oxidant in MEA systems, the model predicted that the effect of HCO$_3^-$ ions in solution was to provide an additional source of H$^+$ ions through dissociation.

Model predictions showed fair agreement with experimental results, the increased viscosities at MEA concentrations $\geq$ 30 wt% decreasing corrosion rates. According to experimental data from (Amundsen et al., 2009), the viscosity of 50 wt% aqueous MEA solution at 25 °C loaded with 0.5 mol CO$_2$ (mol amine)$^{-1}$ was more than three times that of 20 wt% MEA under the same conditions. As the solution became more viscous, oxidant diffusion rates decreased, thereby decreasing rates of the dissolution and overall corrosion process.

Comparisons between model predictions and the experimental data revealed the strengths of the model such as the ability to clarify the impact of operating parameters on the predicted
corrosion rates. However, it was also evident from the comparisons that the model was also weaker in determining the corrosion rates at high solution temperatures and low MEA concentrations, which is primarily attributed to the limitations of the Kent-Eiseneberg model to provide reliable thermodynamic data for extreme conditions.
6.7. References


7. Chapter 7

Analysis of Time-dependent Corrosion of Iron in MEA- H₂O- CO₂ Systems

This section details the results of 9 sets of experiments carried out in a flow reactor, which was designed and fabricated to enable measurement of dissolved iron concentrations under conditions typical of amine-based CO₂ absorption. This aimed to enable discrimination between current densities leading to dissolution from those resulting in adsorbed products, such as iron (hydr-)oxide or carbonate. This was done to investigate the components of the corrosion processes systematically and elucidate their kinetics, mechanisms and rate determining steps(s), by combining electrochemical techniques with subsequent chemical analysis of solutions by inductively coupled plasma optical emission spectrophotometry (ICP-OES).

The mechanisms of iron and carbon steel corrosion in aqueous-CO₂ systems has been deliberated and debated for several decades, with particular attention being given to CO₂
absorbing amine solutions in recent years. Extensive research of CO\textsubscript{2}-induced steel corrosion has been carried out, primarily because of its great importance in the oil and natural gas industry; unfortunately, conflicting corrosion rates as functions of process parameters and various mechanisms have been reported. In order to reconcile the seemingly contradictory reports, it is important to note that the term ‘corrosion’ in CO\textsubscript{2} systems is as a result of several reactions as outlined in Chapter 5 & 6. Several CO\textsubscript{2} dependent chemical, electrochemical and mass transport processes occur simultaneously in the aqueous solution at the iron | solution interface. Each of these reactions responds differently to changes in CO\textsubscript{2} loading, temperature, solution flow rate and other operating parameters, which may result in changes to the concentrations in solution species. Whilst insoluble corrosion products such as FeCO\textsubscript{3} and Fe(OH)\textsubscript{2} have been identified in various locations on amine plants (DuPart and Rooney, 1993), there are also soluble products such as Fe\textsuperscript{2+} resulting from the corrosion reactions. So far, very few publications have addressed the experimental quantification of these soluble products.

The ICP-OES was used to determine dissolved (Fe\textsuperscript{II}) concentrations in the amine solution after constant potential electrolyses (chronoamperometry), enabling the charge yield for dissolution to be determined by relating the amount of charge passed to the amount of iron dissolved. The combined use of conventional electrochemical methods, as well as mass loss determination by chemical analysis provided a more accurate method for dissolution rate measurement than the commonly used Tafel extrapolation method.

The first task was to study the effect of the electrode potential on the corrosion and passivation behaviour. A matrix of experiments was designed to establish the effects on the corrosion rate of operating parameters: solution temperature, CO\textsubscript{2} loading, amine concentration, oxygen content and solution flow rates. The effects of these experimental
variables had been studied previously with the RDE system (Chapter 5), which was not able to determine partial current densities due to Fe\(^{II}\) dissolution.

Once the baseline of the corrosion behaviour of iron in the industry standard solvent MEA had been firmly established, a series of experiments were conducted to compare that to the behaviour in other promising and commercially available solvents: (MDEA), (AEP) and (AMP). According to (Kohl and Nielsen, 1997), most of the equipment and piping in CO\(_2\) absorption plants are fabricated from carbon steel, so it was also imperative to establish the corrosion rate of carbon steel under similar operating conditions. Most of the previous studies on steel corrosion in aqueous MEA have focused on carbon steel with 0.20 % carbon (Nainar and Veawab, 2009; Veawab et al., 1999), which together with carbon steel with 0.35 % carbon and stainless steel, was included in this study.

The majority of the experiments were based on ca. 1 hour electrochemical measurements on iron/steel specimens with the surfaces ‘cleaned’ beforehand, representative of new processing equipment and piping at the start of plant operation. In order to simulate typical CO\(_2\) absorption plant conditions, it was also deemed important to carry out long term measurements, over a period of 28 days. These series of experiments, conducted at open circuit potential, aimed to establish the longer term corrosion behaviour and to gain information on the effects of degradation products accumulating in the aqueous solution.

### 7.1. Electrochemical Behaviour of Iron in Large Scale Electrode

Figure 7-1 shows the cyclic voltammogram \((dE/dt = 10 \text{ mV s}^{-1})\) recorded for the iron electrode, as 4 dm\(^3\) of aqueous solution containing 30 wt% MEA fully saturated with CO\(_2\) (25°C, pH 8.03) was circulated through the reactor at a linear velocity of 0.5 mm s\(^{-1}\). The iron
electrode was ‘cleaned’ cathodically by applying a potential of -1.00 V (AgCl|Ag) for 10 minutes to reduce any (hydr-)oxides formed spontaneously in air; 

\[ E_{\text{AgCl}/\text{Ag}} \text{(SHE)} / V = 0.2197 - 0.0592 \log(C^+) \]

After this procedure, the open circuit potential was measured as -0.75 V. The electrode potential was scanned from a negative potential limit of -1.00 V to a positive limit of 0.00 V, a potential window in which the anodic behaviour of iron could be studied without the evolution of oxygen \((E_{O2/H2O} = +0.55 \text{ V})\). The potential-pH diagram for a Fe-H2O-CO2 system (Figure 5-9) was used to assign reactions to the main features of Figure 7-1.

![Figure 7-1](image)

Figure 7-1: Cyclic voltammograms of an iron electrode in 30 wt% MEA + H2O + CO2 at 10 mV s\(^{-1}\) \((T = 25^\circ\text{C}, \text{pH} 8.03)\) with a linear velocity of 0.5 mm s\(^{-1}\).

The cyclic voltammogram exhibited the same shape and form as those obtained from the RDE system under similar operating conditions \((25^\circ\text{C}, \text{pH} 8.01)\). On the positive-going potential sweep from the negative potential limit of -1.00 V, cathodic current densities resulted from hydrogen evolution from the reduction of H2O and H\(^+\) ions. At potentials > -
0.78 V, anodic current densities were measured due to the dissolution of iron \((E_{Fe^{2+}/Fe} = -0.79 \text{ V})\) occurring simultaneously with other oxidation reactions, such as the precipitation of FeCO₃ \((E_{FeCO_3/Fe} = -0.86 \text{ V})\), based on \([\text{HCO}_3^-]\) of 1.96 M obtained from the Kent-Eisenberg model described in Chapter 6. The anodic domain was characterised by three features: at ca. -0.72 V (I), a current density peak of 23.7 A m⁻² at ca. -0.51 V (peak II), and (III) at ca. -0.28 V. The current density peak (II) was attributed to the dissolution of iron by reaction (7.1) and FeCO₃ formation when its solubility product was exceeded sufficiently; at more positive potentials, this was followed by a passive region due to the formation of (hydr-)oxides on the iron surface.

\[
Fe \leftrightarrow Fe^{2+} + 2e^- \tag{7.1}
\]

On the negative-going scan from the positive potential limit of 0 V, there was a reduction peak (IV) at ca. -0.42 V followed by an additional peak (V) at ca. -0.54 V, as previously detected with the RDE system. As described in Chapter 5, this peak resulted from the simultaneous reduction of (hydr-)oxide such as Fe₂O₃ and Fe(OH)₃ that reactivated the oxidative dissolution reaction of Fe to Fe²⁺, giving rise to a net positive current density.

### 7.2. Effect of Electrode Potential

The anodic domain of iron in aqueous MEA-CO₂ systems was studied by chronoamperometry, recording current responses over a 1 hour period to a range of potentials. To complement the chronoamperometric data, known aliquots of the aqueous amine solution were extracted from the reactor outlet at 10 minute intervals for subsequent analysis by the ICP-MS to measure dissolved Fe²⁺ ion concentrations. This enabled the
potential range for active iron dissolution to be defined within which subsequent experiments could be conducted.

Figure 7-2: Effect of potential on chronoamperograms obtained on iron electrode at \(-0.80\, \text{V} \leq E \leq -0.20\, \text{V}\) in contact with 30 wt\% MEA + H\(_2\)O + CO\(_2\) \((T = 25^\circ\text{C}, \text{pH} 8.03)\) with a linear velocity of 0.5 mm s\(^{-1}\).

Figure 7-2 shows the chronoamperometric \((j-t)\) data for Fe in 30 wt\% MEA fully saturated with CO\(_2\) \((25 \, \text{C, pH} \, 8.03)\), for potentials between \(-0.80\, \text{V}\) and \(-0.20\, \text{V}\). Potentials of \(-0.80\, \text{V}\) and \(-0.75\, \text{V}\) produced low cathodic (negative) current densities, resulting in relatively small concentrations of dissolved Fe\(^{II}\), as shown in Figure 7-4. The cathodic current measured was due to the applied potential at \(-0.80\, \text{V}\) being more negative than the equilibrium potential for iron dissolution \((E_{\text{Fe}^{2+}/\text{Fe}} = -0.79 \, \text{V} \) at dissolved Fe\(^{II}\) activity of \(10^{-4}\) and pH 8.03\) and while that of \(-0.75\, \text{V}\) was less negative than \(E_{\text{Fe}^{2+}/\text{Fe}}\), the applied overpotential was not significant enough to induce a net anodic current. However, the total dissolved Fe\(^{II}\) ions in solution increased significantly as the potential became less negative. The total amount of dissolved iron detected in the solution at the end of the measurement was 130.4 mg m\(^{-2}\) at \(-0.80\, \text{V}\) and
315.6 mg m\(^{-2}\) -0.75 V. As \(E_{H_2O/H_2} > E_{Fe^{1+}/Fe}\), net current densities occurred in the potential window \(E_{H_2O/H_2} > E > E_{Fe^{2+}/Fe}\).

Figure 7-3: Effect of potential on the charge density-time data for iron electrode at -0.80 V ≤ E ≤ -0.20 V in 30 wt% MEA + H\(_2\)O + CO\(_2\) (\(T = 25^\circ\)C, pH 8.03) with a linear velocity of 0.5 mm s\(^{-1}\).

