DEVELOPMENT OF A MECHANISTIC CORROSION MODEL FOR CARBON STEEL IN MEA-BASED CO\textsubscript{2} ABSORPTION PROCESS

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Ameerudeen Najumudeen, candidate for the degree of Master of Applied Science in Industrial Systems Engineering, has presented a thesis titled, *Development of a Mechanistic Corrosion Model for Carbon Steel in MEA-Based CO₂ Absorption Process*, in an oral examination held on July 19, 2012. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

This work developed a mechanistic corrosion model that can be used to predict corrosion rate of carbon steel in the carbon dioxide (CO₂) absorption processes using aqueous solutions of monoethanolamine (MEA). The developed model enhances the capacity of the existing corrosion model developed by Veawab (2000) by incorporating three additional features including the presence of iron carbonate (FeCO₃) on the metal surface and the presence of dissolved oxygen (O₂) and heat-stable salts (HSSs) in the aqueous MEA solutions. The model was developed in Matlab, and comprises three sub-models, i.e. vapour-liquid equilibrium (VLE), species diffusion through a porous film, and electrode kinetics on the metal-solution interface. Two VLE sub-models, i.e. the Kent-Eisenberg (K-E) and the electrolyte non-random two-liquid (e-NRTL), are built into the model. The inputs required for model simulation are three process variables of the CO₂ absorption process, i.e. solution temperature, MEA concentration, and CO₂ loading of the MEA solution. The outputs from the model simulation can be presented as species concentrations in bulk solution and at the metal-solution interface, polarization curves, and corrosion rate. Simulation results show that the model using the e-NRTL sub-model better describes the experimental polarization curves obtained from the literature than the model using the K-E sub-model. The presence of either dissolved O₂ or acetic acid (as HSS) does not affect corrosion of carbon steel, whereas the presence of the FeCO₃ film on the metal-solution interface retards the diffusion of oxidizing agents and, in turn, reduces corrosion rate. Sensitivity analysis for parametric effects on corrosion was also carried out to reveal primary oxidizing agents contributing to corrosion in various operating conditions.
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DEDICATION

I dedicate this thesis to my parents,

Mr. Najumudeen SardarKhan and Mrs. SulaigaBanu Mohamed Yussof

for all their encouragement, support, and understanding throughout my life.
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Figure A.1 Regression of open circuit potential (E) as a function of CO$_2$ loading
NOMENCLATURE

\( a \) Atomic weight (g/mol)

\( c_i \) Concentration of \( i^{th} \) species (kmol/m\(^3\))

CR Corrosion rate

D Density (g/cm\(^3\))

\( D_i \) Diffusion coefficient of the \( i^{th} \) species (m\(^2\)/s)

\( D_{\text{ref}} \) Diffusion coefficient at reference state (m\(^2\)/s)

\( D_{\text{eff}} \) Effective diffusion coefficient (m\(^2\)/s)

DEA Diethanolamine

E Electrode potential (V)

\( E_0 \) Standard electrode potential (V)

\( E_a \) Activation energy (J/mol)

\( E_{\text{corr}} \) Corrosion potential (V)

\( E_{\text{rev}} \) Equilibrium potential (or Reversible potential) (V)

\( f_i \) Correction factor for the \( i^{th} \) key influencing parameter

F Faraday’s constant (C/mol)

\( \Delta G^0 \) Standard change in Gibbs free energy (kJ/mol)

\( \Delta G \) Change in Gibbs free energy at non-standard state (kJ/mol)

\( \Delta H^0 \) Standard change in enthalpy of formation (kJ/mol)

HSS Heat stable salts

\( i_0 \) Equilibrium exchange current density (A/cm\(^2\))

\( i_a \) Anodic current density (A/cm\(^2\))
\(i_c\)  Cathodic current density \((A/cm^2)\)

\(i_{corr}\)  Corrosion current density \((A/cm^2)\)

\(i_{lim}\)  Limiting current density \((A/cm^2)\)

\(k\)  Boltzmann constant \((J/K)\)

\(k_c\)  Chemical reaction rate constant \((1/s)\)

\(K_{sp}\)  Solubility product constant \(((kmol/m^3)^2)\)

MDEA  Methyldiethanolamine

MEA  Monoethanolamine

mmpy  Millimeters per year

mpy  Mils per year

\(n\)  Number of electrons

\(N_i\)  Diffusion flux \((m^2/s)\)

\(pCO_2\)  Partial pressure of \(CO_2\) \((bar)\)

\(Q\)  Amount of charge transferred \((Coulombs)\)

\(R\)  Gas constant \((J/K mol)\)

\(r_b\)  Rate of backward reaction

\(r_f\)  Rate of forward reaction

\(T\)  Temperature \((K)\)

\(t\)  Temperature \((^\circ C)\)

\(t\)  Time \((s)\)

\(w\)  Weight percent of MEA

\(x_i\)  Mole fraction of \(i^{th}\) species

\(z\)  Equivalent weight \((g/mol)\)
Greek Letters:

$\alpha$  Transport constant

$\alpha_{CO_2}$  CO$_2$ loading (mol CO$_2$/mol MEA)

$\beta$  Symmetry factor

$\beta_a$  Anodic Tafel slope (mV/decade of current density)

$\beta_b$  Cathodic Tafel slope (mV/decade of current density)

$\varepsilon$  Porosity

$\kappa$  Permeability

$\eta$  Overpotential (V)

$\mu$  Viscosity (Ns/m$^2$)
1. INTRODUCTION

1.1 CO₂ absorption process

The carbon dioxide (CO₂) absorption process using aqueous solutions of alkanolamine has long been used for gas treating. Acid gases such as CO₂ and hydrogen sulphide (H₂S) are removed from natural gas to enhance its quality and to minimise the operational difficulties that may arise in further processing stages (Kohl and Nielsen, 1997). At present, this process is being adopted in the field of flue gas treatment at major industrial point sources, such as coal-fired power plants, steel manufacturing plants, and cement plants, to reduce emissions of CO₂ into the atmosphere that cause global warming, which, in-turn, causes climate change. The CO₂ removed from the natural gas or flue gas stream can be utilized in the field of Enhanced Oil Recovery (EOR) and in the food and beverage industries.

A simplified process flow diagram of the CO₂ absorption process is shown in Figure 1.1. The feed gas containing CO₂ is introduced to the bottom of the absorber and flows upward towards the top, counter-currently with a CO₂-lean alkanolamine solution (lean solution), which is fed from the top of the absorber. Here, the CO₂ from the feed gas is chemically absorbed into the lean solution. The treated gas containing a lower amount of CO₂ leaves the absorber from the top, while the CO₂-rich alkanolamine solution (rich solution) leaves the absorber from the bottom. At the flash drum, light hydrocarbons are flashed off from the rich solution. This is applied only for natural gas treating and not for flue gas treatment. The rich solution is then heated at the lean-rich heat exchanger and fed to the top of the regenerator.
Figure 1.1: A simplified process diagram of the alkanolamine-based acid gas treating plant (modified from Kohl and Nielsen, 1997)
At the regenerator, the rich solution flows downward and is heated by a stream of hot gaseous mixture that contains water vapour, CO$_2$, and alkanolamine and is produced from the reboiler. As a result, desorption of CO$_2$ takes place, and CO$_2$ is stripped out of the rich solution. The hot gaseous mixture leaves the regenerator top and is sent to the reflux condenser to recover water and alkanolamine. The recovered compounds are collected in the reflux accumulator and ultimately sent back to the regenerator. This is to maintain the concentration of alkanolamine solution in service. After regeneration, the rich solution becomes deprived of CO$_2$ and is called the lean solution. This hot lean solution is pumped to the lean-rich heat exchanger and then to the cooler to reduce its temperature before being re-introduced to the top of the absorber for reuse.

To achieve a removal target of CO$_2$ absorption, use of an efficient CO$_2$ absorption solvent is essential. Common solvents are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), methyldiethanolamine (MDEA) and piperazine (PZ). Each solvent has its inherent advantages and disadvantages. For example, compared to other solvents, MEA has higher reaction rate with CO$_2$ but higher heat of CO$_2$ reaction, which increases the solvent regeneration cost. MDEA has lower heat of reaction with CO$_2$ but the rate of CO$_2$ reaction is lower, which increases capital cost due to a larger size of absorber. Therefore, in recent years, mixtures of these alkanolamines have been used to enhance CO$_2$ absorption capacity and kinetics and reduce heat of reaction with CO$_2$ (Kohl and Nielson, 1997).
1.2 Corrosion in alkanolamine plants

The CO\textsubscript{2} absorption process using aqueous alkanolamine solutions has its inherent problems, such as corrosion, alkanolamine loss, foaming, and plugging of the equipment. Corrosion is the focus of this thesis since it is one of the most severe operational difficulties that directly impacts a plant’s economics. It can cause shutdown of plant operation, heavy economic loss, or even severe safety hazards including fatalities (Kohl and Nielson, 1997; DuPart et al., 1993).

Carbon steel is the major material of construction for the entire plant. Like any other chemical reaction, corrosion accelerates with an increase in temperature, and, thus, a few process areas that operate at high temperatures are prone to severe corrosion. Due to the susceptibility to corrosion, these process areas are usually constructed with corrosion resistant alloys or stainless steel. Two major types of corrosion are reported to be encountered in the alkanolamine-based acid gas plants, namely wet acid gas (or CO\textsubscript{2}) corrosion and alkanolamine solution corrosion (Kohl and Nielson, 1997).

1.2.1 Wet CO\textsubscript{2} corrosion

Wet CO\textsubscript{2} corrosion occurs predominant in the process areas where CO\textsubscript{2} reacts with carbon steel in an aqueous CO\textsubscript{2} environment with little or no alkanolamine (Kohl and Nielson, 1997). As illustrated in Figure 1.1, wet CO\textsubscript{2} corrosion is mainly present at the top area of the regenerator and in the condenser and the reflux accumulator. In the case of natural gas treating plants, wet CO\textsubscript{2} corrosion also occurs at the bottom of the absorber, close to the feed gas inlet, where the feed gas is water-saturated.
The wet CO₂ corrosion of carbon steel occurs when the CO₂ dissolves in water to form carbonic acid (H₂CO₃) (Reaction 1.1), which, in turn, ionizes partially to form a hydrogen ion (H⁺) and bicarbonate ion (HCO₃⁻) (Reaction 1.2) (Nyborg, 2002; Nesic et al. 2002).

\[ CO₂ + H₂O \leftrightarrow H₂CO₃ \]  (1.1)

\[ H₂CO₃ \leftrightarrow H^+ + HCO₃^- \]  (1.2)

The increase in H⁺ plays a major role in the wet CO₂ corrosion of carbon steel where the H⁺ accepts electrons from iron (Fe), thereby oxidizing it to ferrous ions (Fe²⁺) and forming atomic hydrogen (H⁰) (Reaction 1.3).

\[ 2H^+ + Fe \rightarrow Fe^{2+} + 2H^0 \]  (1.3)

The atomic hydrogen usually forms molecular hydrogen (H₂) as per Reaction 1.4. However, it may migrate into the metal lattice and induce hydrogen-induced cracking (Kohl and Nielson, 1997).

\[ 2H^0 \rightarrow H₂ \]  (1.4)

Beyond a pH value of 4, bicarbonate ions are further reduced to carbonate ion (CO₃²⁻), thereby producing more hydrogen ions and increasing the corrosion rate (Reaction 1.5) (Nesic et al., 2001).

\[ HCO₃^- \leftrightarrow H^+ + CO₃^{2-} \]  (1.5)

The rate of corrosion due to this mechanism would increase with the increase in temperature and CO₂ partial pressure (Kohl and Nielson, 1997).
1.2.2 Alkanolamine solution corrosion

Pure alkanolamines and aqueous alkanolamine solutions are not corrosive. However, when alkanolamines contain a certain amount of CO$_2$, they become corrosive (Kohl and Nielson, 1997). This type of corrosion is called alkanolamine solution corrosion. As illustrated in Figure 1.1, alkanolamine solution corrosion occurs predominant in the piping sections of the rich solution from the bottom of the absorber to the regenerator, the rich alkanolamine side of the lean-rich heat exchanger, and the hot, bottom part of the regenerator. A number of factors induce severe alkanolamine solution corrosion, such as high temperature in the regenerator, high CO$_2$ loading at the bottom of the absorber, process contaminants (including heat-stable salts and other degradation products) present in the alkanolamine solution, concentration of alkanolamine solution, and type of alkanolamine used (Kohl and Nielson, 1997).