At potentials less negative than -0.70 V, net anodic (positive) current densities were measured due to the dissolution of iron as iron(II)\(_{aq}\), the subsequent precipitation of FeCO\(_3\), Fe\(_2\)(OH)\(_2\)CO\(_3\), Fe(OH)\(_2\) and (or) passivation of oxides on the electrode surface. The current densities initially exhibited a maximum value, followed by a sharp decrease within 100 s, after which it continued to decline at a slower rate. This decrease in current density with time was indicative of a passivation or precipitation process on the surface of the iron electrode. The net charged passed was anodic (calculated by integrating current-time data) and increased from -0.70 V to -0.55 V, then started to decrease from -0.55 V to -0.20 V (Figure 7-3).

The total concentration of Fe\(^{II}\) ions measured also increased within the potential range of -0.70 V to -0.55 V and then decreased gradually between -0.55 V and -0.20 V (Figure 7-4).
The charge yield of the dissolution reaction was calculated by relating the charge that would have been passed theoretically for the dissolution of elemental Fe to the measured Fe\textsuperscript{II} ions in solution by the ICP-OES, to the total charge passed (recorded in the chronoamperogram).

Figure 7-4: Effect of potential on Fe\textsuperscript{II} concentration-time data for iron electrode at -0.80 V ≤ E ≤ -0.20 V in contact with 30 wt% MEA + H\textsubscript{2}O + CO\textsubscript{2} (T = 25 C, pH 8.03) with a linear velocity of 0.5 mm s\textsuperscript{-1}.

The dissolution charge yield increased from -0.70 V to -0.55 V and then decreased at potentials less negative than -0.55 V. The observed decrease in dissolution rate and anodic current densities at potentials less negative than -0.55 V coincided with the occurrence of the anodic peak (II), which was attributed to the active-passive transition of iron due to its passivation by oxides and hydroxides. Figure 7-5 shows images of the iron electrode after constant potential electrolys and demonstrates the increasingly passive behaviour at potentials less negative than -0.55 V. This behaviour validated the results from the cyclic voltammograms shown in Figure 7-1. Thus, the potential of -0.60 V was selected as a suitable potential for the subsequent constant electrode potential electrolys in the active region, in which iron dissolution dominated the resulting anodic current. This chosen potential also falls within the small potential range (-0.88 V ≤ E ≤ -0.52 V) in which the precipitation of
protective FeCO$_3$, Fe$_2$(OH)$_2$CO$_3$ and Fe(OH)$_2$ ((7. 2) – (7. 4) is predicted thermodynamically according to the potential-pH diagram for Fe-CO$_2$-H$_2$O systems, an example of which is shown in Figure 5-9.

\[
Fe^{2+} (aq) + CO_3^{2-} (aq) \leftrightarrow FeCO_3 (s) \quad (7. 2)
\]

\[
Fe^{2+} + FeCO_3 + 2OH^- \leftrightarrow Fe_2(OH)_2 CO_3 \quad (7. 3)
\]

\[
Fe^{2+} (aq) + 2OH^- (aq) \leftrightarrow Fe(OH)_2 (aq) \quad (7. 4)
\]

Figure 7-5: Images of iron electrode in 30 wt% MEA + H$_2$O + CO$_2$ at pH 8.03 and \( T = 25^\circ C \), with a solution velocity of 0.5 mm s$^{-1}$ (Re = 1.69) after constant electrolyses at -0.70 V, -0.60 V, -0.50 V & -0.40 V.
7.3. Effect of Solution Velocity

7.3.1. Reactor Characterisation with Mass Transport Correlations

As outlined below, the hydrodynamic behaviour of the reactor was characterised using a set of mass transport equations, which relate the hydrodynamic conditions to the geometry of the reactor and the characteristics of the amine solution.

The equivalent hydrodynamic diameter, $d_e$ for the reactor compartment of electrode-membrane distance $d$ and electrode width $w$ was obtained with the following equation (7.5):

$$d_e = \frac{4 \text{(cross sectional area)}}{\text{wetted perimeter}} = \frac{2wd}{(w+d)} \quad (7.5)$$

The mass transport coefficient $k_{m}$, is a heterogeneous rate constant which characterises the mass transport conditions of the reactor under defined conditions such as amine composition, temperature and solution velocity. The mass transport coefficient, $k_{m,x}$ at distance ‘$x$’ from the inlet of the reactor, was estimated from the appropriate correlation for the (laminar) hydrodynamic properties of the reactor and is a function of dimensionless quantities that were used to characterise fluid flow regimes in the flow reactor:

- Reynolds number, defined as the ratio of the inertial forces to viscous forces, where $u$ is the linear velocity and $v$ is the kinematic viscosity of the solution:

  $$\text{Re} = \frac{ud_e}{v} \quad (7.6)$$

- Schmidt number: the ratio of the (momentum) kinematic viscosity, $v$ to the diffusivity coefficient, $D_i$ for species $i$, and is used to characterise fluid flow regimes in which there are simultaneous momentum and mass diffusion convection processes.
\[ \text{Sc} = \frac{v}{D_i} \]  

(7.7)

- Sherwood number represents the ratio of the total mass transfer rate (convective plus diffusion) to the diffusion transfer rate alone:

\[ \text{Sh}_x = \frac{k_{m,x} d_e}{D_i} \]  

(7.8)

Figure 7-6: Dependences of Sherwood number on Reynold number and distance from inlet of the flow reactor based on the reactor geometry, solution flowrate 0.01 - 0.1 m s\(^{-1}\) and MEA solution viscosity \((3.22 \times 10^{-6} \text{ m}^2 \text{ s}^{-1})\).

For a parallel plate electrochemical reactor with a small inter-electrode gap, the dimensionless group correlation for fully developed laminar flow \((\text{Re} < 2000)\) is given by equation (7.9) (Pickett, 1979; Walsh, 1993; Rousar et al., 1971; Rousar, 1986):

\[ \text{Sh}_x = 1.23 \left( \text{Re} \cdot \text{Sc} \cdot \frac{d_e}{x} \right)^{1/3} \]  

(7.9)

The Reynolds and Sherwood numbers were calculated from equations (7.6) and (7.9), based on the reactor geometry and solution velocity of 0.01 - 0.1 m s\(^{-1}\). The kinematic viscosity of
30 wt% MEA at 25°C with 0.5 mol CO₂ (mol amine)⁻¹ was calculated using published viscosity and density data (Amundsen et al., 2009). The results are shown in Figure 7-6.

The mass transport coefficients, \( k_m \) (displayed in Figure 7-8) were then determined by manipulations of the dimensionless group mass transport correlations (7.9) and equation (7.8) and averaged over the electrode surface.

7.3.2. Reactor Characterisation by the Reduction of Hexacyanoferrate(III)

For hydrodynamic systems in which the mass transport correlations cannot be predicted adequately from published correlations, mass transport coefficients can also be determined experimentally by using a diffusion limited current technique, usually based on the reduction of hexacyanoferrate(III) ions (\( \text{Fe(CN)}_6^{3-} \)) or the oxidation of hexacyanoferrate(II) ions (\( \text{Fe(CN)}_6^{4-} \)) at a platinum, gold or nickel electrode (Walsh, 1993; Colli et al., 2013; Wragg and Leontaritis, 1997):

\[
\text{Fe(CN)}_6^{3-} + e^- \leftrightarrow \text{Fe(CN)}_6^{4-} 
\]

(7.10)

According to (Walsh, 1993), the reduction of hexacyanoferrate(III) ions gives better results than the oxidation of hexacyanoferrate(II) ions, as metal oxide formation may affect the kinetics of the latter, depending on the working electrode material. Due to the alkalinity of the hexacyanoferrate(III/II) solutions, at the appropriate potentials, hexacyanoferrate(III) can be reduced with close to 100 % current efficiency. In addition, in the absence of the hydrogen evolution reaction, the reduction of \( \text{Fe(CN)}_6^{3-} \) displays a distinctive mass transport limited current, as shown in Figure 7-7.
Figure 7-7: Cyclic voltammograms of an iron electrode in contact with 50 mol m$^{-3}$ of K$_3$Fe(CN)$_6$ / 100 mol m$^{-3}$ of K$_4$Fe(CN)$_6$ and 1000 mol m$^{-3}$ of Na$_2$CO$_3$ at pH 11.3 with a flow rate of 0.1 mm s$^{-1}$.

Thus, as a method of comparison to the mass transport correlations described above, the flow reactor was also characterised by the reduction of hexacyanoferrate(III). 2 dm$^3$ of solution containing 50 mol m$^{-3}$ K$_3$Fe(CN)$_6$, 100 mol m$^{-3}$ K$_4$Fe(CN)$_6$ and a supporting electrolyte of Na$_2$CO$_3$ at pH 11.3 was circulated through the reactor at various solution linear velocities between 0.1 to 0.8 mm s$^{-1}$. Cyclic voltammograms were determined from a negative potential limit of -0.80 V to a positive limit of 0.80 V and the mass transport limiting reduction current plateaux were measured as functions of solution velocity (Figure 7-7).

The (local) mass transport coefficient $k_{m,x}$ is related the mass transport limited current density $j_{LIM,x}$ to the reactant concentration change in the bulk solution (Wragg and Leontaritis, 1997), where $c_\infty$ is the bulk concentration of the electro-active species.
By relating the magnitude of the mass transport limited current to the solution flow rates, the mass transport coefficient, $k_m$ for hexacyanoferrate(III) was obtained from (7. 11) and the corresponding values for Fe$^{II}$ were calculated using (7. 12). The mass transport coefficient values for Fe(CN)$_6^3$ and Fe$^{II}$ obtained by the mass transport correlation and reduction of hexacyanoferrate (III) are shown as a function of solution flow rates in Figure 7-8. The diffusion coefficients for the Fe(CN)$_6^3$ ions and Fe$^{II}$ ions were obtained from (Books et al., 2006) and (Reddi and Inyang, 2000) respectively.

\[ k_{m,Fe^{2+}} = k_{m,Fe(CN)_6^{3-}} \frac{D_{Fe^{2+}}}{D_{Fe(CN)_6^{3-}}} \] (7. 12)

The mass transport coefficient, $k_m$ is also given by equation (7. 13), from which the thickness of the Nernst diffusion layer $\delta_N$ was calculated and displayed in Figure 7-9.

\[ k_{m,Fe^{2+}} = \frac{D_{Fe^{2+}}}{\delta_N} \] (7. 13)

There was a discrepancy between the values of the mass transport coefficient calculated by the reduction of Fe(CN)$_6^3$ and the values predicted by mass transfer correlations, due to flow not being well developed, because of entry and exit flow dominating mass transport within the short reactor (Pickett and Ong, 1974).

As shown in Figure 7-9, increasing solution velocity decreased the thickness of the Nernst diffusion layer at the iron metal | solution interface.
Figure 7-8: Mass transfer coefficient versus linear velocity for Fe(CN)$_6^{3-}$ measured during hexacyanoferrate(III) reduction and the corresponding values calculated for Fe$^{II}$ with comparisons to the calculations based on mass transport correlations.

Figure 7-9: Effect of solution velocity on the diffusion layer thickness for Fe$^{II}$ measured by the reduction of hexacyanoferrate(III) with comparisons to the calculations based on mass transport correlations.
7.3.3. Effect of solution flow rate on iron corrosion in MEA+ CO2 solutions

Figure 7-10 shows the effect of solution linear velocity on current densities of iron at -0.6 V (AgCl|Ag) in contact with aqueous 30wt% MEA + CO2, current densities increasing with increasing flow rates.