The mechanism of the alkanolamine solution corrosion differs from the mechanism of wet CO$_2$ corrosion and is not fully understood. According to Reisenfeld and Blohm (1950), the corrosion mechanism involves the release of CO$_2$ from the alkanolamine solution (Reactions 1.6 and 1.7) and its further reaction with water and steel (Reaction 1.8).

\[
RNH_3^+ + HCO_3^- \leftrightarrow RNH_2 + CO_2 + H_2O \quad (1.6)
\]

\[
RNH_3^+ + RNHCOO^- \leftrightarrow 2RNH_2 + CO_2 \quad (1.7)
\]

\[
Fe + CO_2 + H_2O \rightarrow FeCO_3 + 2H^0 \quad (1.8)
\]

where RNH$_3^+$, RNH$_2$, RNHCOO$^-$, and FeCO$_3$ denote protonated alkanolamine ion, alkanolamine, alkanolamine carbamate ion, and iron carbonate, respectively. In 1984,
Kosseim et al. suggested that RNH$_3^+$ could be one of the major oxidizing agents (Reaction 1.9).

\[
Fe + 2RNH_3^+ \rightarrow Fe^{2+} + 2RNH_2 + 2H^0
\]  

(1.9)

In 1993, Dupart et al. suggested carbamate ions could be one of the oxidizing agents because tertiary alkanolamine solutions do not form carbamate ions and are found to be less corrosive than primary alkanolamine solutions. In 2002, Veawab and Aroonwilas developed a mechanistic model to identify major oxidizing agents in the MEA-based CO$_2$ absorption process. They concluded that HCO$_3^-$ and H$_2$O, but not H$_3$O$^+$, are the major oxidizing agents.

1.2.3 Plant experiences

Plant experiences with respect to corrosion problems have been reported in the literature. As summarized in Table 1.1, a variety of solvents, such as MEA, DEA, MDEA, and Sulfinol, have been used to remove CO$_2$ from natural gas. Uniform corrosion was detected in through the entire plants, while localized corrosion, such as pitting and erosion corrosion, were reported at the bottom of the absorber by DuPart et al. (1993) and stress corrosion cracking (SCC) was reported by Sutopo and Safruddin (2000) in both the absorber and regenerator (Table 1.1). Common corrosion mitigation methods include modification of process and equipment design, use of corrosion inhibitors, use of alternative solvents that are less corrosive, use of corrosion resistant materials, and application of chemical passivation onto the process equipment and piping made of steel before plant operation. In most cases, a combination of two or more of these methods is applied.
Table 1.1: Examples of plant experiences on corrosion

<table>
<thead>
<tr>
<th>Reference</th>
<th>Plant</th>
<th>Acid gas</th>
<th>Solvent</th>
<th>Corrosion detected</th>
<th>Corrosion mitigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>DuPart et al.</td>
<td>Acid gas treating plant</td>
<td>45% CO₂ and 20 ppm H₂S</td>
<td>Formulated MDEA</td>
<td>* Pitting and erosion corrosion in high CO₂ loaded alkanolamine at the absorber</td>
<td>* Carbon steel was replaced by 304 stainless steel in areas of CO₂ flashing</td>
</tr>
<tr>
<td>(1993)</td>
<td></td>
<td></td>
<td></td>
<td>* Pitting was caused by CO₂ flashing.</td>
<td>* Reduced flow disruptions by change in design and limiting flow velocity in carbon steel pipeline to 5 ft/s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Erosion was caused by simultaneous abrasion due to high solution velocity.</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>17% CO₂</td>
<td>Formulated MDEA</td>
<td></td>
<td>* Erosion corrosion at the bottom of the absorber due to turbulence of inlet gas and liquid surface</td>
<td>* Farthest holes were welded, and eroded areas were filled with metal impregnated epoxy fillers.</td>
</tr>
<tr>
<td>plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>18% CO₂</td>
<td>25% MEA</td>
<td></td>
<td>* Severe uniform and galvanic corrosion at the bottom of the absorber due to penetration of oxygen through the passive FeCO₃ films</td>
<td>* Design modification of the gas inlet and the lowering of liquid level in the absorber effectively reduced the corrosion problem.</td>
</tr>
<tr>
<td>plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bich et al.</td>
<td>Acid gas treating plant</td>
<td>H₂S and CO₂</td>
<td>MDEA</td>
<td>* Formation of loose scales in rich amine side and subsequent breakdown that resulted in exposure of fresh steel surface to the solution</td>
<td>* Addition of corrosion inhibitor, slip stream filtration, solvent reclaiming, metalizing, and use of stainless steel</td>
</tr>
<tr>
<td>(1996)</td>
<td></td>
<td></td>
<td></td>
<td>* Corrosion rate increased with acid gas loading</td>
<td></td>
</tr>
<tr>
<td>Author(s)</td>
<td>Plant Type (Processing)</td>
<td>Absorbent</td>
<td>Treatments/Issues</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-------------------------</td>
<td>-----------</td>
<td>------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rodriguez and Edwards (1999)</td>
<td>Acid gas treating plant (natural gas processing)</td>
<td>CO₂</td>
<td>DEA - MDEA blend</td>
<td>* Corrosion rate (50 – 60 mpy) in the lean side of the lean-rich heat exchanger</td>
<td></td>
</tr>
<tr>
<td>DeHart et al. (1999)</td>
<td>Acid gas treating plant (CO₂ recovery plant)</td>
<td>3% CO₂</td>
<td>30% MEA</td>
<td>* Uniform and galvanic corrosion found in the bottom of the absorber and in the regenerator</td>
<td></td>
</tr>
<tr>
<td>DeHart et al. (1999)</td>
<td>Acid gas treating plant (CO₂ recovery plant)</td>
<td></td>
<td>Sulfinol</td>
<td>* Heavy FeCO₃ deposition in heat exchanger</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Iron oxide (FeO) and hematite (Fe₂O₃) deposition</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mainly H₂S</td>
<td>DEA</td>
<td>* Iron sulphide (FeS) fouling and reboiler corrosion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Injection of 2 to 4 L/d of oxygen scavenging inhibitors (reduced Fe²⁺ content from 50 to 5 ppm)</td>
</tr>
<tr>
<td>Veldman (2000)</td>
<td>Acid gas treating plant (natural gas processing)</td>
<td>25% CO₂</td>
<td>Sulfinol</td>
<td>* Injection of 0.5 L/d of corrosion inhibitor</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* MEA was replaced with MDEA Type-A and then to MDEA Type-B to avoid SCC and erosion corrosion, respectively.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mainly H₂S</td>
<td>DEA</td>
<td>* Stress Corrosion Cracking (SCC) with MEA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>* Erosion corrosion with MDEA – Type A</td>
</tr>
<tr>
<td>Sutopo and Safruddin (2000)</td>
<td>Acid gas treating plant (natural gas treating)</td>
<td>5.88 to 8% CO₂ and trace of H₂S</td>
<td>MEA and later formulated MDEA</td>
<td>* MEA was replaced with MDEA Type-A and then to MDEA Type-B to avoid SCC and erosion corrosion, respectively.</td>
<td></td>
</tr>
</tbody>
</table>
1.3 Corrosion prediction

Corrosion prediction is essential for the design of process equipment. The knowledge of corrosion prediction for wet CO$_2$ corrosion is more common than for alkanolamine solution corrosion. A number of studies on corrosion prediction modelling for wet CO$_2$ corrosion are available in the literature, whereas only two studies were found on corrosion prediction modelling for alkanolamine solution corrosion.

1.3.1 Corrosion model for wet CO$_2$ corrosion

The corrosion prediction models for wet CO$_2$ corrosion date back to as early as 1975, when de Waard and Milliams developed a semi-empirical CO$_2$ corrosion prediction model that expressed corrosion rate as a function of temperature and CO$_2$ partial pressure, as shown below (de Waard and Milliams, 1975):

$$\log(CR) = 7.96 - \frac{2320}{t+273} - 0.00555t + 0.67\log(pCO_2)$$ \hspace{1cm} (1.10)

where $CR$ is the corrosion rate (mmpy), $t$ is the temperature (°C) and $pCO_2$ is the partial pressure of CO$_2$ (bar). This model was improved by de Waard et al. in 1991, to include the effects of other factors on corrosion rate, such as pH, flow velocity, protective iron carbonate (FeCO$_3$) film formation (or scaling tendency), steel composition, and mass transport which were incorporated into the model using a nomogram. The corrosion rate predicted by the Equation 1.11 is fitted on the nomogram and the corrected corrosion rate is calculated using the nomogram. Following is the improved semi-empirical CO$_2$ corrosion model (de Waard et al. 1991):

$$\log(CR) = 5.8 - \frac{1710}{T} + 0.67\log(pCO_2)$$ \hspace{1cm} (1.11)
where \( CR \) is the corrosion rate (mmpy), \( T \) is the temperature (K) and \( pCO_2 \) is the partial pressure of CO\(_2\) (bar).

Later in 1997, Mishra et al. developed an empirical corrosion prediction equation based on reaction kinetic principles where the corrosion rate is expressed as a function of temperature, pH (concentration of H\(^+\)) and CO\(_2\) partial pressure (Equation 1.12).

\[
CR = C[H^+]^{1.33} pCO_2^{0.67} e^{-Q/kT}
\]  

(1.12)

where \( CR \) is the corrosion rate (mmpy), \( C \) is a constant, \([H^+]\) is the concentration of H\(^+\) (kmol/m\(^3\)), \( pCO_2 \) is the partial pressure of CO\(_2\) in (N/m\(^2\)), \( Q \) is the instantaneous reaction rate constant of CO\(_2\) dissolution in water, \( k \) is the Boltzmann constant (J/K) and \( T \) is the temperature (K).

In 1999, Anderko and Young developed a mechanistic corrosion model composed of thermodynamic and electrochemical components to provide realistic speciation of aqueous system, as well as anodic and cathodic processes at the metal surface. The model was validated against experimental results and used to analyze parametric effects on corrosion rate, such as temperature, CO\(_2\) partial pressure, solution composition, and flow velocity.

In 2001, another mechanistic corrosion model for aqueous CO\(_2\) corrosion was developed by Nesic et al. This model incorporates electrochemical reactions at the metal surface, diffusion of chemical species between bulk and metal surface, diffusion of chemical species across porous FeCO\(_3\) films, electromigration of ions under the influence of the established potential gradients, and the chemical reactions taking place in the bulk solution. This model allows users to specify FeCO\(_3\) film thickness and study its effect on corrosion rate.
Later, in 2003, Nesic and Lee improved the previous model by incorporating the growth of FeCO$_3$ films into the model. The FeCO$_3$ precipitation starts when the solution is supersaturated with Fe$^{2+}$ and CO$_3^{2-}$ ions. It was found from the simulation results that FeCO$_3$ films are formed at high pH, high temperature, high CO$_2$ partial pressure, and high Fe$^{2+}$ concentration.

In 2009, Nesic et al. developed a mechanistic model that uses species transport equations to solve for speciation. This model includes the effects of H$_2$S, O$_2$, and organic acids on corrosion rate. Transport equations were written using Fick’s first and second laws, and electroneutrality was added as a constraint to solve for speciation. The model could predict corrosion rates at various CO$_2$ partial pressures, temperatures, velocities, FeCO$_3$ film thicknesses, and flow velocities.