![Graph showing effect of solution linear velocity on current densities of iron](image)

Figure 7-10: Effect of solution velocity on chronoamperometric data for iron electrode in 30 wt% MEA + H2O + CO2 at pH 8.03 and $T = 25 \, ^\circ C$; -0.60 V (AgCl|Ag).

The bulk concentration of FeII ions increased with solution velocity (Figure 7-13), partly due to the enhanced mass transport of the oxidising species (H+) to the surface of the iron. The charge density (Figure 7-12) and the charge yield of the iron dissolution reaction also increased with solution flow rate, implying that the FeCO3 protective layer formation/precipitation of Fe(OH)2 was impeded by solution flow. FeCO3 precipitation occurred only if the local concentrations of FeII and CO32- ions in the aqueous solution exceeded its solubility product, with sufficient supersaturation to provide a driving force. The temperature dependent solubility product, $K_{sp}$ for FeCO3 formation is $1.27 \times 10^{-11}$ at 25°C (calculated from thermodynamic data in (Benezeth et al., 1985)). The condition for Fe(OH)2 precipitation is outlined in equation (7. 18). In order to determine if the ‘local’ conditions at the iron electrode met the requirements for FeCO3 and Fe(OH)2 nucleation, the FeII ion concentrations
at the electrode surface $[\text{Fe}^{2+}(x=0)]$ was estimated from the flux, $N_{Fe^{2+}}$ and the measured Fe$^{II}$ ion concentration in the bulk solution $[\text{Fe}^{2+}(x=\delta_N)]$ by taking into account the concentration profile across the Nernst diffusion layer.

$$Fe \rightarrow 2e^- + \text{Fe}^{2+}(x=0) \xrightarrow{k_m} \text{Fe}^{2+}(x=\delta_N) \quad (7.14)$$

Figure 7-11 shows a schematic representation of the concentration profile of Fe$^{II}$ across an idealised Nernst diffusion layer at an iron electrode.

![Figure 7-11: Idealised Nernst diffusion layer and concentration profile for Fe$^{II}$ ions required for FeCO$_3$ and Fe(OH)$_2$ precipitation.](image)

A series of equations were employed for the calculation of $[\text{Fe}^{2+}(x=0)]$ and are outlined in (7.15) – (7.17) below:

The flux of Fe$^{II}$ ions from the electrode | solution interface $(x=0)$ into the solution:
\[ N_{Fe^{2+}} = \frac{j_{Fe}}{2F} = \frac{j_{0,Fe} \exp(\beta_{Fe} T_{Fe})}{2F} \] (7.15)

\[ N_{Fe^{2+}} \approx -D_{Fe^{2+}} \frac{\partial [Fe^{2+}]}{\partial x} \approx -D_{Fe^{2+}} \frac{([Fe^{2+}]_{x=0} - [Fe^{2+}]_{x=\delta N})}{\delta N} \] (7.16)

At steady-state and in the absence of Fe\textsuperscript{II} accumulation/precipitation:

\[ [Fe^{2+}]_{x=0} \approx [Fe^{2+}]_{x=\delta N} + \frac{j_{Fe} \delta N}{2F D_{Fe^{2+}}} \] (7.17)

Precipitation of Fe(OH)\textsubscript{2} may occur if:

\[ [Fe^{2+}]_{x=0} \geq 10^{(12.94-2pH)} \text{ mol dm}^{-3} \] (7.18)

Precipitation of Fe\textsubscript{2}(OH)\textsubscript{2}CO\textsubscript{3} may occur if:

\[ [Fe^{2+}]_{x=0} \geq 10^{(10.70-2pH)} \text{ mol dm}^{-3} \] (7.19)

Precipitation of FeCO\textsubscript{3} may occur if:

\[ [Fe^{2+}]_{x=0} \cdot [CO_3^{2-}] \geq K_{sp} \] (7.20)

However, all three processes require supersaturation as a driving force for phase formation.

The resulting calculations for the Fe\textsuperscript{II} concentration at the surface of the electrode, \([Fe^{2+}]_{x=0}\) obtained at each linear solution velocity was summarised in Table 7-1. The equilibrium concentration of the CO\textsubscript{3}\textsuperscript{2-} ions was calculated by the Kent Eisenberg model described in Chapter 6. At each of the flow rates studied within this work, the \([Fe^{2+}]_{x=0}\), \([CO_3^{2-}]\) and \([OH^-]\) species exceeded the solubility products, \(K_{sp}\), of \([Fe^{2+}]_{x=0}\) \([CO_3^{2-}]\) and/or \([Fe^{2+}]_{x=0}\)\([OH^-]\), i.e. the thermodynamic condition required for Fe(OH)\textsubscript{2} and FeCO\textsubscript{3} precipitation to occur.
Turbulent solution flow conditions (Re $>$ 2200 for channel flow) at higher flow rates has been reported (Revie, 2015) to cause mechanical disruption to the FeCO$_3$ film, decreasing the barrier of the passive film to the diffusion of oxidising agents to the underlying iron surface. However, this was unlikely to be the case in this flow system, as the hydrodynamic conditions remained under laminar flow conditions (Re $\leq$ 6.47) even at the maximum flow rate studied (Figure 7-10). However, the increase in dissolution charge yield for Fe$^{II}_{aq}$ formation with increasing solution velocity was most probably due to a decrease in the supersaturation level at the metal | solution interface, through the increased mass transport of Fe$^{II}$ away from the iron surface.

![Figure 7-12](image)

Figure 7-12: Effect of solution velocity on charge density-time data for iron electrode in 30 wt% MEA + H$_2$O + CO$_2$ at pH 8.03 and T = 25 °C, at -0.60 V (AgCl|Ag).
Figure 7-13: Effect of solution velocity on time dependence of mass of Fe$^{II}$ dissolved from iron electrode in 30 wt% MEA + H$_2$O + CO$_2$ at pH 8.03 and T = 25 °C; -0.60 V (AgCl|Ag).

Table 7-1: Effect of solution velocity on the conditions required for FeCO$_3$ and Fe(OH)$_2$ precipitation by determining the [Fe$^{II}$] at the iron electrode surface, equilibrium [CO$_3^{2-}$] from the Kent Eisenberg model and the results from iron electrode in 30 wt% MEA + H$_2$O + CO$_2$ (T = 25 °C, pH 8.03) at -0.60 V (AgCl|Ag).

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$^1$ Calculations based on $k_m$ from the reactor characterisations based on mass transport correlations.
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### 7.4. Temperature Effect - Full CO$_2$ saturation

Figure 7-14 shows the effect of temperature on current density-time data at a potential of -0.60 V (AgCl|Ag) in 30 wt% MEA solution at full CO$_2$ saturation. 40 °C represented the absorber conditions while the highest temperature 80 °C was representative of the rich-lean heat exchanger. The chronoamperograms maintained a similar characteristic shape, but the initial maximum current density increased with temperature. The current density decreased rapidly until it reached a minimum current density (close in value at all temperatures), which remained constant for the duration of the experiment.

---

2 Based on the Kent-Eisenberg Model, [CO$_3^{2-}$] was 0.20 M for aqueous 30wt% MEA+CO$_2$, 25°C at pH 8
Effect of temperature on current density – time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a velocity of 0.5 mm s⁻¹.

Both the total charge (Figure 7-15) and dissolved Fe²⁺ ion concentration (Figure 7-16) increased with increasing temperature. The change in dissolved Fe²⁺ with time exhibited a seemingly linear behaviour at 25 °C, but then dissolution rates at higher temperatures (40-80 °C) decreased. The calculated dissolution charge yield for Fe²⁺ₐq species also decreased with temperature; for example, the charge yield decreases from 77.9 % at 40 °C to 65.3 % at 80 °C, due to increased rates of adsorbed product formation.

The following expression for the temperature dependence of the solubility product of FeCO₃ was obtained by (Benezeth et al., 2009) and the calculated values for the temperature range studied within this work are shown in Table 7-3.

\[
\log_{10}K_{sp} = a + b \cdot (T/K)^{-1} + d \cdot \log_{10}(T/K) \tag{7.21}
\]

Elevating the temperature increased the rate of all the processes involved in the corrosion of iron in the aqueous amine solution including mass transport rates, chemical reactions in the bulk solution and electrochemical reactions at the iron | solution interface. As the kinetics of each of these processes increased with temperature, depending on the solubility product of
ferrous carbonate (FeCO$_3$) film formation, increased temperature can either increase or decrease the corrosion rate.

Figure 7-15: Effect of temperature on the charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H$_2$O + CO$_2$ ($T = 25–80$ °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$.

Increasing the temperature promoted higher concentrations of Fe$^{II}$ ions in the aqueous amine solution, and as the local concentrations exceeded the solubility product, FeCO$_3$, the protective film precipitated. The solubility product ($K_{sp}$) is related to the supersaturation ($S$) via reaction (7.22).

$$ S = \frac{[Fe^{2+}]_{x=0} [CO_3^{2-}]}{K_{sp}} \quad (7.22) $$

Once the supersaturation value $S$ exceeded unity, the FeCO$_3$ film could have begun to precipitate on the surface of the iron, probably leading to a decrease in corrosion rates. However, at low concentrations of Fe$^{2+}$$_{(x=0)}$ and CO$_3^{2-}$ that are only slightly above the solubility limit and at low temperatures, the rate of FeCO$_3$ precipitation is slow. Thus, the precipitation kinetics were deemed even more important in determining the protectiveness of the FeCO$_3$ film than just the thermodynamics of the system. (Johnson and Tomson, 1991)
discovered that the most important parameters influencing the kinetics of FeCO$_3$ precipitation are the supersaturation and temperature and they proposed an equation (7. 23) for the precipitation rate:

$$R_{FeCO_3} = \frac{A}{v} \cdot \exp^{54.8-123.0 \cdot \frac{K_{sp}}{RT} \cdot (S^2 - 1)^2}$$ (7. 23)

The nucleation and growth of the FeCO$_3$ film are slow processes that are enhanced by increasing the solution temperature. The nucleation of crystalline films such as FeCO$_3$ has proven to be challenging to model mathematically and it is also generally accepted that the rate of precipitation is dependent primarily on the crystal growth rate (supersaturation) instead of the nucleation rate. In addition to the rate equation (7. 23) proposed by (Johnson and Tomson, 1991), (van Hunnik and Hendriksen, 1996) also proposed a more frequently used equation for the crystal growth rate of FeCO$_3$; both equations have been used to evaluate the effect of temperature on the rate of corrosion based on the Fe$_2^+(x=0)$ and CO$_3^{2-}$ obtained from the experiments.

According to (van Hunnik and Hendriksen, 1996):

$$R_{FeCO_3} = \frac{A}{v} \cdot \exp^{52.4-119.8 \cdot \frac{K_{sp}}{RT} \cdot (S - 1)(1 - S^{-1})}$$ (7. 24)

The FeCO$_3$ film growth rate obtained from equation (7. 23) and (7. 24) based on the Fe$_2^+(x=0)$ data listed in Table 7-2 is plotted as a function of the temperature in Figure 7-17. The results obtained are in agreement with reports from literature that substantial rates of film formation are achieved only at higher temperatures (> 60 C) and high supersaturation, $S$ (Nesic and Lee, 2003). The solubility of FeCO$_3$ is also dependent on the temperature and decreases with increasing temperature (Table 7-3).
Although the dissolution rate increased significantly at higher temperatures (i.e. increased concentration of Fe$^{2+}$ ions in the bulk solution), the formation rate of FeCO$_3$ also accelerated which resulted in a decrease in the dissolution rate at elevated temperatures. This decrease in corrosion rate occurred as a result of the FeCO$_3$ layer acting as a diffusion barrier to the oxidising species and covering at least part of the iron surface, thereby inhibiting the dissolution of underlying metal. Figure 7-18 shows images of the iron electrode after the chronoamperometric experiments; the passive film formation was more evident at higher temperatures. It is also important to note that the film formed at 60$^\circ$C was non-adherent to the metal surface and could easily be wiped off with a cloth, whereas the films formed at 80$^\circ$C were so tough they could be removed only by mechanical polishing.

Figure 7-16: Temperature effect on Fe$^{II}$ concentration-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H$_2$O + CO$_2$ ($T = 25$ C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 

Figure 7-17: Effect of temperature on the FeCO$_3$ precipitation rate at iron electrode in contact with 30 wt% MEA + H$_2$O + CO$_2$ ($T = 25$ °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$ after constant potential electrolyses at -0.60 V (AgCl|Ag).

Figure 7-18: Images of iron electrode in contact with 30 wt% MEA + H$_2$O + CO$_2$ ($T = 25 – 80$ °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$ after constant electrolyses at -0.60 V (AgCl|Ag).
Table 7-2: Effect of temperature on the conditions required for FeCO₃ precipitation by determining the [Fe⁴⁺] at the iron electrode surface, equilibrium [CO₃²⁻] from the Kent Eisenberg model and the results from iron electrode in contact with 30 wt% MEA + H₂O + CO₂ (T = 25 °C, pH 8.03) at -0.60 V.

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Table 7-3: Effect of temperature on the solubility product, $K_{sp}$ (calculated from thermodynamic data in (Benezeth et al., 2009))

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7.5. Effect of CO$_2$ loading

The effect of CO$_2$ loading ($\alpha$) on the corrosion rate of iron in the aqueous 30wt% MEA solutions was investigated at loadings of 0.4, 0.2, 0.0 and compared to the results at full CO$_2$ loading ($\alpha \approx 0.6$). The desired CO$_2$ loadings were achieved according to the CO$_2$ solubility data in 30 wt% MEA obtained by (Tong et al., 2012) and (Jou et al., 1995), included in Appendix (I). As an example, according to Jou et al., a CO$_2$ partial pressure 8.96 Pa would be required to achieve a CO$_2$ loading of 0.203 mol CO$_2$ (mol MEA)$^{-1}$ at 40°C.

There was a significant difference between the current-time behaviour of the iron maintained potentiostatically at -0.60 V in loaded and unloaded amine solutions (Figure 7-19). In the absence of CO$_2$ ($\alpha = 0.0$, pH 12.31), the current-time transients resulted in a net cathodic charge which increased in value with increasing temperature. Although MEA in itself is non-corrosive in the absence of CO$_2$ and iron dissolution was not predicted thermodynamically at pH 12.3, at lower temperatures (25-40°C), there was a relatively small amount of dissolved Fe$^{II}$ ions detected in the amine solution that increased linearly with time (Figure 7-21). At elevated temperatures (60-80°C), [Fe$^{II}$] decreased with time, i.e. there was a net loss of dissolved Fe$^{II}$, presumably due to its precipitation / adsorption. In unloaded MEA solutions, total dissolved Fe$^{II}$ concentrations decreased with increasing temperature.

In CO$_2$ loaded MEA solutions ($\alpha = 0.4$, pH 9.90 and $\alpha = 0.2$, pH 10.70), the current-time transients maintained the characteristic anodic behaviour as seen previously at full CO$_2$ saturation ($\alpha = 0.6$, pH 8.03) (Figure 7-22 & Figure 7-25). The net anodic charge and total dissolved Fe$^{II}$ ion concentration increased with CO$_2$ loading and linearly with temperature (Figure 7-23 - Figure 7-27). For example, the total dissolved Fe$^{II}$ concentration at 80°C at the end of the chronoamperometric measurement was 1.534 g m$^{-2}$ at $\alpha = 0.2$, 2.815 g m$^{-2}$ at
α = 0.4, 6.364 g m⁻² at α = 0.8. The transformation in the corrosion behaviour of iron in MEA solutions on absorption of CO₂ was due to the changes in the ionic composition of the amine solution resulting from the reaction of the amine and CO₂. As described previously in Chapter 5 and Chapter 6, as the CO₂ loading is increased, so do equilibrium concentrations of hydrogen carbonate ion (HCO₃⁻) and protonated amine (RNH₃⁺), which subsequently dissociate to form hydrogen ions (H⁺). The reduction of H⁺ ions serves as the main reduction reaction, so increasing its rate by increasing its effective concentration, thereby increasing dissolution rates.

At lower temperatures, it was difficult to distinguish the effect of CO₂ loading on the dissolution charge yield; however, at higher temperatures (60-80 °C), both the total charge and the dissolution charge yield increased significantly with CO₂ loading. It is clear from the results (Figure 7-28) that the dissolution reaction was enhanced by CO₂ absorption; for example, the total charge for the chronoamperogram of iron in 30 wt% MEA at full saturation (80 °C) was 33 691 C sm⁻² (dissolution charge yield was 65.3 %), while that of α = 0.2 was 21 020 C m⁻² (dissolution charge yield is 25.3 %).

In addition to iron dissolution, the solubility of FeCO₃ is also strongly dependent on the CO₂ loading and pH of the system. According to (Nordsveen et al., 2003), FeCO₃ precipitation can occur only at a pH which exceeds a critical value, which depends on the temperature and Fe^{II} concentration. At a pH above this critical pH, once the saturation of Fe^{II} and CO₃²⁻ is exceeded, precipitation can occur. According to thermodynamic predictions from the potential-pH diagram for Fe-CO₂-H₂O (Figure 5-9), this critical pH is ca. 6.4 and for P(CO₂) = 0.1 MPa. The rate of FeCO₃ precipitation also increased with CO₂ loading (Figure 7-33) due to the increased concentration of CO₃²⁻ ions in the bulk solution and Fe^{II} ions at the surface of the iron from the increased corrosion rate.
Figure 7-19: Chronoamperometric data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, pH 12.31, α = 0) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-20: Charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in contact with 30 wt% MEA + H₂O (T = 25-80 °C, pH 12.31, α = 0) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-21: Corrosion-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, pH 12.31, α = 0) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-22: Chronoamperometric data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O ($T = 25$-$80$ °C, pH 10.70, $\alpha = 0.2$) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-23: Charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O ($T = 25$-$80$ °C, pH 10.70, $\alpha = 0.2$) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-24: Fe²⁺ concentration-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O ($T = 25$-$80$ °C, pH 10.70, $\alpha = 0.2$) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-25: Chronoamperogram for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, pH 9.90, α = 0) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-26: Charge density-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, pH 9.90, α = 0.4) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-27: Fe²⁺ concentration-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T = 25-80 °C, pH 9.90, α = 0.4) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-28: Effect of CO₂ loading on the Fe^{II} concentration-time data for iron electrode at -0.60 V (AgCl|Ag) in contact with 30 wt% MEA + H₂O (pH 8.03-12.3, α = 0-0.6) with a solution velocity of 0.5 mm s⁻¹ for a) 25 °C b) 40 °C c) 60 °C d) 80 °C.
Figure 7-29: Effect of CO₂ loading on current density - time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (pH 8.03-12.3, α = 0-0.6) with a solution velocity of 0.5 mm s⁻¹ for a) 25 °C b) 40 °C c) 60 °C d) 80 °C.
Figure 7-30: Effect of CO₂ loading on charge density-time data for iron electrode at -0.60 V (AgCl/Ag) in 30 wt% MEA + H₂O (pH 8.03-12.3, α = 0-0.6) with a solution velocity of 0.5 mm s⁻¹ for a) 25 °C b) 40 °C c) 60 °C d) 80 °C
Figure 7-31: Effect of CO$_2$ loading and temperature on total dissolved [Fe$^{2+}$] from iron electrode in 30 wt% MEA + H$_2$O (T = 25-80 °C, $\alpha = 0-0.6$) at -0.60 V (AgCl|Ag) with a solution velocity of 0.5 mm s$^{-1}$.

Figure 7-32: Effect of CO$_2$ loading and temperature on total charge density for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H$_2$O (T= 25-80 °C, $\alpha = 0-0.6$) with a solution velocity of 0.5 mm s$^{-1}$. 
Effect of CO$_2$ loading on the FeCO$_3$ precipitation rate at the iron electrode in 30 wt% MEA + H$_2$O + CO$_2$ ($T = 80$ °C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$ after constant potential electrolyses at -0.60 V (AgCl|Ag).

### 7.6. Effect of Oxygen Content

Figure 7-34 shows the effect of oxygen on current density - time data for iron at -0.6 V in 30 wt% MEA at full CO$_2$ saturation (pH = 8.03, $\alpha = 0.60$, $T = 25$-80 °C). An anoxic system was created to exclude the influence of oxygen by bubbling high purity nitrogen, prior to CO$_2$ being introduced to the system and maintaining a flow of nitrogen instead of air throughout the reactor system. Although the absence of oxygen had a considerable effect on the corrosion of iron in aqueous solutions, the chronoamperograms exhibited similar forms in both atmospheres, suggesting that the mechanism for iron dissolution and precipitation was the same in the presence and absence of oxygen. The data displayed a maximum initial value which decreased rapidly due to the passivation of the metal surface; however, the minimum current density was significantly greater in the presence of oxygen.
Thus, the possibility of Fenton’s reaction was considered. The oxidation of organic substrates by Fe^{II} ions and H_{2}O_{2} (resulting from the reduction of oxygen via reaction (7.23)) was first described by (Fenton, 1876) after observing the oxidation of tartaric acid by hydrogen peroxide in the presence of Ferrous ions. Fenton’s mechanism is initiated by the formation of hydroxyl radical via the reaction (7.26).

$$O_{2} + 2H^{+} + 2e^{-} \rightarrow H_{2}O_{2}$$ \hfill (7.25)

Fenton’s reaction:

$$Fe^{2+} + H_{2}O_{2} \rightarrow Fe^{3+} + HO^{'} + OH^{'}$$ \hfill (7.26)

$$Fe^{3+} + H_{2}O_{2} \rightarrow Fe^{2+} + HOO^{'} + H^{+}$$ \hfill (7.27)

Initiating radicals hydroxyl (HO') and hydroperoxyl (HOO') could then react with MEA to form oxidative degradation products such as ammonia or organic acids via a hydrogen abstraction mechanism as shown in Figure 7-35. (Petryaev et al., 1984) proposed that at pHs ≥ 6, MEA forms a five-member ring by forming hydrogen bonds between HN---O or OH---
N. Free radicals such as hydroxyl and hydroperoxyl then abstract a hydrogen atom from the nitrogen, α-carbon or the β-carbon (Lawal and Idem, 2006). The newly formed amine radical can then transfer the radical internally through the ring structure, which subsequently results in cleavage of the N- -C bond (Chi and Rochelle, 2002). The main degradation products formed are an amine, an aldehyde or aldehyde radical. The aldehyde radical, if formed, would then abstract hydrogen from another molecule of MEA, forming an MEA radical and aldehyde.