1.3.2 Corrosion model for alkanolamine solution corrosion

The model for alkanolamine solution corrosion by Veawab and Aroonwilas (2002) was developed specifically for MEA-H$_2$O-CO$_2$ environments. It accounts for thermodynamic equilibrium of chemical species in bulk solution and electrochemical reactions on the metal-solution interface. The electrolyte Non-Random Two Liquid (NRTL) model was employed for estimating the equilibrium concentrations of the chemical species present in the solution. The mixed potential theory was applied to represent kinetics of electrochemical reactions on the metal-solution interface during corrosion processes. HCO$_3^-$ and H$_2$O were identified as the major oxidizing agents, whereas H$_3$O$^+$ was found to play only a minor role in corrosion in this environment.
In 2008, Nouri et al. developed a semi-empirical corrosion prediction model for DEA-H₂O-CO₂ systems. This predictive model was a modification of the de Waard and Milliams model (1975). The corrosion rate obtained from the de Waard and Milliams model was fixed as the base corrosion rate \( CR_{\text{base}} \), and the modified corrosion rate \( CR_{\text{modified}} \) was the product of the base corrosion rate and the individual correction factors (as shown in Equation 1.14) for the effects of all key influencing variables, such as partial pressure of CO₂, partial pressure of H₂S, H₂S/CO₂ ratio, temperature, pH, presence of protective films, free water, water composition, oil wetting, presence of glycol and methanol, addition of corrosion inhibitors, and material type. The base corrosion rate prediction equation is given in Equation 1.11, while the modified corrosion rate equation is expressed in Equation 1.13.

\[
CR_{\text{modified}} = CR_{\text{base}} \prod_{i=1}^{n} f_i
\]

(1.13)

where \( n \) is the total number of key influencing variables and \( f_i \) is the correction factor of the \( i^{th} \) key influencing variable. The correction factors for all key influencing parameters were obtained either from plant data or laboratory experiments.

### 1.4 Research motivation and objectives

Current knowledge of corrosion prediction for alkanolamine solution corrosion is very limited. As discussed in Section 1.3, there are only two works in the literature in attempts were made to predict the corrosion rate of carbon steel in alkanolamine-based acid gas treating plants. The limitations of the work done by Veawab and Aroonwilas (2002) are that the model does not account for three factors that may contribute to corrosion, i.e. the presence of dissolved O₂, FeCO₃ film formation on the metal surface,
and the presence of heat-stable salts, which are the degradation products of the solution. The corrosion predictive model developed by Nouri et al. (2008) was built in the form of a semi-empirical model that was regressed from plant corrosion data and the operating conditions specifically of acid gas treating plants using aqueous solutions of DEA. There are two main limitations of this model. First, the model might not be applicable to flue gas treatment operations, of which the process conditions differ from acid gas treating plants. Second, the model might not be applicable to other solvents, especially MEA, which is considered a benchmark solvent for flue gas treatment.

To extend the knowledge of corrosion prediction for alkanolamine solution corrosion, this work aims at improving the mechanistic corrosion model of Veawab and Aroonwilas (2002) by developing a mechanistic corrosion model of carbon steel for MEA-based CO₂ capture plants for flue gas treatment that incorporates three factors into the model, *i.e.* the presence of dissolved O₂, FeCO₃ film formation on the metal surface, and the presence of heat-stable salts. This work implements a mechanistic-type of model, not a semi-empirical model, for two main reasons: First, the mechanistic model can be extended to other solvents by altering the vapour-liquid equilibrium data without modification of the model structure. Second, the mechanistic model does not require for model regression a significant quantity of corrosion data from plant operations, which are currently not available for flue gas treatment operations. MEA was chosen as the CO₂ absorption solvent for this work because of its promise as a cost-effective solvent for CO₂ capture in flue gas treatment applications.

This thesis is divided into 5 chapters. Chapter 2 provides principles of corrosion and a literature review on available vapour-liquid equilibrium models, corrosion and
diffusion models, and corrosion due to heat-stable salts. Chapter 3 describes the model development and implementation. Chapter 4 presents and discusses the simulation results. Chapter 5 concludes the findings of this work and provides recommendations for future work.
2. FUNADAMENTALS AND LITERATURE REVIEW

2.1 Electrochemical nature of corrosion

A metallic corrosion process is electrochemical in nature and involves transfer of electrons at the metal-solution interface. It consists of anodic and cathodic reactions. An anodic reaction (oxidation) occurs when any chemical species donates an electron ($e^-$) to acquire a more positive charge. A cathodic reaction (reduction) occurs when any chemical species accepts an $e^-$ to acquire a more negative charge (Jones, 1992). Consider corrosion of zinc (Zn) in nitric acid (HNO$_3$) as an example. The overall corrosion reaction (Reaction 2.1), yielding zinc nitrate (Zn(NO$_3$)$_2$) and hydrogen gas (H$_2$), is composed of oxidation (Reaction 2.2) and reduction (Reaction 2.3) reactions.

\[ Zn + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2 \]  \hspace{1cm} (2.1)

\[ Zn \rightarrow Zn^{2+} + 2e^- \]  \hspace{1cm} (2.2)

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (2.3)

2.1.1 Electrode potentials

Electrochemical thermodynamics gives an understanding of energy changes involved in the electrochemical reactions. This energy change directly relates to the driving force for electrode (or corrosion) reactions and dictates reaction spontaneity. Though thermodynamics can predict the feasibility of any corrosion reaction, it cannot predict the rate of the corrosion reaction. Actual corrosion rate is governed by the kinetics of electrochemical reaction.
When a conducting metal is immersed in an electrolyte that has ionic conductivity, two half-cell reactions, one anodic and one cathodic, will occur. Each reaction has its inherent electrode potential called its half-cell electrode potential or electromotive force \((emf)\). The difference in the potential of the two half-cell reactions constitutes the electrochemical potential or the cell potential \((E)\) as given below (Jones, 1992):

\[
E = E_a + E_c
\]  
(2.4)

where \(E_a\) and \(E_c\) represent anodic and cathodic half-cell electrode potentials, respectively. Free energy change accompanying the electrochemical reaction is related to the electrochemical potential of that reaction as expressed by the following relationship (Jones, 1992):

\[
\Delta G = -n F E
\]  
(2.5)

where \(\Delta G\) is the Gibb’s free energy change (kJ/mol), \(n\) is the number of electrons exchanged in the reaction, \(F\) is the Faraday’s constant (96,485 C/mol) and \(E\) is the electrochemical potential (V).

### 2.1.2 Nernst equation

Consider the following reaction where \(A, B, C,\) and \(D\) are the chemical species involved in the reaction, and \(a, b, c,\) and \(d\) are the number of moles of the respective reacting chemical species.

\[
aA + bB \leftrightarrow cC + dD
\]  
(2.6)

The free energy changes at standard \((\Delta G^0)\) and non standard \((\Delta G)\) states are given below.

\[
\Delta G^0 = (c \Delta G^0_C + d \Delta G^0_D) - (a \Delta G^0_A + b \Delta G^0_B)
\]  
(2.7)
\[ \Delta G = (c \Delta G_C + d \Delta G_D) - (a \Delta G_A + b \Delta G_B) \]  

The change of free energy from standard to non-standard state \( (\Delta G - \Delta G^0) \) can be determined by Equation (2.9).

\[ (\Delta G - \Delta G^0) = [c(\Delta G_C - \Delta G^0_C) + d(\Delta G_D - \Delta G^0_D)] - [a(\Delta G_A - \Delta G^0_A) + b(\Delta G_B - \Delta G^0_B)] \]  

(2.9)

Taking the chemical species \( C \) as an example and using its concentration \([C]\), the following relationship can be written:

\[ c(\Delta G_C - \Delta G^0_C) = RT \ln [C]^c \]  

(2.10)

where \( R \) is the universal gas constant (J/mol K) and \( T \) is the absolute temperature (K). By writing the same relation for the other three chemical species, the following expression can be written:

\[ \Delta G - \Delta G^0 = RT \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} \]  

(2.11)

The Nernst equation can be written by substituting Equation (2.5) into (2.11) (Jones, 1992).

\[ E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} \]  

(2.12)

where \( E^0 \) is the standard electrode potential (V). The Nernst equation relates the electrochemical potential to the concentration of the reactants and the products of any electrochemical reaction.

### 2.1.3 Electrochemical kinetics

Electrochemical reactions either donate or accept electrons. Thus, the rate of the electron flow can be termed as the reaction rate. The rate of electron flow is conveniently measured as current \( (I) \) in amperes, where one ampere is equal to one coulomb of charge.
per second. The proportionality between the current and mass of the substance that reacts electrochemically \((m)\) is given by Faraday’s laws (Jones, 1992).

Faraday’s first law:

The mass of a substance altered at an electrode \((m)\) during electrolysis is directly proportional to the quantity of electricity transferred \((Q)\) at that electrode. The quantity of electricity refers to the quantity of electrical charge, typically measured in coulombs.

\[ m \propto Q \]  \hspace{1cm} (2.13)

The above expression can be rewritten in terms of current and time as given below:

\[ m \propto It \]  \hspace{1cm} (2.14)

Faraday’s second law:

For a given quantity of electricity, the mass of an elemental material altered \((m)\) at an electrode is directly proportional to the element's equivalent weight \((z)\), which is the ratio of its atomic weight \((a)\) to its valency \((n)\):

\[ m \propto z \]  \hspace{1cm} (2.15)

After substituting \( z = \frac{a}{n} \) into equation (2.15) and combining equations (2.14) and (2.15), the following expression can be written:

\[ m = \frac{Iia}{nF} \]  \hspace{1cm} (2.16)

where \( F \) is the proportionality constant, called Faraday’s constant \((F = 96485\ C/mol)\).

The expression for corrosion rate can be arrived at by dividing equation (2.16) by time \((i)\) and surface area \((A)\) as given below (Jones, 1992):

\[ CR = \frac{m}{iA} = \frac{ai}{nF} \]  \hspace{1cm} (2.17)
where \( i \) is the current density (A/cm\(^2\)) and is written as current per unit area \( \left( i = \frac{I}{A} \right) \)

Corrosion rate can be calculated as a function of current density. The current density is in the range of \( 10^{-9} \) up to several A/cm\(^2\). The corrosion rate can be conveniently expressed in terms of penetration as shown below (Jones, 1992).

\[
CR = 0.00327 \frac{ai}{nD}
\]

(2.18)

where \( CR \) is the corrosion rate (mmpy) and, \( D \) is the density of the metal (g/cm\(^3\)).

### 2.1.4 Exchange current density

When an electrochemical reaction is said to be in equilibrium, the rate of the forward half-cell reaction \( (r_f) \) is equal to the rate of the backward half-cell reaction \( (r_b) \). Such rate is proportional to the equilibrium exchange current density \( (i_0) \) as expressed below (Jones, 1992):

\[
r_f = r_b = \frac{i_0}{nF}
\]

(2.19)

where \( i_0 \) is defined as (Bockris and Reddy, 1970):

\[
i_0 = Fk_c c_A \exp \left( \frac{-\beta F \eta}{RT} \right)
\]

(2.20)

where \( k_c \) is the reaction rate constant, \( c_A \) is the concentration of the reactant (kmol/m\(^3\)), \( \beta \) is the symmetry factor, and \( \Delta \phi_e \) is the equilibrium potential (V).

It is not possible by any instrument to measure the absolute value of \( i_0 \), since there is no net transfer of electrons. The theoretical calculation of \( i_0 \) is limited by the lack of
knowledge of reaction rate constant, $k_c$. The easiest way to obtain the value of $i_o$ is from the polarization curves.

### 2.1.5 Electrochemical polarization

Equilibrium potential or reversible potential ($E_{rev}$) is the potential exhibited by the electrode in the absence of an external current. Electrochemical polarization is the variation in electrochemical potential ($E$) from the equilibrium potential ($E_{rev}$), and it is conveniently measured in volts (V) or millivolts (mV). Two modes of electrochemical polarization are defined: cathodic polarization and anodic polarization. Cathodic polarization is caused by an addition of electrons resulting in a negative charge buildup at the cathode. Anodic polarization occurs by the removal of electrons resulting in a positive charge buildup at the anode (Bockris and Reddy, 1970 and Jones, 1992).