![Chemical structures](image)

**Figure 7-35:** Hydrogen abstraction mechanism for the oxidative degradation of MEA (Petryaev et al., 1984)

A similar effect of oxygen was observed for the CO₂ loadings of 0.20 and 0.40. The increase in corrosion rate in the presence of oxygen is attributed to the increased concentration of oxidising agents in the aqueous amine solution. As described in *Chapter 5*, the presence of oxygen enhances the rates of the O₂ reduction reaction, which in turn increases the iron corrosion rate at open circuit.
Figure 7-36: Effect of CO₂ loading on charge-time data for iron electrode at -0.60 V (AgCl|Ag) in 30 wt% MEA + H₂O (T= 40 °C, pH 8.03, α = 0.6) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-37: Effect of CO₂ loading on Fe^{II} concentration - time data for iron electrode at -0.60 V in 30 wt% MEA + H₂O (T = 40 °C, pH 8.03, α = 0.6) with a solution velocity of 0.5 mm s⁻¹.
7.7. Effect of MEA concentration

The effect of MEA concentration on the oxidation kinetics of iron and precipitation of FeCO$_3$ was consistent with that of voltammetric behaviour of the Fe RDE (Chapter 5). The chronoamperometric experiments were carried out in 5 – 50 wt% MEA at full CO$_2$ saturation (25 – 80 °C); Figure 7-38 - to Figure 7-55 summarise the results.

The current-time transients (Figure 7-38 and Figure 7-41) for low MEA concentrations (5 – 10 wt%) exhibited current densities that rose initially to a maximum, followed by sharp decreases to current densities values close to zero. At 80 °C, the chronoamperometric data also displayed a sharp peak at 789 s (5 wt%) and 600 s (10 wt%), signifying dissolution of the underlying iron surface which was being covered progressively with a FeCO$_3$ passive layer. The formation of FeCO$_3$ was also evidenced in Fe$^{II}$ concentration-time curves: at low temperatures (25-40 °C), Fe$^{II}$ concentrations increased linearly with time, but at higher temperatures (60-80 °C), Fe$^{II}$ dissolution rates reached a maximum, then started to decline sharply. At high temperatures, this loss of Fe$^{II}$ in the aqueous amine solution could be attributed to the precipitation of FeCO$_3$ on the surface, which acted as a local sink for Fe$^{II}$ and CO$_3^{2-}$ ions.

At higher MEA concentrations (≥ 20 wt%), the chronoamperometric data were similar to those for 30 wt%; the current density decreased with time to a certain value, at which it remained approximately constant, and the dissolved [Fe$^{II}$] concentration in solution increased with time and temperature.

At full CO$_2$ loading and temperatures of 25-80 °C, Fe$^{II}$ concentrations increased from 5 – 40 wt% and then decreased at concentrations >40 wt%. It is also important to note that there was a significantly larger increase in Fe$^{II}$ concentrations between 20 wt% and 30 wt%. This
trend was similar to that from the voltammetric results with the rotating disc electrode; however, the Fe$^{II}$ ion concentration was found to be a maximum at [MEA] of 40 wt% as opposed to 30 wt% with the RDE system.

The charge density-time data had the same form as the Fe$^{II}$ concentration-time plots, in which the total charge increased at lower concentrations (≤40 wt%), then decreased at higher MEA concentrations. However, the charge yield due to dissolution decreased with increasing [MEA]; for example, at 25 °C the charge yield due to dissolution was 31.25% at 5 wt% MEA and 20.8% at 50 wt%.
Figure 7-38: Effect of temperature on current density –time data for iron electrode at -0.60 V (AgCl|Ag) in 5 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-39: Effect of temperature on charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 5 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-40: Temperature effect on Fe²⁺ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 5 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-41: Effect of temperature on current density - time for iron electrode at -0.60 V (AgCl|Ag) in 10 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-42: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 10 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-43: Temperature effect on Fe²⁺ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 10 wt% MEA + H₂O + CO₂ (T = 25 – 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-44: Effect of temperature on current density-time data for iron electrode at -0.6 V (AgCl/Ag) in 20 wt% MEA + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-45: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl/Ag) in 20 wt% MEA + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-46: Temperature effect on Fe⁺⁺ concentration-time data for iron electrode at -0.6 V (AgCl/Ag) in 20 wt% MEA + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-47: Effect of temperature on current density-time data for iron electrode at -0.6 V (AgCl|Ag) in 40 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-48: Effect of temperature on charge density-time data for iron electrode -0.6 V (AgCl|Ag) in 40 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-49: Temperature effect on the Fe²⁺ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 40 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-50: Effect of temperature on current density - time data for iron electrode at -0.6 V (AgCl|Ag) in 50 wt% MEA + H₂O + CO₂ (T = 25-80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-51: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 50 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-52: Temperature effect on Fe^{II} concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 50 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-53: Effect of [MEA] on Fe$^{II}$ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 5-50wt% MEA + H$_2$O + CO$_2$ (pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$.  


Figure 7-54: Effect of [MEA] on current density - time data for iron electrode at -0.6 V (AgCl|Ag) in 5–50 wt% MEA + H₂O + CO₂ (pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-55: Effect of [MEA] on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 5 - 50wt% MEA + H₂O + CO₂ (pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
7.8. **Effect of Metal Type**

Although carbon steel is the most commonly used material for the piping and equipment in CO₂ absorption plants (DuPart and Rooney, 1993), pure iron was used for most experiments for which results are reported in this thesis, to elucidate its electrochemical behaviour in aqueous amine-CO₂ solutions, before introducing the additional complexity of alloying elements. However, most of the published experimental results have been focused on the behaviour of carbon steel 1020 (Carbon Steel S355), so it was included in this work for comparison purposes. Carbon steel 1038 (Carbon Steel EN8) is an additional type of steel that presently is being utilised in amine-based absorption processes (Sun et al., 2011); however, its corrosion behaviour in amine solvents has yet to be reported. Comparisons were also made to stainless steel AISI 304, one of the most commonly utilised stainless steels, used in the most corrosive locations in CO₂ absorption plants.

The constant potential measurements of carbon steel S355 and EN8 in aqueous 30 wt% MEA solutions fully loaded with CO₂ resulted in chronoamperograms similar to that of iron (Figure 7-57 & Figure 7-60). The total anodic charges (Figure 7-58 & Figure 7-61) and Fe²⁺ concentration-time data (Figure 7-59 & Figure 7-62) also increased with temperature. Overall, the corrosion rates in S355 and EN8 were slightly lower than that of pure Fe; for example, at 80 °C, the total dissolved Fe²⁺ concentration at the end of the procedure was 6.364 g m⁻² in iron, 5.865 g m⁻² in S355 and 5.544 g m⁻² for EN8.

Figure 7-63 - Figure 7-65 demonstrate the effect of temperature on stainless steel 304 in 30 wt% MEA at full CO₂ saturation; as expected, Fe²⁺ concentrations were significantly lower than for iron and carbon steel. In contrast to the corrosion behaviour in iron and carbon steel, the total charge and Fe²⁺ dissolution rate decreased with increasing temperature. As predicted by the potential-pH diagram in Figure 7-56 for the Fe-Cr-Ni-H₂O system, the results
suggested that the ca. 18 % Cr in the bulk AISI 304 / UNS S30400 stainless steel (0.07 % C, 0.75 % Si, 2.00 % Mn, 0.045 % P, 0.030 % S, 17.5/19.5 % Cr, 8.0/10.5 % Ni, 0.10 % N) resulted in a passive layer whose composition was dominated by chromium. As a more active metal than iron, the surface concentration is enhanced to > 50 %; the results in Figure 7-63 suggest the passive layer hindered the iron dissolution process, increasingly so with increasing temperature. The concentrations of chromium and manganese in solution were also monitored by the ICP, but were considered insignificant. Hence, stainless steel offers a potential solution to corrosion in alkanolamine-based CO2 capture processes, but at significantly greater capital cost (ca. $2 000 t^{-1}) compared to carbon steels (ca. $200 t^{-1}; LME, 2016).

![Potential-pH diagram for Fe-Cr-Ni-H2O system at 298 K, 0.1 MPa and dissolved activities = 10^{-4}.](image)

**Figure 7-56:** Potential-pH diagram for Fe-Cr-Ni-H2O system at 298 K, 0.1 MPa and dissolved activities = 10^{-4}.
Figure 7-57: Effect of temperature on current density – time data for carbon steel S355 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-58: Effect of temperature on charge density – time data for carbon steel S355 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-59: Temperature effect on the dissolved Fe²⁺ concentration-time data for carbon steel S355 electrode at -0.6 V (AgCl|Ag) in 30wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-60: Effect of temperature on current density – time data for carbon steel EN8 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-61: Effect of temperature on charge density – time data for carbon steel EN8 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-62: Temperature effect on Fe²⁺ concentration-time data for carbon steel EN8 electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-63: Effect of temperature on current density - time data for stainless steel electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-64: Effect of temperature on charge density – time data for stainless steel electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25-80 C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-65: Temperature effect on dissolved Fe⁺⁺ concentration - time data for stainless steel electrode at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-66: Effect of steel composition on the corrosion-time curve obtained on iron electrode at -0.6 V (AgCl|Ag) in contact with 30 wt% MEA + H₂O + CO₂ (pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
7.9. Effect of Amine Type

As discussed in the literature review (Chapter 3), there are several other amines and blends that are being developed currently and considered to replace MEA as the benchmark for the CO$_2$ absorption process. Chronoamperometric measurements were made with the iron electrode at -0.60 V in solutions of 30 wt% methyldiethanolamine (MDEA), 30 wt% 2-amino-2-methyl-1-propanol (AMP) & 30 wt% aminoethylpiperazine (AEP) at full CO$_2$ saturation (25-60 °C). A total amine concentration of 30 wt% and full CO$_2$ saturation provided directly comparable conditions to the previous studies on MEA, from which the influence of amine type could be considered with a negligible influence of operating parameters. The results for the MDEA system are displayed in (Figure 7-67 - Figure 7-69), AEP in (Figure 7-70 - Figure 7-72) and AMP in (Figure 7-73 - Figure 7-75).

The relative dissolution rates of iron in the amine solutions depended on both the amine type and temperature (Figure 7-77). In comparison to the other amines, MEA was the most ‘aggressive’ towards iron at elevated temperatures (60-80 °C), while the highest Fe$^{II}$ concentrations were determined in MDEA at lower temperatures (25-40 °C).

Sterically-hindered amines such as AMP and cyclic amines AEP have gained substantial interest recently due to superior CO$_2$ absorption capacity, as well as low degradation rates. Significantly lower corrosion rates were observed in both AEP and AMP solutions, with AMP solutions yielding the lowest corrosion rates at all temperatures studied.