The electrochemical polarization can be categorized into two types: activation polarization and concentration polarization. The activation polarization occurs when the rate of electron transfer at the metal-solution interface is lower than the rate of chemical species transport from the bulk solution to the interface. This causes the corrosion rate of the metal to depend mainly on the rate of electron transfer at the interface. On the contrary, concentration polarization occurs when the rate of electron transfer at the metal-solution interface is greater than the rate of chemical species transport from the bulk solution to the interface. The corrosion takes place almost instantaneously, and the corrosion rate depends mainly on the rate of chemical species transfer from the bulk solution to the interface. Note that, in some cases, both activation and concentration
polarizations are present at the electrode surface. This type of polarization is called combined polarization (Oldham and Myland, 1993 and Jones, 1992).

2.2 Vapour-liquid equilibrium models

There are three main types of vapour-liquid equilibrium (thermodynamic) models that are available for aqueous alkanolamine-CO$_2$ systems. The first type is a solubility model, which follows a regression-based approach. The equilibrium constants are fitted into the CO$_2$ partial pressure and solubility data. An example of this model is the Kent and Eisenberg model developed in 1976. This model correlated the vapour-liquid equilibrium data for the absorption of CO$_2$ in alkanolamines. The model could predict the equilibrium solubility of CO$_2$ in aqueous alkanolamine solutions, and it was able to predict the solubility data outside the range of existing data with a higher confidence interval. For computational simplicity, the solution was assumed to behave ideally, i.e., the activity coefficients were assumed to be unity (Kent and Eisenberg, 1976; Hessen et al., 2009).

The second type of model is the excess Gibbs energy model. The activity coefficients of all chemical species are calculated as a function of excess Gibbs energy. An example of this model is the Deshmukh-Mather model developed by Deshmukh and Mather in 1981. The model predicted the activity coefficients of all the chemical species except water, which is assumed to behave ideally. More sophisticated models, such as the electrolyte-NRTL model, were developed later. Unlike the Deshmukh-Mather model, the electrolyte-NRTL model assumes water to have non-ideal behaviour, and the binary interaction parameters between all chemical species (including water) are taken into
account to predict the activity coefficients. The model is accurate in predicting speciation, since it calculates the actual activity coefficients of all chemical species in the system (Deshmukh and Mather, 1981; Chen and Evans, 1986; Austgen et al., 1989; Hessen et al., 2009).

The third type of model is an Equation of State (EOS) model. An EOS model is used to represent both liquid and vapour phases of the system. The main advantage of EOS models over the excess Gibbs energy models is that the EOS model can be used to predict the activity coefficients of chemical species at a wide range of temperatures and pressures for both binary and multi-component vapour-liquid equilibrium (Solbraa, 2002; Huttenhuis et al., 2008).

2.3 Corrosion prediction models

There are three types of corrosion prediction models available in the literature. They are empirical, semi-empirical, and mechanistic models. Although aqueous CO₂ environments can cause pitting corrosion, mesa attack, flow-induced corrosion, and uniform corrosion (Fosbol et al., 2009), due to the predominance of uniform corrosion and the complexity of model development for localized corrosion, all corrosion prediction models for aqueous CO₂ environments to date were developed for uniform corrosion. The three types of corrosion prediction models are discussed below.

2.3.1 Empirical model

The empirical corrosion predictive model is the simplest to develop. It is purely data driven and requires a large amount of corrosion data that are either obtained from
actual plant operations or from laboratory experiments. The model can be expressed, with little or no significant difference, as a linear or non-linear mathematical correlation of the corrosion rates and the variables. The drawbacks of this type of model are that they require a large set of data for various operating conditions that affect the corrosion rate, their confidence intervals are low, and they cannot be extended to other systems easily. Even with a slight change in the operating conditions, the corrosion rate prediction can be largely deviant. They extrapolate poorly outside the conditions present in their database (Fosbol et al., 2009). An example of an empirical corrosion model for an aqueous CO₂-H₂S-O₂ environment is the model developed by Lyle and Shutt (1998) as presented below:

\[
CR = 8.6988 + 9.856 \times 10^{-3} [O_2] + 1.48 \times 10^{-7} [O_2]^2 - 1.30865 (pH) \\
+ 0.04934 [CO_2] [H_2S] - 4.8231 \times 10^{-5} [CO_2] [O_2] \\
- 2.372 \times 10^{-3} [H_2S] [O_2] - 1.113 \times 10^{-3} [O_2] (pH)
\]  

(2.21)

where \( CR \) is the corrosion rate (mpy), \([O_2]\) is the concentration of oxygen in gas phase (ppmv), \([H_2S]\) is the concentration of hydrogen sulfide in the gas phase (psi), and \([CO_2]\) is the concentration of carbon dioxide in gas phase (psi).

### 2.3.2 Semi-empirical model

The semi-empirical model is the mathematical correlation that consists of two components: an empirical correlation for base corrosion rate and correction factor(s). The empirical correlation is regressed from the corrosion data from either plant operations or experiments. The correction factor represents physical or chemical phenomena involved in corrosion processes, such as FeCO₃ film formation, flow velocity, pH, and/or the
presence of inhibitors. An example of the semi-empirical corrosion model is the model developed by Nouri et al. (2008) as previously given in Equation 1.14.

The main drawback of the empirical model is that it relies on a large set of corrosion data. The semi-empirical model, however, can be used to predict the corrosion rate outside the variable ranges used during model development with higher confidence than the empirical model. This is because its correction factors are represented by parameters from physical chemistry. This type of model is preferred by industry since it is less time consuming and simpler to develop than the purely theory-driven mechanistic models. In addition, it can extrapolate better than the empirical models (Fosbol et al., 2009; de Waard and Milliams, 1975; de Waard et al., 1991).

2.3.3 Mechanistic model

Mechanistic corrosion models differ from the empirical and semi-empirical models in that they are built on theory of corrosion processes and do not require any corrosion data for model development. These models have good extrapolation capacity and can be modified to simulate other systems. However, they do require an understanding of fundamental science relating to kinetics, thermodynamics, heat transfer, mass transfer, and many different fields of engineering and science. This type of model is usually developed at educational institutions (Fosbol et al., 2009; Nesic et al., 2001).
2.4 Diffusion model

2.4.1 Solubility product constant

Precipitation is one of the phase transitions and is considered to be heterogeneous equilibrium. Consider an example of calcium carbonate precipitation due to the reaction between aqueous calcium ($Ca^{2+}$) and carbonate ions ($CO_3^{2-}$):

$$Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightleftharpoons K_w CaCO_3_{(s)}$$  \hspace{1cm} (2.22)

The equilibrium constant for this heterogeneous equilibrium is called the solubility product constant ($K_{sp}$), which is expressed as (Brady and Holum, 1988):

$$K_{sp} = c_{Ca^{2+}} \cdot c_{CO_3^{2-}}$$  \hspace{1cm} (2.23)

where $c_{Ca^{2+}}$ is the concentration of $Ca^{2+}$ ions (kmol/m$^3$) and $c_{CO_3^{2-}}$ is the concentration of $CO_3^{2-}$ ions (kmol/m$^3$).

The precipitation of any insoluble salt depends on the value of $K_{sp}$. That is, when $K_{sp}$ is less than 1, the solution is unsaturated and precipitation will not occur. When $K_{sp}$ is equal to 1, the solution is saturated and precipitation will start to occur. When the concentration of any reactant chemical species increases slightly or when $K_{sp}$ is greater than 1, the solution is supersaturated and precipitation will occur at the suitable nucleation sites.

The principle of $K_{sp}$ was used by Nordsveen et al. (2003) to determine if iron carbonate ($FeCO_3$) precipitation occurs in an aqueous $CO_2$ system. The reaction for iron carbonate precipitation is given below:

$$Fe^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightleftharpoons K_w FeCO_3_{(s)}$$  \hspace{1cm} (2.24)
FeCO₃ gets precipitated only when the solution is supersaturated, or, in other words, FeCO₃ precipitation occurs only when the product of local concentrations of Fe²⁺ and CO₃²⁻ ions is greater than the value of \( K_{sp} \left( \left( c_{Fe^{2+}} \times c_{CO_3^{2-}} \right) > K_{sp} \right) \) (Nordsveen et al., 2003).

The solubility product constant was expressed as a function of ionic strength and temperature as given below (Sun et al, 2009):

\[
\log K_{sp} = -59.3498 - 0.041377T - \frac{2.1963}{T} + 24.5724\log(T) + 2.518I^{0.5} - 0.657I \tag{2.25}
\]

where \( T \) is the temperature (K) and \( I \) is the ionic strength (kmol/m³). The ionic strength is defined as:

\[
I = \frac{1}{2} \sum c_i z_i^2 \tag{2.26}
\]

where \( c_i \) is the concentration of the \( i^{th} \) chemical species (kmol/m³) and \( z_i \) is the charge on the \( i^{th} \) chemical species.

For an appreciable amount of precipitation to occur, the solution should be in a supersaturated state. Supersaturation (S) is defined as a ratio of the product of molar concentration of reacting chemical species to the solubility product constant that was estimated using Equation (2.26) (Nordsveen et al., 2003):

\[
S = \frac{c_{Fe^{2+}} c_{CO_3^{2-}}}{K_{sp}} \tag{2.27}
\]

Rate of iron carbonate film growth (\( R_{gr,FeCO_3} \)) was expressed as a function of supersaturation and solubility product constant by two different researchers as given below:
Expression given by Johnson and Tomson (1991):

\[
R_{\text{FeCO}_3} = Ae^{54.8 \frac{123}{RT}} K_{sp} (S^{1/2} - 1)^2
\]  

(2.28)

Expression given by van Hunnik et al (1996):

\[
R_{\text{FeCO}_3} = Ae^{52.4 \frac{119.8}{RT}} K_{sp} (S - 1)(1 - S^{-1})
\]  

(2.29)

where \( A \) is the surface area of pores per unit volume (\( m^2/m^3 \)), \( R \) is the universal gas constant (\( J/mol \ K \)), and \( T \) is the temperature (\( K \)).

2.4.2 Transport process

The precipitation of FeCO\(_3\) film occurs when the solution is supersaturated and the nucleation site is available on the steel surface for the growth of FeCO\(_3\) film. This film is neither very intact nor very loose. The tenacity of the film depends on the film forming conditions such as temperature, pH, and local concentration of reacting chemical species. The film is partially passive in nature, which helps in minimizing corrosion by making some areas of the steel surface unavailable for corrosion (Nesic et al., 2002). Thus, the formed FeCO\(_3\) film aids in the reduction of corrosion since the oxidizing agents have to diffuse across the porous film to reach the metal surface in order to get reduced electrochemically (Nesic et al., 2001 and Nesic et al., 2002). This process has been modeled by a few researchers and will be briefly explained in this section.