Whilst the charge density resulting from iron in MEA and AEP solutions were very close in magnitude, the charge yield due to dissolution in AEP was significantly lower than that of MEA. For example, the total charge in MEA solutions was $3.4 \times 10^4 \text{ C m}^{-2}$ with a dissolution yield of 65.3 %, while the total charge in AEP was $3.6 \times 10^4 \text{ C m}^{-2}$ and the yield was 29.8 %,
resulting in lower corrosion rates in in AEP. The lowest charge current densities and dissolution rates were determined in aqueous AEP solutions.

Although AEP has not been featured in any previous corrosion studies based on the CO$_2$ capture process, (Veawab et al., 1999) conducted potentiodynamic tests on carbon steel in MEA, MDEA and AMP. The results by (Veawab et al., 1999) indicated that the highest corrosion rates were in MEA, followed by AMP and then MDEA had the lowest corrosion rate (MEA > AMP > MDEA). Whilst MEA solutions exhibited the highest dissolution rates at higher temperatures (60-80 °C), this was followed by MDEA, then AEP and AMP (MEA > MDEA > AEP > AMP). At lower temperatures (25-40 °C) the corrosion rates in the amine solutions are in the order MDEA > MEA > AEP > AMP.

The decrease in corrosion rates in MDEA at elevated temperatures, in comparison to MEA is consistent with the results of (Veawab et al., 1999), (Tomoe et al., 1996) and (DuPart and Rooney, 1993). It was suggested that MDEA, a tertiary amine, is less corrosive due to its inability to form carbamates (RNHCOO$^-$), which would subsequently undergo hydrolysis to form HCO$_3^-$ (Veawab et al., 1999) also proposed that the influence of the amine type on the dissolution rates was as a result of the total amount of CO$_2$ absorbed. They measured a total CO$_2$ loading of 0.243 mol CO$_2$ (mol MDEA)$^{-1}$, which was significantly lower than the 0.565 mol mol$^{-1}$ loading in MEA solutions under CO$_2$ saturation. However, it is possible to achieve significantly higher CO$_2$ loadings in MDEA solutions. Although tertiary amines have a low reactivity to CO$_2$ due to the inability to form carbamates, there is also preferential formation of HCO$_3^-$ via the direct hydrolysis of CO$_2$. In fact, one of the main advantages associated with the use of tertiary amines is their relatively superior capacity to absorb CO$_2$ up to a loading of 1 mol CO$_2$ (mol tertiary amine)$^{-1}$. Hence, it was expected that the corrosion rate would increase in the MDEA systems as observed at 25 °C and 40 °C.
AMP solutions also have a higher absorption capacity due to the lower stability of the car bamates formed, which readily hydrolyses to form HCO$_3^-$ ions. Thus, the reason for significantly lower corrosion rates observed in AMP systems is unclear, as it was also expected that higher equilibrium concentrations of HCO$_3^-$ ions would result in higher dissolution rates.

Whilst it was evident from the results that the corrosion behaviour of iron in amine solutions can be attributed partly to the CO$_2$ loading capabilities, it was also clear that the amines also have additional and amine-specific interactions with iron.
Figure 7-67: Effect of temperature on current density – time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% MDEA + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-68: Effect of temperature on charge density - time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% MDEA + H₂O + CO₂ (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-69: Temperature effect on Fe²⁺ concentration - time data for iron electrode at -0.6 V (AgCl|Ag) in 30wt% MDEA + H₂O + CO₂ (T = 25°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-70: Effect of temperature on current density-time data of iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AEP + H₂O + CO₂ (T = 25 - 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-71: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AEP + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-72: Temperature effect on Fe²⁺ concentration - time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% AEP + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-73: Effect of temperature on current density – time data for iron electrode at -0.6 V (AgCl|Ag) in 30wt% AMP + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-74: Effect of temperature on the charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in 30wt% AMP + H₂O + CO₂ (T = 25 – 80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Figure 7-75: Temperature effect on Fe²⁺ concentration - time data for iron electrode at -0.6 V (AgCl|Ag) in 30wt% AMP + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-76: Effect of amine type on current density – time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% [Amine] (T = 25-80 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
Figure 7-77: Effect of amine type on Fe$^{II}$ concentration-time data for iron electrode at -0.6 V (AgCl|Ag) in 30 wt% [Amine] ($T = 25 - 80^\circ$C, pH 8.03) with a solution velocity of 0.5 mm s$^{-1}$. 
Figure 7-78: Effect of amine type on charge density-time data for iron electrode at -0.6 V (AgCl|Ag) in contact with 30 wt% [Amine] (T = 25 - 80°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.
7.10. **Longer Term Corrosion Measurements**

The corrosion behaviour of both iron and carbon steel S355 in aqueous 30 wt% MEA solution at full CO₂ saturation (α = 0.60, T = 25°C) was determined at open circuit potential over a 28 day period and Fe²⁺ concentrations were measured using ICP-OES. In order to maintain a constant loading, CO₂ was purged continuously in the amine solution while the pH of the solution was monitored throughout the duration of the experiment. Figure 7-79 shows the open circuit potential (OCP) measured and the resulting corrosion-time curves over the 28 day period are shown in Figure 7-80.

![Graph showing the open circuit potential](image)

Figure 7-79: Time dependence of open circuit potentials of iron and steel electrodes at -0.6 V (AgCl|Ag) in 30 wt% MEA + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

The iron electrode maintained an OCP of -0.76 ± 0.07 V (AgCl|Ag) for the first 22 days, which then increased slowly from a value of -0.75 V to -0.68 V by the end of the experiment. On the other hand, the steel sample displayed an OCP that remained relatively constant at -
0.73 ± 0.03 V for the first 21 days then at day 22 increased in value suddenly to -0.39 V, followed by a slow increase to -0.31 V at the end of the experiment.

Figure 7-80: Time-dependence of iron(II) concentrations dissolved from iron and steel S355 electrodes at -0.6 V (AgCl|Ag) in contact with 30 wt% MEA + H₂O + CO₂ (T = 25 °C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹.

Initially, the measured Fe²⁺ concentration was almost identical for steel and iron samples. However, as time progressed, the dissolution rates on both electrodes diverged, with the rate of dissolution being generally higher for the steel sample than for iron. However, while the rate of iron corrosion appeared to increase with time, that of steel appeared to decrease after 22 days, coinciding with the sudden change in the steel’s OCP and can be attributed to the formation of a protective passive layer. A thick black corrosion product which covered the entire surface of the steel exposed to the amine solution was visible even to the naked eye, whereas the passive layer formed on the iron sample was less visible (Figure 7-82).

Although the characterization of the passive film was not within the scope of this work, according to the potential-pH diagram for Fe-CO₂-H₂O systems, at the initial OCP of -0.73±0.03V, the carbon steel sample as for iron, was predicted thermodynamically to correspond to
active iron dissolution and FeCO$_3$ precipitation. Lastly, it is also important to note that as time progressed, the initially clear solution amine solution with a slight yellow tint became increasingly darkened in colour with time (Figure 7-81). It was unclear if this was due to an accumulation of contaminants resulting from the oxidative and CO$_2$–induced degradation of MEA, or from the accumulation of corrosion products in solution.

Figure 7-81: Images of the flow reactor system for the longer term studies at open circuit potential for a) 7 days b) 14 days c) 28 days
Figure 7-82: Images of the iron and carbon steel S355 electrodes after immersion in 30 wt% MEA + H₂O + CO₂ (T = 25°C, pH 8.03) with a solution velocity of 0.5 mm s⁻¹ at open circuit potential for 28 days.
7.11. References


8. Chapter 8

Conclusions and Future Work

The principal results of the project are summarised in the three objectives:

1. Quantification of the electrochemical kinetics and mechanisms of iron oxidation and hence corrosion rates, in aqueous MEA-CO$_2$-H$_2$O systems, as a function of experimental variables.


3. Description of the dependence of iron(II) dissolution rates on experimental variables, using a specially-designed electrochemical flow reactor with subsequent analysis of dissolved iron(II) concentrations, enabling deconvolution of total oxidation current densities in the small scale electrochemical experiments, into rates of reactions leading to adsorbed and dissolved products.
8.1. **Summary of this project**

As iron is the main component of carbon steel materials used for fabrication of most equipment in amine scrubbing plants, this project aimed to elucidate experimentally, supported by thermodynamic and electrochemical modelling, the electrochemical behaviour of iron in aqueous MEA-CO$_2$-H$_2$O solutions.

8.2. **Rotating Disc Electrode and Electrochemical Quartz Crystal Results**

One of the main objectives of this project was to quantify the electrochemical behaviour of iron in aqueous MEA-CO$_2$-H$_2$O systems and hence its corrosion rates, as functions of experimental variables. Hence, the kinetics of iron oxidation in aqueous MEA solutions were determined by cyclic voltammetry with a RDE and an EQCM as functions of electrochemical parameters. Electrode potential-pH and activity-pH diagrams for Fe-H$_2$O systems and Fe-water–CO$_2$ systems were used to assist with reaction assignments. The results obtained showed that the active to passive transition of iron in MEA was strongly dependent on both the hydrodynamic conditions of the system and on the composition of MEA solutions. In unloaded MEA solutions at pH ca. 12, iron exhibited passive electrochemical behaviour implying a negligible corrosion rate. However, on loading the MEA solution with CO$_2$, protonated amine (RNH$_3^+$) and hydrogen carbonate ions (HCO$_3^-$) are formed, which subsequently dissociate to produce hydrogen ions (H$^+$). This resulted in a decrease in the bulk pH from ca. 12 in unloaded solutions to ca. 8 in fully CO$_2$-saturated solutions, switching the system from a passive to an active state, in which active dissolution was thermodynamically favourable.

Based on the voltammograms of iron in MEA solutions fully loaded with CO$_2$, it was established that the active dissolution and passivation of iron involves a minimum of two stages due to the appearance of at least two anodic current peaks. The first anodic stage occurred in a potential range in which only Fe$^{II}$ oxidation products were predicted thermodynamically.
first anodic stage was also assigned to a surface transformation as the charge and magnitude of
the current peak within this stage was independent of the RDE rotation rate and pH whilst it
increased linearly with potential scan rate and temperature. As a result of these observations,
and in accordance with the thermodynamic predictions, the first stage of oxidation was
assigned to formation of a pre-passive layer of Fe(OH)$_2$ by

$$\text{Fe} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + 2\text{e}^- \quad (8.1)$$

The second oxidation stage also occurred within a potential range at which only Fe$^{II}$ species
are predicted; current densities ($j_{pII}$) increased linearly with rotation rate ($f_{1/2}$), suggesting that
diffusion at the electrode surface limited iron oxidation rates. The results from the EQCM
clearly indicated a mass loss associated with this second stage, so it was attributed to the iron
dissolution as the predominant process, through this passive layer via the reaction:

$$\text{Fe} \leftrightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (8.2)$$

The anodic reaction rates within the active region were also strongly dependent on the solution
temperature, as the charge density within the region of iron dissolution doubled at 80°C in
comparison to 25°C.

The effect of pH was distinguished from that of CO$_2$ by studying the behaviour of iron in CO$_2$-
free solutions of MEA which had been adjusted to the same pH as that of fully CO$_2$ saturated
solutions with the addition of H$_2$SO$_4$. In the absence of CO$_2$, even at the same pH, the
electrochemical behaviour was fundamentally different, resulting in significantly lower current
densities in the potential range associated with the dissolution of Fe to Fe$^{II}_{(aq)}$.