Modeling of metal corrosion covered with a layer of porous film involves transport equations for all the chemical species and then solving them simultaneously with the electroneutrality equation (Nesic et al., 2001 and Nesic et al., 2003). The
transport equation consists of three components: accumulation \( \frac{\partial (\epsilon c_i)}{\partial t} \), net flux \( \frac{\partial (\kappa c_i)}{\partial x} \), and chemical reaction term \( \epsilon R_i \) and is written in the form given below:

\[
\frac{\partial (\epsilon c_i)}{\partial t} = -\frac{\partial (\kappa c_i)}{\partial x} + \epsilon R_i \tag{2.30}
\]

where \( \epsilon \) is the porosity of the film, \( c_i \) is the concentration of the \( i^{th} \) chemical species (kmol/m\(^3\)), \( \kappa \) is the surface permeability of the film, \( x \) is the spatial coordinate, and \( R_i \) is the net rate of the chemical reaction. When the system is in equilibrium, there is no net rate of formation or depletion of chemical species, so the chemical reaction term \( (\epsilon R_i) \) of equation (2.31) will be equal to ‘0’. The net flux term in equation (2.31) has two components: the effective diffusion component \( \left( (D_i + D_t) \frac{\partial c_i}{\partial x} \right) \) and electromigration component \( \left( z_i u_i F c_i \frac{\partial \Phi}{\partial x} \right) \) as given below (Nesic et al., 2002):

\[
\frac{\partial (\kappa c_i)}{\partial x} = N_i = -(D_i + D_t) \frac{\partial c_i}{\partial x} - z_i u_i F c_i \frac{\partial \Phi}{\partial x} \tag{2.31}
\]

where \( N_i, D_i, D_t, z_i, u_i, F, \) and \( \Phi \) are the net flux (mol/m\(^2\)s), molecular diffusion coefficient (m\(^2\)/s), turbulent diffusion coefficient (m\(^2\)/s), electrical charge of the \( i^{th} \) chemical species, mobility of the \( i^{th} \) chemical species, Faraday’s constant, and electric potential (V), respectively.

The values of a few parameters, such as \( D_i \) and \( z_i \), can be found in the literature, but for other parameters, like \( D_t \) and \( u_i \), correlations are available (Nesic et al, 2001; Nesic et al., 2002). For computational simplicity, the electromigration term
in equation (2.32) is often replaced with a simple electroneutrality equation by assuming that regardless of how small the volume of the electrolyte may be, it is always electrically neutral, and, hence, there is no significant separation of charges leading to electromigration (Nesic et al., 2001).

Electroneutrality equation:

\[ \Sigma_i z_i c_i = 0 \]  

(2.32)

So for \( n \) number of chemical species, there would be \( n \) number of species transport equations and one electroneutrality equation, which would act as a constraint. These sets of equations would be solved simultaneously to obtain the surface concentrations of all the chemical species.

2.5 Corrosion in presence of Heat Stable Salts (HSSs)

The process contaminants also influence the corrosion rate in alkanolamine plants. The process contaminants can be classified into two types. The first type of contaminants enters the process stream along with the feed gas or through make-up solution or through make-up water. The second type of contaminants is formed as a result of thermal or chemical degradation of the alkanolamines or other chemical species in the solution. Heat stable salts (HSSs) are irreversibly formed degradation products (Srinivasan, 2006). Examples of HSSs are acetate, oxalate, malonate, and formate. Most of them are organic acids that increase the corrosion rate either by undergoing direct reduction at the metal surface or by dissociating to produce a proton that, in turn, is reduced at the metal surface (George et al., 2004). Srinivasan (2006) stated that the
presence of HSSs increases the solution viscosity, reduces the absorption capacity of the alkanolamine solution, and increases the conductivity of the solution, and that, in turn, increases the rate of corrosion.

The presence of acetic acid (HAc) in CO₂ corrosion of carbon steel has been studied by George et al. (2004). They proposed two different mechanisms through which the acetic acid might increase the corrosion rate. The first scenario occurs when acetic acid dissociates and acts only as a source of protons, which, in turn, get reduced on the steel surface. The second scenario occurs when acetic acid gets reduced directly on the metal surface. The results obtained by George et al. (2004) support the former scenario.

George et al. (2004) also considered the reduction of protons to be a concentration polarization type of reaction under the limiting current conditions. The limiting current is calculated from the equation given below:

\[ i_{\text{lim(HAc)}} = k_m F [HAc]_b \]

The overall current density of the proton reduction is given as:

\[ \frac{1}{i_{(H^+)}} = \frac{1}{i_{a(H^+)}} + \frac{1}{i_{\text{lim(H^+)}} + i_{\text{lim(HAc)}}} \]

Thus, the authors arrived at the current density of protons in the presence of acetic acid. They solved the model by using the electroneutrality principle to predict the corrosion rate. The simulation results were compared with the experimental results and were found to be in good agreement.
3. MODEL DEVELOPMENT

3.1 Scheme of the corrosion process

Figure 3.1 depicts the overall corrosion process that was modeled in this work. The corrosion process constitutes a number of activities taking place in three layers connected in series: bulk solution, porous film or corrosion product (iron carbonate, FeCO₃) and interface between metal and corrosion film. In the bulk solution, twelve chemical species exist as a result of carbon dioxide (CO₂) absorption into the aqueous solution of alkanolamine, which, in this case is monoethanolamine (MEA or RNH₂). These chemical species are MEA, protonated amine (MEA H⁺ or RNH₃⁺), amine carbamate (MEACOO⁻ or RNHCOO⁻), undissociated water (H₂O), dissolved CO₂, bicarbonate ion (HCO₃⁻), carbonate ion (CO₃²⁻), hydronium ion (H₃O⁺), hydroxyl ion (OH⁻), and heat-stable salts (which, in this case, are acetic acid (CH₃COOH)), oxygen (O₂), and ferrous ion (Fe²⁺). Due to their concentration gradients, the chemical species diffuse between the bulk solution and the metal-FeCO₃ interface through the porous FeCO₃ layer. At the interface, electrochemical corrosion reactions take place. Oxidizing agents, which, in this case, are assumed to be H₂O, HCO₃⁻, H₃O⁺, and O₂, undergo reduction reactions by oxidizing iron (Fe) and accepting electrons, while the metal undergoes oxidation reactions, producing ferrous ion (Fe²⁺). Fe²⁺, in turn, travels through the porous FeCO₃ layer to the bulk solution.
Figure 3.1: Schematic representation of corrosion of metal in MEA-CO$_2$-H$_2$O system
3.2 Model framework

The model framework comprises three main model components: input, calculation models, and output, as illustrated in Figure 3.2. The input requires information of typical operating conditions of the MEA-based CO₂ absorption process, including process (solution) temperature, MEA concentration, and CO₂ loading in the MEA solution. The calculation model consists of three sub-models: Vapour-Liquid Equilibrium (VLE) sub-model, diffusion of chemical species through porous FeCO₃ layer sub-model, and electrochemical corrosion sub-model. The VLE sub-model is used for determining speciation or concentrations of all chemical species existing in the bulk solution. Two VLE sub-models are available in the model framework, a Kent-Eisenberg (K-E) based-model and an Electrolyte Non-Random Two Liquid (e-NRTL)-based model. The K-E model assumes ideal liquid, meaning the activity coefficients of all chemical species are unity, whereas the NRTL model considers interactions among chemical species in the bulk solution, which causes the departure from the unity activity coefficients. Both VLE sub-models incorporate the VLE data from literature and the principle of mass balances for carbon atoms and for MEA, as well as the principle of electroneutrality of charged species. The bulk concentrations of chemical species obtained from the VLE sub-model are subsequently used in the diffusion sub-model. The diffusion sub-model is built on the modified Fick’s law of diffusion to map the concentration gradients of chemical species across the porous FeCO₃ layer and to determine the concentrations of available oxidizing agents on the metal-surface interface, which are further used in the electrochemical corrosion sub-model. The electrochemical
Figure 3.2: Framework of the mechanistic corrosion model

**Inputs**
- Solution temperature
- MEA concentration
- CO$_2$ loading in solution

**Calculation model**

**Vapor-Liquid Equilibrium (VLE) sub model**
- Speciation in bulk solution
- Based on K-E model or e-NRTL model
- Mass balance for Carbon and MEA
- Electroneutrality of charged species

**Diffusion sub model**
- Concentration gradient of chemical species across FeCO$_3$ films
- Concentration of oxidizing agents at the metal-solution interface
- Modified Fick’s laws

**Electrochemical sub model**
- Kinetics of oxidation of metal and reduction of oxidizing agents
- Mixed potential theory
- Nernst equation

**Output**
- Speciation in the bulk solution and at the metal-surface interface
- Polarization curves
- Corrosion rate
corrosion sub-model accounts for the electrochemical reactions (oxidation of metal and reduction of oxidizing agents) on the metal surface, which is represented by the mixed potential theory. The electrode kinetic parameters such as $i_0$ and $E_{rev}$ for all the electrochemical reactions were regressed from data in the literature using the Nernst equation. The output simulation results can be presented as species concentrations in the bulk solution and at the metal-solution interface, polarization curves, and corrosion rate.

3.3 Vapour-liquid equilibrium (VLE) model

3.3.1 Chemical reactions in bulk solution

Once CO$_2$ from the gas stream is absorbed into an aqueous solution of MEA, the following are the reactions that take place in the bulk MEA solution (Austgen et al., 1989):

*Dissociation of protonated MEA:*

$$\text{MEA}H^+ + H_2O \rightleftharpoons K_1 \rightarrow H_3O^+ + \text{MEA}$$  \hspace{1cm} (3.1)

*Reversion of MEA Carbamate:*

$$\text{MEA}COO^- + H_2O \rightleftharpoons K_2 \rightarrow \text{MEA} + HCO_3^- \hspace{1cm} (3.2)$$

*Hydrolysis of CO$_2$:*

$$\text{CO}_2 + 2H_2O \rightleftharpoons K_3 \rightarrow HCO_3^- + H_3O^+ \hspace{1cm} (3.3)$$

*Dissociation of water:*

$$2H_2O \rightleftharpoons K_4 \rightarrow H_3O^+ + OH^- \hspace{1cm} (3.4)$$

*Dissociation of bicarbonate ion:*

$$HCO_3^- + H_2O \rightleftharpoons K_5 \rightarrow CO_3^{2-} + H_3O^+ \hspace{1cm} (3.5)$$
where $K_i$ is the equilibrium constant of reversible reaction at equilibrium. The $K_i$ of the above reactions can be expressed in terms of activity coefficient ($\gamma_i$) and mole fraction of chemical species ($x_i$) as given below:

\[
K_1 = \frac{\left( \gamma_{\text{MEA}} x_{\text{MEA}} \right) \left( \gamma_{H,O^+,H,O} x_{H,O^+} \right)}{\left( \gamma_{\text{MEAH}^+,\text{MEA}^-} \right) \left( \gamma_{H,O^+,H,O} \right)}
\] (3.6)

\[
K_2 = \frac{\left( \gamma_{\text{MEA}} x_{\text{MEA}} \right) \left( \gamma_{\text{HCO}_3^-} x_{\text{HCO}_3^-} \right)}{\left( \gamma_{\text{MEACOO}^-,\text{MEACOO}^-} \right) \left( \gamma_{H,O^+,H,O} \right)}
\] (3.7)

\[
K_3 = \frac{\left( \gamma_{H,O^+,H,O} x_{H,O^+} \right) \left( \gamma_{\text{HCO}_3^-} x_{\text{HCO}_3^-} \right)}{\left( \gamma_{\text{CO}_2^-} x_{\text{CO}_2^-} \right) \left( \gamma_{H,O^+,H,O} \right)^2}
\] (3.8)

\[
K_4 = \frac{\left( \gamma_{H,O^+,H,O} x_{H,O^+} \right) \left( \gamma_{\text{OH}^-} x_{\text{OH}^-} \right)}{\left( \gamma_{H,O^+,H,O} \right)^2}
\] (3.9)

\[
K_5 = \frac{\left( \gamma_{H,O^+,H,O} x_{H,O^+} \right) \left( \gamma_{\text{CO}_3^-} x_{\text{CO}_3^-} \right)}{\left( \gamma_{\text{HCO}_3^-} x_{\text{HCO}_3^-} \right) \left( \gamma_{H,O^+,H,O} \right)}
\] (3.10)

As per the above five chemical reactions, there are 9 chemical species present in the bulk solution of which 8 are independent species and 1 (H$_2$O) is a dependant species.

To quantify bulk concentrations of all chemical species, three additional equations, as listed below, are required:

**Electroneutrality / Charge Balance:**

\[
\left( \gamma_{\text{MEACOO}^-,\text{MEACOO}^-} \right) + \left( \gamma_{\text{HCO}_3^-} x_{\text{HCO}_3^-} \right) + \left( \gamma_{\text{OH}^-} x_{\text{OH}^-} \right) + 2 \left( \gamma_{\text{CO}_3^-} x_{\text{CO}_3^-} \right) - \left( \gamma_{\text{MEAH}^+,\text{MEA}^-} \right) - \left( \gamma_{H,O^+,H,O} x_{H,O^+} \right) = 0
\] (3.11)
Mass balance for MEA:

\[
\left(\gamma_{\text{MEA}} x_{\text{MEA}}\right)_{\text{Total}} - \left(\gamma_{\text{MEA}} x_{\text{MEA}}\right) - \left(\gamma_{\text{MEAH}^+} x_{\text{MEAH}^+}\right) - \left(\gamma_{\text{MEACOOO}} x_{\text{MEACOOO}}\right) = 0 \quad (3.12)
\]

Mass balance for carbon atoms:

\[
\alpha_{\text{CO}_2} \left(\gamma_{\text{MEA}} x_{\text{MEA}}\right)_{\text{Total}} - \left(\gamma_{\text{MEACOOO}} x_{\text{MEACOOO}}\right) - \left(\gamma_{\text{HCO}_3^-} x_{\text{HCO}_3^-}\right) - \left(\gamma_{\text{CO}_2} x_{\text{CO}_2}\right) = 0 \quad (3.13)
\]

where \(\alpha_{\text{CO}_2}\) is the \(\text{CO}_2\) loading in bulk solution.

### 3.3.2 Kent-Eisenberg (K-E) model

In the Kent-Eisenberg (K-E) model, the MEA solution is assumed to behave ideally such that activity coefficients \((\gamma_i)\) of all chemical species present in the solution are unity. The temperature dependence of the equilibrium constants \((K_i)\) is given by the following expression (Austgen et al., 1989):

\[
\ln K_i = C_{1,i} + C_{2,i} \left(\frac{1}{T}\right) + C_{3,i} \ln T + C_{4,i} T
\]

(3.14)

where \(C_{1,i}, C_{2,i}, C_{3,i}, \text{ and } C_{4,i}\) are given in Table 3.1.

Note that the values of \(K_i\) reported by Austgen et al. (1989) were used instead of those in the work of Kent and Eisenberg (1976) because the developed corrosion model was built based on chemical reactions using \(\text{H}_3\text{O}^+\) (similar to the work of Austgen et al.) not \(\text{H}^+\), which was used in the K-E model (1976).
Table 3.1: Temperature dependence of equilibrium constants for chemical reactions in e-NRTL model (Austgen et al., 1989)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation of protonated MEA</td>
<td>$K_1$</td>
<td>2.1211</td>
<td>-8189.38</td>
<td>0.0</td>
<td>-0.007484</td>
</tr>
<tr>
<td>Reversion of MEA Carbamate</td>
<td>$K_2$</td>
<td>2.8898</td>
<td>-3635.09</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Hydrolysis of CO$_2$</td>
<td>$K_3$</td>
<td>231.465</td>
<td>-12092.10</td>
<td>-36.7816</td>
<td>0.0</td>
</tr>
<tr>
<td>Dissociation of water</td>
<td>$K_4$</td>
<td>132.899</td>
<td>-13445.90</td>
<td>-22.4773</td>
<td>0.0</td>
</tr>
<tr>
<td>Dissociation of bicarbonate ion</td>
<td>$K_5$</td>
<td>216.049</td>
<td>-12431.70</td>
<td>-35.4819</td>
<td>0.0</td>
</tr>
</tbody>
</table>
3.3.3 Electrolyte Non-Random Two-Liquid (e-NRTL) model

The Electrolyte Non-Random Two-Liquid (e-NRTL) model was developed by Austgen et al. in 1989 to represent the vapour-liquid equilibria in acid gas-alkanolamine-water systems. The activity coefficients of chemical species in the bulk solution are not unity and can be calculated by accounting for both long-range ion-ion interaction and local interactions between all true liquid-phase species. Details of the determination of activity coefficients can be found in Veawab (2000). All speciation results from the e-NRTL model were obtained from Veawab (2000).

3.3.4 Mathematical solving for speciation

Equations obtained from equilibrium constants:

\[ F(1) = 1 - \frac{\left(\gamma_{\text{MEA}}x_{\text{MEA}}\right)\left(\gamma_{\text{H}_2\text{O},\text{H}^+}x_{\text{H}_2\text{O}}\right)}{K_1\left(\gamma_{\text{MEAH}^+}x_{\text{MEAH}^+}\right)\left(\gamma_{\text{H}_2\text{O}}x_{\text{H}_2\text{O}}\right)} \]  
(3.15)

\[ F(2) = 1 - \frac{\left(\gamma_{\text{MEA}}x_{\text{MEA}}\right)\left(\gamma_{\text{HCO}_3^-,\text{HCO}_3^-}x_{\text{HCO}_3^-}\right)}{K_2\left(\gamma_{\text{MEACOO}^-,\text{MEACOO}^-}x_{\text{MEACOO}^-}\right)\left(\gamma_{\text{H}_2\text{O}}x_{\text{H}_2\text{O}}\right)} \]  
(3.16)

\[ F(3) = 1 - \frac{\left(\gamma_{\text{H}_2\text{O},\text{H}^+}x_{\text{H}_2\text{O}}\right)\left(\gamma_{\text{HCO}_3^-,\text{HCO}_3^-}x_{\text{HCO}_3^-}\right)}{K_3\left(\gamma_{\text{CO}_2^-\text{CO}_2^-}x_{\text{CO}_2^-}\right)\left(\gamma_{\text{H}_2\text{O}}x_{\text{H}_2\text{O}}\right)^2} \]  
(3.17)

\[ F(4) = 1 - \frac{\left(\gamma_{\text{H}_2\text{O},\text{OH}^-}x_{\text{H}_2\text{O}}\right)\left(\gamma_{\text{OH}^-}\text{H}^-\text{OH}^-\right)}{K_4\left(\gamma_{\text{H}_2\text{O}}x_{\text{H}_2\text{O}}\right)^2} \]  
(3.18)

\[ F(5) = 1 - \frac{\left(\gamma_{\text{H}_2\text{O},\text{H}^+}x_{\text{H}_2\text{O}}\right)\left(\gamma_{\text{CO}_2^-\text{CO}_2^-}x_{\text{CO}_2^-}\right)}{K_5\left(\gamma_{\text{HCO}_3^-,\text{HCO}_3^-}x_{\text{HCO}_3^-}\right)\left(\gamma_{\text{H}_2\text{O}}x_{\text{H}_2\text{O}}\right)} \]  
(3.19)
Electroneutrality / Charge Balance:

\[
F(6) = \left( \gamma_{MEACOO} x_{MEACOO} \right) + \left( \gamma_{HCO_3} x_{HCO_3} \right) + \left( \gamma_{OH} x_{OH} \right) + 2 \left( \gamma_{CO_3^2} x_{CO_3^2} \right) - \left( \gamma_{MEAH} x_{MEAH} \right) - \left( \gamma_{H,O^+} x_{H,O^+} \right)
\]  

(3.20)

Mass balance for MEA:

\[
F(7) = \left( \gamma_{MEA} x_{MEA} \right)_{Total} - \left( \gamma_{MEA} x_{MEA} \right) - \left( \gamma_{MEAH} x_{MEAH} \right) - \left( \gamma_{MEACOO} x_{MEACOO} \right)
\]  

(3.21)

Mass balance for carbon atoms:

\[
F(8) = \alpha_{CO_2} \left( \gamma_{MEA} x_{MEA} \right)_{Total} - \left( \gamma_{MEACOO} x_{MEACOO} \right) - \left( \gamma_{HCO_3} x_{HCO_3} \right) - \left( \gamma_{CO_3^2} x_{CO_3^2} \right) - \left( \gamma_{CO_2} x_{CO_2} \right)
\]  

(3.22)

The above equations were normalized and rewritten in a convenient mathematical form. Then, these equations were solved simultaneously using the Newton – Raphson method (Chapra and Canale, 2010). The algorithm for solving the set of eight non-linear equations simultaneously is given below in Figure 3.3.

The simulation was carried out by varying input parameters (temperature, CO₂ loading, and MEA concentration). The initial guess values for speciation [\(x_i\)] had to be given as input in the form of a 8x1 matrix. The then program returned the value of the function \(F(1)\) to \(F(8)\). The gradient of the functions \(F(1)\) to \(F(8)\) was found and stored as a 8x8 matrix, [\(F\)]. This matrix was used to iterate for the next value of concentration \([x_{i+1}]\). The program was stopped when the relative error was less than 0.01. Thus, the obtained output is the concentration of 8 chemical species at the bulk (speciation).
Figure 3.3: Algorithm to solve for speciation
3.4 Dissolved O\textsubscript{2} content in bulk solution

The concentration of dissolved oxygen in the bulk solution was calculated using the expression below (Green and Perry, 2007):

\[ x_{O_2} = \exp\left( A + \frac{B}{T} + C \times \ln T + D \times T \right) \]  

(3.23)

where \( x_{O_2} \) is the mole fraction of oxygen, the values of constants \( A, B, C, \) and \( D \) are \(-171.2542, 8391.24, 23.24323, \) and \( 0 \) respectively, and \( T \) is the absolute temperature (K). The above mole fraction of oxygen is the amount of oxygen that is dissolved under the oxygen partial pressure of 1 atm. However, the concentration of oxygen in the flue gas is typically 3.81\% by volume (Abu-Zahra et al., 2007). Therefore, in this model, the resulting \( x_{O_2} \) was subsequently multiplied with a factor of 0.0381 to obtain the actual dissolved oxygen.

3.5 Diffusion model

3.5.1 FeCO\textsubscript{3} layer formation

According to Wang et al. (1995), FeCO\textsubscript{3} film forms on the metal surface when the solution temperature exceeds 80°C. The thickness of the FeCO\textsubscript{3} film varies with the solution temperature, \( i.e. \) the film grows thicker at higher temperatures. The temperature dependence of the film thickness can be illustrated in Table 3.2 and Figure 3.4. The film thickness was, in this work, regressed to obtain an empirical equation as a function of temperature (\( T \) in °C) as given below:

\[ \text{Film thickness (\( \mu \text{m} \))} = 0.017 \times t^2 - 1.578 \times t + 17.329 \]  

(3.24)
Table 3.2: Thickness of FeCO$_3$ film at various temperatures (Wang et al., 1995)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Film thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>0.1</td>
</tr>
<tr>
<td>90</td>
<td>13.2</td>
</tr>
<tr>
<td>100</td>
<td>29.5</td>
</tr>
<tr>
<td>110</td>
<td>49</td>
</tr>
<tr>
<td>120</td>
<td>72.7</td>
</tr>
<tr>
<td>130</td>
<td>101.3</td>
</tr>
<tr>
<td>140</td>
<td>129</td>
</tr>
</tbody>
</table>
Figure 3.4: FeCO$_3$ film thickness as a function of temperature

(Data taken from Wang et al., 1995)
The growth of the film reduces the corrosion rate as the transport of the species from the bulk solution to the metal surface is slowed.

3.5.2 Species transport equation

The model was set to calculate the thickness of the film when the temperature exceeds 80°C. The oxidizing agents diffuse across the film to reach the metal surface in order to get reduced. As a result, the concentration gradients of oxidizing agents are established. To map the concentration gradient, the modified Fick’s law was used.