The rate of iron dissolution was controlled primarily by the kinetics of one or several reactions
which result in the evolution of hydrogen. The hydrogen evolution reaction is considered to
the predominant cathodic reaction, the rate of which is limited by the diffusion of H$^+$ ions to
the iron electrode surface from the bulk solution.
However, it has been established that the mechanism by which H\(^+\) ions are supplied to the electrode surface in aqueous CO\(_2\) solutions differs from that in strong acid solutions, in which the diffusion of H\(^+\) ions is the principal rate controlling reaction. In MEA-CO\(_2\)-H\(_2\)O systems, the flux of H\(^+\) ions was increased by the presence of the reaction products, RNH\(_3^+\) and HCO\(_3^-\), resulting in high dissolution current densities in the presence of CO\(_2\) as compared to those in MEA solutions with pHs adjusted by H\(_2\)SO\(_4\). The presence of the protonated amine and hydrogen carbonate ions provides a reservoir of H\(^+\) ions, thereby increasing the corrosion rate by serving as an additional source of H\(^+\) ions via dissociation. Measurements in NaHCO\(_3\) / Na\(_2\)CO\(_3\) solutions at pH ca. 8 showed a linear dependence of \(j_{\text{pH}}\) on HCO\(_3^-\) concentrations, also leading to the conclusion that the kinetics of the iron dissolution is related to a process under HCO\(_3^-\) ion transport control.

In MEA-CO\(_2\)-H\(_2\)O solutions, the Fe dissolution process was inhibited by the formation of a passive film. At the outer layer, precipitation of FeCO\(_3\) is thermodynamically feasible if the concentration of dissolved Fe\(^{\text{II}}\)\(_{\text{(aq)}}\) ions at the iron | solution interface exceeds the solubility limit. The appearance of a third oxidation stage in quiescent solutions accompanied with a relative mass gain within this region implied the precipitation of FeCO\(_3\) via:

\[
Fe^{2+}_{\text{(aq)}} + CO_3^{2-}_{\text{(aq)}} \leftrightarrow FeCO_3_{(s)} \tag{8.4}
\]

or,

\[
Fe^{2+} + HCO_3^- + OH^- \rightarrow FeCO_3 + H_2O \tag{8.5}
\]

The precipitation of FeCO\(_3\) on the iron surface was induced only at high local concentrations of both Fe\(^{\text{II}}\)\(_{\text{(aq)}}\) and CO\(_3^{2-}\) / HCO\(_3^-\) ions. Thus, the disappearance of the third oxidation stage
with rotation of the RDE was attributed to dispersion of Fe$^{II}$\textsubscript{(aq)}, decreasing the local supersaturation and so preventing FeCO$_3$ precipitation.

Based on the potentiodynamic study of iron in aqueous MEA solutions, it was clear that operating parameters such as temperature, CO$_2$ loading amine concentration and oxygen content significantly altered the electrochemical response. The changes in the electrochemical behaviour can be attributed to the impact on the solution chemistry and ionic composition. A Kent-Eisenberg type model was used to estimate the concentrations of the solutions species in the bulk solution as a function of the operating parameters. The electrochemical measurements were analysed using the Tafel extrapolation method; analysis of the resulting kinetic data enabled corrosion rates to be predicted as functions of the experimental variables.

Kinetic analysis of the experimental results showed that temperature and CO$_2$ loading were the most significant parameters affecting corrosion rates of iron / steel in MEA-CO$_2$-H$_2$O. For example, corrosion rates of iron in fully CO$_2$-saturated MEA solutions increased from 6.2 mm a$^{-1}$ at 25$^\circ$C to 17.7 mm a$^{-1}$ at 80$^\circ$C, compared with 0.3 mm a$^{-1}$ in unloaded EA solutions at 25$^\circ$C. Increasing the CO$_2$ loading increased the iron oxidation rate, principally by shifting the solution pH and increasing the rate of the hydrogen evolution reaction. At amine concentrations less than 30 wt%, the corrosion rates increased with increasing MEA concentration, while at concentrations more than 30 wt%, corrosion rates decreased implying a more complex behaviour that had not been observed previously in Fe-MEA-H$_2$O studies in which it had been concluded that corrosion rates increased with amine concentration.

As expected, addition of (dissolved) oxygen increased iron corrosion rates, e.g. from 5.8 mm a$^{-1}$ to 6.2 mm a$^{-1}$ in 30 wt% MEA system at 25$^\circ$C, due to its acting as an additional oxidant.

As expected for a system exhibiting dissolution-precipitation-passivation behaviour, current densities due to iron dissolution increased with increasing mass transport rate coefficients,
which also decreased Fe^{II} concentrations at the iron | solution interface, minimising or even preventing FeCO_3 precipitation.

8.3. Mechanistic Modelling

A mechanistic model was developed for the uniform corrosion of iron in MEA-CO_2-H_2O based on the proposed corrosion mechanisms from the voltammetric results. The model was constructed by taking into account the CO_2 absorption equilibrium reactions and the electrochemical reactions at the iron | solution interface, with the aim to predict concentrations of the solution species and corrosion rates as a function of operating conditions.

Equilibrium concentrations of the amine species (RNH_2, RNH_3^+, RNHCOO^-), carbon(IV) species (HCO_3^-, CO_3^{2-}) and hydrogen ions (H^+) were calculated with the Kent-Eisenberg type model, the results of which were in accordance with the experimental data for the pH and CO_2 loading. The electrochemical reactions incorporated in the model were the anodic dissolution of iron and the cathodic reduction of H^+, direct water reduction and the reduction of oxygen. The corrosion model was developed by simulating polarization curves based on the species concentrations and the transport limited current densities of the iron RDE defined by the Levich equation. Values of exchange current densities and transfer coefficients for iron oxidation and reduction of protons, water and oxygen were obtained from the literature.

The thermodynamic speciation model predictions agreed well with the experimental data based on the solution pH and CO_2 loading and the concentrations of RNH_3^+, HCO_3^- and consequently H^+ were predicted to increase with CO_2 loading and temperature. The electrochemical model predictions were in modest to fairly good agreement with experimental data, with the model generally predicting higher corrosion rates than experimental data. This discrepancy was attributed to the model neglecting the effect of FeCO_3 precipitation, which would have partially passivated the iron surface and impeded the active dissolution process.
In addition to predicting corrosion rates, the mechanistic model was also used to deconvolute the effects of CO$_2$ loading and MEA concentrations on the iron corrosion rates and mechanisms. Contrary to suggestions in literature that the direct reduction of HCO$_3^-$ participates in the corrosion process and acts as the primary oxidant in CO$_2$ loaded amine systems, the direct reduction of HCO$_3^-$ did not have to be considered to account for the higher corrosion rates, which would otherwise have been significantly higher than the experimental results. The model predicted that the primary role of HCO$_3^-$ in the corrosion process was to provide an additional reservoir of H$^+$ ions via dissociation.

The mechanistic model also clarified the decrease in corrosion rates observed at higher MEA concentrations as being due to increased viscosities, thereby decreasing rates of oxidant diffusion, Fe$^{II}$ dissolution and corrosion.

8.4. Electrochemical Flow reactor

The final objective for this project was to investigate the components of the corrosion process and elucidate their kinetics, mechanisms and rate determining steps. Hence, it was important to combine electrochemical techniques with chemical analysis of sample solutions by inductively coupled plasma optical emission spectrophotometry (ICP-OES) to discriminate between total oxidation current densities from those leading to dissolution, rather than adsorbed products such as Fe(OH)$_2$ or FeCO$_3$. Thus, an electrochemical flow reactor was designed and built in-house to enable the measurement of dissolved iron concentrations under typical amine-based CO$_2$ absorption conditions. ICP-OES was used to measure dissolved Fe$^{II}$$_{(aq)}$ concentrations in the amine solutions after constant potential measurements, enabling the charge yield for the dissolution to be determined by relating the amount of charge passed to the amount of dissolved Fe$^{II}$$_{(aq)}$ measured.
The mass transport behaviour of the reactor was characterised as a function of solution flow rate by the transport controlled reduction of hexacyanoferrate(III) ions at a platinised titanium electrode. This enabled predictions of the conditions required for FeCO$_3$ and Fe(OH)$_2$ precipitation, as well as the rate of FeCO$_3$ precipitation from the current fluxes and measured dissolved Fe$^{II}$$_{(aq)}$ concentrations in solution.

Based on measurements conducted to study the effect of the electrode potential, the potential of -0.60 V (AgCl|Ag) was chosen as a suitable potential for the subsequent constant electrode potential measurements within the active region, in which iron dissolution dominated the anodic current measured. In the potential range -0.88 V $\leq$ E $\leq$ -0.52 V, precipitation of protective FeCO$_3$ and Fe(OH)$_2$ was predicted thermodynamically.

In a complementary set of results to those obtained using the RDE, increasing solution flow rates increased corrosion rates, partly by enhanced mass transport of the oxidising species to the surface of the iron and prevention or decreased of FeCO$_3$ supersaturation.

Increasing the temperature and CO$_2$ loading enhanced iron dissolution rates, whilst the rate of formation of FeCO$_3$ was also increased. The supersaturation of FeCO$_3$ was exceeded at lower temperatures ($\leq$ 60$^\circ$C) and high CO$_2$ loading. However, the precipitation rate was significantly lower than the corrosion rate, resulting in the formation of non-adherent FeCO$_3$ films, in agreement with reports from the literature. At 80$^\circ$C and high CO$_2$ loadings, a more adherent film was formed, resulting in a significant decrease in corrosion rates, in accordance with the conditions of formation for a protective FeCO$_3$ film reported in the literature.

As for the voltammetric measurements, corrosion rates increased with MEA concentrations from 5 – 40 wt%, then corrosion rates decreased at concentrations > 40 wt%. At low MEA concentrations, increasing equilibrium concentrations of H$^+$ ions with increasing MEA concentrations, led to increased corrosion rates. However, increased viscosity of the solutions...
at MEA concentrations > 40 wt%, resulted in dissolution rates being limited by the decreased mass transport rates of the oxidising species $H^+$, $H_2O$ and $O_2$ to the iron electrode. It is important to note that concentrations of MEA solutions used in amine scrubbing plants have been limited to ca. 30 wt %, specifically to limit corrosion rates. Hence, this finding that corrosion rates are lowered at higher MEA concentrations due to increasing viscosity may be of significant economic impact to the CO$_2$-capture industry, as higher CO$_2$ absorption capacities are attainable at higher amine concentrations, thereby decreasing sizes and hence costs of absorber-desorber equipment.

The type of amine also affected corrosion rates. Significantly lower corrosion rates were measured in the other commercially-available solvents tested: methyl diethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP) and aminoethylpiperazine (AEP). Iron corrosion rates in the amine solutions fully saturated with CO$_2$ decreased in the order: MEA > MDEA > AEP > AMP at higher temperatures (60-80 °C) and MDEA > MEA > AEP > AMP at lower temperatures (25-40 °C). Thus, sterically hindered amines such as AMP and cyclic amines AEP may provide a suitable alternative to MEA, due to their high CO$_2$ absorption capacity and resistance to degradation. However, all these benefits associated with the use of alternative amines come at a considerably higher cost. Carbon steel exhibited similar dissolution rates to those of iron, whereas those for stainless steel were significantly lower. Hence, stainless steel offers a potential solution to corrosion in the amine scrubbing process, but at significantly higher costs.