Fick’s first law states that diffusion flux ($N$) of any species is directly proportional to the species concentration ($c$) gradient (Bird et al., 2001):

$$N = -D \frac{\partial c}{\partial x}$$  \hspace{1cm} (3.25)

Fick’s second law describes the change of species concentration with respect to time ($t$) and distance ($x$) (Bird et al., 2001):

$$\frac{\partial c}{\partial t} = -D \frac{\partial N}{\partial x}$$  \hspace{1cm} (3.26)

To combine both Fick’s laws, Equations (3.25) and (3.26) are merged:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$  \hspace{1cm} (3.27)

where $D$ is the diffusion coefficient of species. However, when the species diffusion takes place in any aqueous solution across a porous medium, the porosity of the film and the viscosity of the solution must be taken into account. Therefore, instead of $D$, the effective diffusion coefficient ($D_{eff}$), which is a function of the temperature and viscosity of the solution, to be calculated. Since an electrochemical reaction is taking place at the
interface, which results in the depletion of the species at the interface, the kinetics of the reaction should be taken into account to establish equilibrium at the interface. Thus, combined Fick’s law can be modified to the form shown below (Nesic et al, 2001):

\[
\frac{\partial \varepsilon c_i}{\partial t} = D_{\text{eff}} \frac{\partial \kappa N_i}{\partial x} + k_i c
\]  

(3.28)

where \( k_i \) is the reaction rate constant and \( \kappa \) is the permeability, which can be written as a function of porosity of the FeCO\(_3\) film (\( \varepsilon \)) as shown below:

\[
\kappa = \varepsilon^{3/2}
\]  

(3.29)

Therefore, the modified equation used in this model is expressed as:

\[
\frac{\partial c}{\partial t} = D_{\text{eff}} \varepsilon^{0.5} \frac{\partial^2 c}{\partial x^2} + k_i c
\]  

(3.30)

where \( \varepsilon \) was corrected with \( \varepsilon_1 \) correction factor to compensate the surface coverage at low porosities as shown below (Nesic et al., 2001):

\[
\varepsilon = 0.1 + 0.9 \varepsilon_1
\]  

(3.31)

\[
\varepsilon_1 = A \varepsilon^{-B \varepsilon - C(pH+D)} + E
\]  

(3.32)

where \( A = 580, B = 0.045, C = 1.5, D = -2.2, E = 0.06 \) and \( t \) is the temperature (°C).

The values of \( k_i \), rate constant for the electrochemical reactions were calculated from the rate constant expression (Levenspiel, 1999):

\[
k_i = \frac{r_i}{a_i^n}
\]  

(3.33)

where \( r_i \) is the reaction rate, which, in this, case is the equilibrium exchange current density (\( i_0 \)), \( a_i \) is the concentration of species \( i \), and \( n \) is the order of the reaction. Thus, equation (3.33) can be rewritten as:
3.5.3 Solving transport equation

For a steady state condition, the change in species concentration with time is assumed to be zero. This makes the left hand side of equation (3.61) become zero. Since the concentration is only a function of distance from the metal surface, the partial differential equation can be rewritten as an ordinary differential equation as shown below:

\[
\frac{d^2c}{dx^2} + \left(\frac{k_i}{D_{\text{eff}}\varepsilon^{0.5}}\right)c = 0
\]  

The above differential equation was solved using the Euler method (Chapra and Canale, 2010) to determine the concentration of the oxidizing agents at the surface of the metal. This method gives the concentration of any species as a function of distance from the interface at equilibrium. The initial condition for the concentration is the bulk concentration of the chemical species.

The value of \(D_{\text{eff}}\) for a given species can be determined from the diffusion coefficient of the given species in water \((D_{\text{ref}})\) at a reference temperature \((T_{\text{ref}})\), viscosity of MEA solution \((\mu_{\text{ref}})\) at a reference temperature \((T_{\text{ref}})\), and viscosity of MEA solution \((\mu)\) at any temperature \((T)\) as per the following relationship (George et al., 2004):

\[
D_{\text{eff}} = D_{\text{ref}} \frac{T}{T_{\text{ref}}} \frac{\mu_{\text{ref}}}{\mu}
\]  

(3.36)
Table 3.3: Diffusion coefficients of various species in water at 25°C

<table>
<thead>
<tr>
<th>Species</th>
<th>Diffusion coefficient (m²/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>1.96 E-09</td>
<td>Nesic et al., 2001</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1.11 E-09</td>
<td>Nesic et al., 2001</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>9.20 E-10</td>
<td>Nesic et al., 2001</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>9.31 E-09</td>
<td>Nesic et al., 2001</td>
</tr>
<tr>
<td>OH⁻</td>
<td>5.26 E-09</td>
<td>Nesic et al., 2001</td>
</tr>
<tr>
<td>O₂</td>
<td>2.10 E-09</td>
<td>Nesic et al., 2001</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>7.20 E-10</td>
<td>Nesic et al., 2001</td>
</tr>
<tr>
<td>MEA</td>
<td>1.08 E-09</td>
<td>Lide, 2004</td>
</tr>
</tbody>
</table>
where the values of $D_{ref}$ are provided in Table 3.3 and the values of $\mu$ (in Ns/m$^2$) can be determined from the following equation (Weiland et al., 1998; Amundsen et al., 2009):

$$\mu = \mu_{H_2O} \times \left( \frac{[(a.w_1 + b)T + (c.w_1 + d)][\alpha(e.w_1 + f.T + g) + 1]w_1}{T^2} \right)$$  \hspace{1cm} (3.37)

where $\mu_{H_2O}$ is the viscosity of water (kg/m s) at any given temperature $T$, $T$ is the given temperature (K), $\alpha$ is the CO$_2$ loading (mol CO$_2$/mol MEA), $w_1$ is the concentration of MEA solution (wt%), and $a$, $b$, $c$, $d$, $e$, $f$, and $g$ are constant values: 0, 0, 21.186, 2373, 0.01015, 0.0093, -2.2589, respectively (Amundson et al., 2009). The value of $\mu_{H_2O}$ can be determined as a function of the temperature as shown below (Amundson et al., 2009):

$$\mu_{H_2O} = \mu_{H_2O,20^\circ C} \times 10^{-1} \left( \frac{1.3277(20-t) - 0.001053(t-20)^2}{t-105} \right)$$  \hspace{1cm} (3.38)

where $\mu_{H_2O,20^\circ C}$ is the viscosity of water at 20°C (0.001002 Ns/m$^2$) and ‘t’ is the temperature (°C).

3.6 Electrochemical corrosion model

3.6.1 Electrochemical reactions

Five electrochemical reactions, i.e., one anodic and four cathodic reactions, are assumed to occur at the metal-solution interface:

Anodic reaction:

Oxidation of iron:

$$Fe \xrightarrow{k_a} Fe^{2+} + 2e^-$$  \hspace{1cm} (3.39)
Cathodic reactions:

**Reduction of hydronium ion:**

\[
2H_3O^+ + 2e^- \xrightleftharpoons[k_b]{k_a} 2H_2O + H_2 \tag{3.40}
\]

**Reduction of bicarbonate ion:**

\[
2HCO_3^- + 2e^- \xrightleftharpoons[k_{c^-}]{k_c} 2CO_3^{2-} + H_2 \tag{3.41}
\]

**Reduction of water:**

\[
2H_2O + 2e^- \xrightleftharpoons[k_{d^-}]{k_d} 2OH^- + H_2 \tag{3.42}
\]

**Reduction of dissolved oxygen:**

\[
O_2 + 2H_2O + 4e^- \xrightleftharpoons[k_{e^-}]{k_e} 4OH^- \tag{3.43}
\]

### 3.6.2 Determination of electrode kinetic parameters and corrosion rate

The mixed potential theory was incorporated into the corrosion model to determine the concentration of \(Fe^{2+}\) and \(i_{corr}\) (or corrosion rate). It states that the sum of the rate of the oxidation reactions is equal to the sum of the rate of the reduction reactions. In an aqueous MEA-CO\(_2\) environment, it was assumed that the oxidation reaction is the conversion of Fe to \(Fe^{2+}\) while the reduction reactions involve four reactions due to the presence of four oxidizing agents including \(H_3O^+, HCO_3^-\), \(H_2O\), and dissolved \(O_2\). The reduction reactions of \(H_3O^+, HCO_3^-\), and \(H_2O\) were assumed to be under activation or charge-transfer control, whereas the reduction of \(O_2\) is under both charge-transfer and diffusion control. Note that the corrosion model for the environment containing HSS is explained in detail in Section 3.7.
\[ \Sigma i_{\text{oxidation}} = \Sigma i_{\text{reduction}} \]  
\[ \Sigma i_{\text{oxidation}} = i_{\text{Fe}^+/\text{Fe}^{2+}} \]  
\[ \Sigma i_{\text{reduction}} = i_{H_2O^+/H_2} + i_{HCO_3^-/CO_3^{2-}} + i_{H_2O/OH^-} + i_{O_2/OH^-} \]  

where:

\[ i_{H_2O^+/H_2} = i_{0,H_2O^+/H_2} \times 10^{((E-E_{\text{rev},H_2O^+/H_2})/\beta_{H_2O^+/H_2})} \]  
\[ i_{HCO_3^-/CO_3^{2-}} = i_{0,HCO_3^-/CO_3^{2-}} \times 10^{((E-E_{\text{rev},HCO_3^-/CO_3^{2-}})/\beta_{HCO_3^-/CO_3^{2-}})} \]  
\[ i_{H_2O/OH^-} = i_{0,H_2O/OH^-} \times 10^{((E-E_{\text{rev},H_2O/OH^-})/\beta_{H_2O/OH^-})} \]  
\[ \frac{1}{i_{O_2/OH^-}} = \frac{1}{i_{(a)O_2/OH^-}} + \frac{1}{i_{\text{lim},O_2}} \]  

where:

\[ i_{(a)O_2/OH^-} = i_{0,O_2/OH^-} \times 10^{((E-E_{\text{rev},O_2/OH^-})/\beta_{O_2/OH^-})} \]  
\[ i_{\text{lim},O_2} = nk_m F[O_2]_b \]  

where \( i \) is the current density of a reaction (\( \mu \text{A/cm}^2 \)), \( i_0 \) is the equilibrium exchange current density of a reaction (\( \mu \text{A/cm}^2 \)), \( E \) is the equilibrium potential (V), \( E_{\text{rev}} \) is the reversible electrode potential (V), \( \beta \) is the symmetry factor, \( i_{\text{lim},O_2} \) is the limiting current density for oxygen reduction (\( \mu \text{A/cm}^2 \)), \( i_{(a)} \) is the current density from activation controlled reduction, \( i_{\text{lim}} \) is the current density from diffusion controlled reduction (limiting current density), \( k_m \) is the mass transfer coefficient of oxygen (1/s), \([O_2]_b\) is the
bulk concentration of oxygen (kmol/m$^3$), $n$ is the number of electrons transferred in the reduction reaction, and $F$ is the Faraday’s constant (C/mol).

The $i_0$ is analogous to the rate of the reaction (Veawab, 2000) and can be written in the form of an Arrhenius expression:

$$i_0 = k_0 a_i^n e^{-\frac{E_a}{RT}}$$  \hspace{1cm} (3.53)

where $k_0$ is the frequency factor (1/s), $a_i$ is the concentration of $i^{th}$ species (kmol/m$^3$), $n$ is the reaction order, which, in this case, is assumed to be pseudo first order ($n = 1$) for all reactions, $E_a$ is the activation energy (kJ/mol), which was assumed to be constant and independent of temperature, $R$ is the universal gas constant (J/mol K), and $T$ is the absolute temperature (K).

For the reduction of $\text{H}_3\text{O}^+$, $\text{HCO}_3^-$, and $\text{H}_2\text{O}$, the values of $E_a$ were determined from Equation 3.53 using the values of $i_0$, $k_0$, and $a_i$ at a given $T$ obtained from Veawab (2000) and Veawab and Aroonwilas (2002). By using the calculated $E_a$, $i_0$ can be determined under any condition. The electrochemical kinetic parameters are listed in Table 3.4. For the reduction of $\text{O}_2$, the $i_0$ and $E_a$ values were taken from Bockris and Khan (1993), while $k_0$ was back-calculated using Equation (3.53).