### 8.5. Future Work Proposals

Being the most extensively used amine for CO$_2$ capture, MEA acts as the benchmark for the amine scrubbing process, so was the primary focus of most of the studies within this thesis. In more recent years, several other promising solvents such as methyl diethanolamine (MDEA),
2-amino-2-methyl-propanol (AMP) and piperazine (PZ) have been poised possibly to replace MEA as the primary solvent of choice, based on their efficiencies and superior CO₂ adsorption capacities. However, the electrochemical kinetics of iron and steel in these alternative amines has yet to be studied significantly.

Due to the limitations of the electrochemical apparatus, the experimental studies in this thesis were restricted to a maximum of 80°C, whilst the operating temperature of an absorption plant’s stripper is typically 120°C. Based on the results from the higher temperature measurements (60-80°C) in the electrochemical flow reactor, it is possible that the corrosion rates may decreased significantly under amine regenerating conditions, due to the precipitation of FeCO₃. Therefore, it may also be important to investigate the kinetics at higher solution temperatures (80°C-120°C).

Whilst the soluble corrosion products resulting from the corrosion reaction have been quantified within this thesis, efforts must also be devoted to identifying the insoluble corrosion products such as FeCO₃ and Fe(OH)₂ as functions of the operating conditions. In a complementary set of studies to the electrochemical techniques used within this thesis, it is also recommended that analytical techniques such as in-situ (Fourier Transform Infrared) FT-IR spectroscopy be employed to characterize the corrosion products formed on the surface of the electrode during electrochemical oxidation as function of experimental variables. This can be used to define further the favourable conditions under which protective FeCO₃ layers may be formed, which is key to decrasing corrosion rates in CO₂ - containing systems.

Based on the comprehensive results on the kinetics of iron in MEA-CO₂ systems, the effect of MEA concentrations on predicted iron corrosion rates raises questions on the effectiveness of the MEA concentrations in amine scrubbing plants being limited to 30wt%, specifically to limit corrosion issues. However, it is also important to note that concentrated amine solutions are also more prone to degradation. According to some suggestions from the literature, degradation
products and contaminants, particularly heat stable salts, enhance corrosion rates in MEA plants either by decreasing solution pHs or by forming complexes with iron. Ultimately, future research should aim at addressing both the degradation and corrosion processes in amine scrubbing plants, leading to the development of more robust, less prone to degradation and less corrosive amines for the CO₂ absorption process.

The mechanistic corrosion model needs to be developed further into a macro-kinetic model describing the electrochemical flow reactor, in order to predict the time-dependent iron corrosion in amine-CO₂ systems. The model should also be extended to include the use of other amines and to determine the conditions under which FeCO₃ could precipitate.

Finally, based on the information obtained, strategies to mitigate or minimise steel corrosion and amine decomposition should be devised.
9. Chapter 9

Appendices
### I. CO₂ Solubility Data

Table 9-1: Solubility data in a solution of MEA (30 mass %) and water (70 mass %) at T = 25°C from (Jou et al., 1995)

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<th>PCO₂ (kPa)</th>
<th>αCO₂</th>
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<tbody>
<tr>
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<tr>
<td>0.00927</td>
<td>0.323</td>
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<tr>
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<td>0.439</td>
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<td>0.494</td>
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<tr>
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<td>6425</td>
<td>1.109</td>
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</table>

Table 9-2: Solubility data in a solution of MEA (30 mass %) and water (70 mass %) at T = 40°C from (Jou et al., 1995) and (Tong et al., 2012)

<table>
<thead>
<tr>
<th>Reference: Jou et al., 1995</th>
<th>Reference: Tong et al., 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCO₂ (kPa)</td>
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Table 9-3: Solubility data in a solution of MEA (30 mass %) and water (70 mass %) at T = 60°C from (Jou et al., 1995)

<table>
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<tr>
<th>PCO₂ (kPa)</th>
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<td>0.0564</td>
</tr>
<tr>
<td>0.0193</td>
<td>0.119</td>
</tr>
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<td>0.0579</td>
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Table 9-4: Solubility data in a solution of MEA (30 mass %) and water (70 mass %) at T = 80°C from (Jou et al., 1995)

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II. Cyclic Voltammetry Data

Table 9-5: Effects on $j_{PII}$ of rotation rate, temperature (25-80 °C) and aqueous MEA concentration (10-60 wt%) for Fe RDE in MEA + H₂O + CO₂ at pH 8.01; 10 mV s⁻¹.

<table>
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<th>10</th>
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<tr>
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<td></td>
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<td>540</td>
<td>26.24</td>
<td>41.55</td>
<td>33.07</td>
</tr>
<tr>
<td>240</td>
<td>14.11</td>
<td>29.02</td>
<td>20.54</td>
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<table>
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<td>26.76</td>
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<table>
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<td>960</td>
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<td>92.16</td>
</tr>
<tr>
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<td>32.04</td>
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<td>240</td>
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<td>0</td>
<td>12.05</td>
<td>21.64</td>
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<table>
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<th>[MEA] / wt%</th>
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<td>60</td>
<td>16.18</td>
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<tr>
<td>0</td>
<td>33.68</td>
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III. Effect of MEA Concentration

Figure 9-1: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at $f = 1500$ rpm in MEA+ CO$_2$ at pH 8.01 and $T = 25 \, ^\circ C$; 10 mV s$^{-1}$. 

Figure 9-2: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at $f = 1500$ rpm in MEA+ CO$_2$ at pH 8.01 and $T = 25 \, ^\circ C$; 10 mV s$^{-1}$. 

Figure 9-3: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at f = 1500 rpm in MEA+ CO$_2$ at pH=8.01 and T = 40 °C; 10 mV s$^{-1}$

Figure 9-4: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at f = 1500 rpm in MEA+ CO$_2$ at pH=8.01 and T = 40 °C; 10 mV s$^{-1}$
Figure 9-5: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at f = 1500 rpm in MEA+ CO$_2$ at pH~8.01 and T = 60 °C; 10 mV s$^{-1}$.

Figure 9-6: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at f = 1500 rpm in MEA+ CO$_2$ at pH~8.01 and T = 60 °C; 10 mV s$^{-1}$. 
Figure 9-7: Effect of (5-30 wt%) MEA concentration on cyclic voltammograms of iron RDE rotating at $f = 1500$ rpm in MEA+ CO$_2$ at pH $\sim 8.01$ and $T = 80$ °C; 10 mV s$^{-1}$.

Figure 9-8: Effect of (30-60 wt%) MEA concentration on cyclic voltammograms of an iron RDE rotating at $f = 1500$ rpm in MEA+ CO$_2$ at pH $\sim 8.01$ and $T = 80$ °C; 10 mV s$^{-1}$. 
IV. The influence of ionic composition on the electrochemical behaviour of iron in sodium carbonate-hydrogen carbonate solutions at pH 8.01

Figure 9-9: Effect of NaHCO$_3$ + Na$_2$CO$_3$ concentration on cyclic voltammograms of an iron RDE rotating at $f = 1500$ rpm in MEA+ CO$_2$ at pH≈8.01 and $T = 80^\circ C$; 10 mV s$^{-1}$.

Figure 9-10: Effect of NaHCO$_3$ concentration on current density for peak II of stationary Fe electrode in NaHCO$_3$ + Na$_2$CO$_3$ solutions ($T = 25^\circ C$, pH 8.01).
V. Kinetic Data obtained from Polarization curves

Table 9-6: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at \( f = 1500 \) rpm in 10 wt% MEA+ \( \text{CO}_2 \) at pH-8.01; 10 mV s\(^{-1}\)

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Rotation/RPM</th>
<th>( b_0/\text{mV dec}^{-1} )</th>
<th>( b_1/\text{mV dec}^{-1} )</th>
<th>( E_{\text{corr}}/\text{mV} )</th>
<th>( j_{\text{corr}}/\mu\text{A cm}^{-2} )</th>
<th>Corrosion rate/mm y(^{-1})</th>
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<tbody>
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<td>25</td>
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<td>481.38</td>
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<td>240</td>
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<td>348.95</td>
<td>4.087</td>
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<tr>
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<td>159.85</td>
<td>-762.24</td>
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Table 9-7: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at \( f = 1500 \) rpm in 20 wt% MEA+ \( \text{CO}_2 \) at pH-8.01; 10 mV s\(^{-1}\)

<table>
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<th>Temperature/°C</th>
<th>Rotation/RPM</th>
<th>( b_0/\text{mV dec}^{-1} )</th>
<th>( b_1/\text{mV dec}^{-1} )</th>
<th>( E_{\text{corr}}/\text{mV} )</th>
<th>( j_{\text{corr}}/\mu\text{A cm}^{-2} )</th>
<th>Corrosion rate/mm y(^{-1})</th>
</tr>
</thead>
<tbody>
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<td>25</td>
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Table 9-8: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at f = 1500 rpm in 30 wt% MEA + CO₂ at pH = 8.1; 10 mV s⁻¹

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<th>b₁/ mV dec⁻¹</th>
<th>Eₑcorr/ mV</th>
<th>jₑcorr/ µA cm⁻²</th>
<th>Corrosion rate/ mm y⁻¹</th>
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Table 9-9: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at $f = 1500$ rpm in 40 wt% MEA+ CO$_2$ at pH~8.01; 10 mV s$^{-1}$

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<th>$I_{corr}$/ µA cm$^{-2}$</th>
<th>Corrosion rate/mm y$^{-1}$</th>
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Table 9-10: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at $f = 1500$ rpm in 50 wt% MEA + CO$_2$ at pH $\approx 8.01$; 10 mV s$^{-1}$

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<th>$b_{-}$/ mV dec$^{-1}$</th>
<th>$b_{+}$/ mV dec$^{-1}$</th>
<th>$E_{corr}$/ mV</th>
<th>$j_{corr}$/ µA cm$^{-2}$</th>
<th>Corrosion rate/ mm y$^{-1}$</th>
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Table 9-11: Summary of kinetic parameters obtained from the polarization curve of iron RDE rotating at $f = 1500$ rpm in 60 wt% MEA + CO$_2$ at pH $\approx 8.01$; 10 mV s$^{-1}$

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<th>$j_{corr}$/ µA cm$^{-2}$</th>
<th>Corrosion rate/ mm y$^{-1}$</th>
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VI. Thermodynamic Data

Table 9-12: Thermodynamic properties of species in Fe-CO$_2$-H$_2$O systems at 298K (Bard et al., 1985).
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Specific heat capacity values at constant pressure were calculated from the following expression:

$$C_p = A + B \times (10^{-3})T + \frac{C \times (10^5)}{T^2} + D \times (10^{-6})T^2$$

The coefficients of $C_p$ were taken from the HSC software database.
Table 9-13: Specific Heat Capacity Coefficients (HSC Software Database, 2016)

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<th>Species</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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