The value of $E$ was obtained from the literature and regressed as a function of CO$_2$ loading from Veawab (2000) and Soosaiprakasam and Veawab (2008).

$$E = 0.116 \times \alpha_{\text{CO}_2} - 0.6506$$  \hspace{1cm} (3.54)

where $E$ is the open circuit voltage (V) and $\alpha_{\text{CO}_2}$ is the CO$_2$ loading (mol CO$_2$ / mol MEA). The $E_{\text{rev}}$ is the reversible potential (V), which can be calculated from the Nernst equation as shown below:
**Table 3.4:** Electrochemical kinetic parameters

<table>
<thead>
<tr>
<th>Reaction</th>
<th>n</th>
<th>$k_a$ (1/s)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Reduction of $H_3O^+$</td>
<td>1</td>
<td>2.41E+09</td>
<td>1.49E+04</td>
</tr>
<tr>
<td>*Reduction of $HCO_3^-$</td>
<td>1</td>
<td>1.16E+09</td>
<td>3.87E+04</td>
</tr>
<tr>
<td>*Reduction of $H_2O$</td>
<td>1</td>
<td>2.60E-11</td>
<td>6.43E+04</td>
</tr>
<tr>
<td>#Reduction of $O_2$</td>
<td>1</td>
<td>1.69E+03</td>
<td>2.00E+04</td>
</tr>
</tbody>
</table>

* Veawab (2000)

# Bockris and Khan (1993)
\[ E_{rev,i} = E_{T,i}^0 + \frac{RT}{n_i F} \left( \frac{[\text{Products}]}{[\text{Reactants}]^n_i} \right) \]  

(3.55)

where \( E_{T,i}^0 \) is the standard electrode potential (V) at any given temperature; \( R \) is the universal gas constant (J/mol K); \( T \) is the absolute temperature (K); \( n_i \) is the number of electrons taking part in the reaction; \([\text{Products}]\) is the activity of the products, which is the product of activity coefficient and concentration of all the products; \([\text{Reactants}]\) is the activity of the reactants, which is the product of the activity coefficient and concentration of all the reactants; and ‘\( F \)’ is the Faraday’s constant (C/mol).

The \( E_{T}^0 \) was determined using the following equation (Bockris and Reddy, 1970):

\[ \Delta G_{T}^0 = n_i F E_{T}^0 \]  

(3.56)

where \( \Delta G_{T}^0 \) is the Gibbs free energy of formation of any compound at any given temperature, which can be calculated using Equation (3.57):

\[ \Delta G_{T}^0 = T \left[ \frac{\Delta G_{298K}^0}{298} + \Delta H_{298K}^0 \left( \frac{1}{T} - \frac{1}{298} \right) \right] \]  

(3.57)

where \( \Delta G_{298K} \) and \( \Delta H_{298K} \) are standard Gibbs free energy of formation (kJ/mol) at 298 K and standard enthalpy of formation (kJ/mol) at 298 K and \( T \) is the temperature (K). The values of \( \Delta G_{298K}^0 \) and \( \Delta H_{298K}^0 \) are given in Table 3.5. The Gibbs free energy change for any reaction was calculated by:

\[ \Delta G_{\text{reaction}}^0 = \sum \Delta G_{f,\text{products}}^0 - \sum \Delta G_{f,\text{reactants}}^0 \]  

(3.58)

where \( \Delta G_{\text{reaction}}^0 \) is the Gibbs free energy change accompanying the reaction, \( \sum \Delta G_{f,\text{products}}^0 \) is the sum of Gibbs free energy of the products, and \( \sum \Delta G_{f,\text{reactants}}^0 \) is the sum of Gibbs free energy of the reactants.
<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G_{298}^0$ (kJ/mol)</th>
<th>$\Delta H_{298}^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$</td>
<td>-78.90</td>
<td>-89.10</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>-237.00</td>
<td>-286.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-237.00</td>
<td>-286.00</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>-586.80</td>
<td>-692.00</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>-527.80</td>
<td>-677.10</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>-157.20</td>
<td>-230.02</td>
</tr>
</tbody>
</table>

Table 3.5: Gibbs free energy and enthalpy of formation of various compounds (Moore, 1983)
The value of \( \beta \) was determined with the following equation:

\[
\beta = \frac{2.303RT}{\alpha}
\]  

(3.59)

where \( \alpha \) is the transport coefficient, which is 0.5 for cathodic reactions and 1.5 for anodic reactions (Wang, 1999).

Once all parameters were determined, the \( i_{Fe/Fe^{2+}} \) was calculated from the sum of all cathodic currents in Equation (3.46). The value of \( i_{0,Fe/Fe^{2+}} \) was regressed from Veawab (2000) while the value of \( \beta \) was calculated from Equation (3.59). The obtained values were substituted into the Nernst equation (Equation 3.55) to calculate the concentration of \( Fe^{2+} \) ions.

To estimate the corrosion rate of the metal, two methods were employed. First, the value of corrosion current density \( i_{corr} \) was determined from the sum of all cathodic currents of all reduction reactions. Second, the value of \( i_{corr} \) was obtained from the polarization curves, which were established using the following relationship:

\[
E - E_{rev} = \beta \left( \log \frac{i}{i_0} \right)
\]  

(3.60)

Any polarization curve starts at point, \( (E_{rev}, i_0) \) and progresses in the direction of increasing current density with slope \( \beta \) (Veawab, 2000). The values of \( i_{corr} \) and corrosion potential \( (E_{corr}) \) are the intersection point of the simulated anodic and cathodic polarization curves. Corrosion rate was calculated from the value of \( i_{corr} \) as per the following equation.

\[
CR = 0.00327 \frac{a_i}{n D} i_{corr}
\]  

(3.61)
where \( CR \) is the corrosion rate in millimeters per year (mmpy), \( a \) is the atomic weight of corroding metal (g/mol), \( i_{\text{cor}} \) is the corrosion current density (\( \mu A/cm^2 \)), \( n \) is the number of electrons involved in the reaction, and \( D \) is the density of the metal (g/cm\(^3\)). The values of \( a \) and \( D \) of a metal (Fe) were obtained from Lide (2004).

### 3.6.3 Calculation of corrosion rate in presence of acetic acid

When acetic acid was added to the model, the reduction current of H\(_3\)O\(^+\) comprised two parts: activation current density \( (i_{(a)} \) and diffusion limited current density \( (i_{\text{lim}}) \) (George et al., 2004) as written below:

\[
\frac{1}{i_{H_3O^+/H_2}} = \frac{1}{i_{(a)H_3O^+/H_2}} + \frac{1}{i_{\text{lim,}H_3O^+/H_2}} \tag{3.62}
\]

\[
i_{\text{lim,}H_3O^+/H_2} = n k_m F [HAc]_b \tag{3.63}
\]

\[
i_{(a)H_3O^+/H_2} = i_{0,H_3O^+/H_2} \times 10^{((E-E_{\text{rev,H}_3O^+/H_2})/b_{H_3O^+/H_2})} \tag{3.64}
\]

where, \([HAc]_b\) is the bulk concentration of acetic acid (George et al., 2004).
4. SIMULATION RESULTS AND DISCUSSION

A mechanistic corrosion model for carbon steel in a MEA-based CO₂ absorption process was developed in this work. The model is an integration of three sub-models that employs the principles of vapour-liquid equilibrium (VLE), species diffusion through a porous film, and electrode kinetics on the metal-solution interface. The developed VLE Kent-Eisenberg (K-E) sub-model was verified with the original K-E results published in 1976 to ensure the reliability of speciation simulation in determining concentrations of chemical species in the bulk solution of aqueous MEA under the assumption of the presence of unity activity coefficients. To reveal the sensitivity of the two VLE sub-models, the simulated K-E speciation results were then compared with the speciation from the electrolyte non-random two-liquid (e-NRTL) model with the non-unity activity coefficient obtained from Veawab (2000). The speciation results from both the K-E and e-NRTL sub-models were subsequently used for generating polarization curves, as well as relevant corrosion data, of the aqueous MEA-CO₂ environment under given conditions, which were compared with those from the literature. The developed corrosion model was later used to simulate corrosion data under different conditions to study the effects of a porous FeCO₃ layer on the metal surface and dissolved O₂ and heat-stable salt on corrosion. Details of the model verification and corrosion simulation are given below.
4.1 Simulation results of the developed K-E sub-model

4.1.1 Model verification

The developed K-E sub-model was verified with the VLE experimental results produced in the original work of Kent and Eisenberg (1976). Kent and Eisenberg developed a VLE model for aqueous amines-CO$_2$ systems and presented their simulation results in terms of CO$_2$ partial pressure and the respective CO$_2$ loading in the solution (or the amount of CO$_2$ gas absorbed into the solution). As shown in Table 4.1, the amounts of the CO$_2$ absorbed into the solution from Kent-Eisenberg (1976) and from this work are comparable, with a less than 6% difference. This difference might result from the fact that the equilibrium constants used in the developed K-E sub-model were taken from Austgen et al. (1989) instead of Kent-Eisenberg (1976). This is because the CO$_2$ absorption reactions used in this work follow Austgen et al. (1989) in that they involve hydronium ions (H$_3$O$^+$), which differs from the K-E model involving hydrogen ions (H$^+$).

4.1.2 Speciation results

After being verified, the developed K-E sub-model was used to determine concentrations of all chemical species in the bulk MEA solution under a wide range of operating conditions of the MEA-based CO$_2$ absorption process for the application of flue gas treatment. These speciation data were plotted against three operating parameters: CO$_2$ loading in the solution, solution temperature, and MEA concentration, for the study of parametric effects on speciation.
**Table 4.1:** Comparison of VLE simulation results with the experiment

<table>
<thead>
<tr>
<th>CO₂ loading (mol CO₂/mol MEA)</th>
<th>Amount of CO₂ absorbed into the solution in various forms (kmol/m³)</th>
<th>% Difference from K-E experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental value (Kent and Eisenberg, 1976)</td>
<td>This work</td>
</tr>
<tr>
<td>0.387</td>
<td>0.9675</td>
<td>0.9109</td>
</tr>
<tr>
<td>0.424</td>
<td>1.0600</td>
<td>1.0079</td>
</tr>
<tr>
<td>0.400</td>
<td>1.0000</td>
<td>0.9478</td>
</tr>
<tr>
<td>0.480</td>
<td>1.2000</td>
<td>1.1332</td>
</tr>
<tr>
<td>0.472</td>
<td>1.1800</td>
<td>1.1304</td>
</tr>
<tr>
<td>0.392</td>
<td>0.9800</td>
<td>0.9285</td>
</tr>
</tbody>
</table>
4.1.2.1 Effect of CO$_2$ loading in the solution

The speciation was simulated for CO$_2$ loading values from 0.10 to 1.00 mol CO$_2$/mol MEA with an interval of 0.05 mol CO$_2$/mol MEA, while the MEA concentration and solution temperature were kept constant. From Figure 4.1, it can be seen that the bulk concentrations of H$_3$O$^+$, HCO$_3^-$, MEAH$^+$, and MEACOO$^-$ increase with CO$_2$ loading. However, those of H$_3$O$^+$ and HCO$_3^-$ are much more sensitive to the CO$_2$ loading than those of MEAH$^+$ and MEACOO$^-$. With the common knowledge that corrosion increases with CO$_2$ loading, this suggests that H$_3$O$^+$ and HCO$_3^-$ could play a more significant role in corrosion than MEAH$^+$ and MEACOO$^-$. It should be noted that HCO$_3^-$ is likely to have more influence on corrosion than H$_3$O$^+$ since HCO$_3^-$ is present in the solution in a much greater quantity than H$_3$O$^+$ (i.e., the mole fraction of HCO$_3^-$ is $10^{-5}$ – $10^{-1}$ while the mole fraction of H$_3$O$^+$ is $10^{-13}$ – $10^{-9}$).

4.1.2.2 Effect of solution temperature

The speciation was simulated for various solution temperatures from 40 to 100$^\circ$C with an interval of 5$^\circ$C, while keeping MEA concentration and CO$_2$ loading constant. Figure 4.2 shows that as the solution temperature increased, the bulk concentrations of H$_3$O$^+$ and HCO$_3^-$ increased. The H$_3$O$^+$ concentration was more sensitive to the change in solution temperature than HCO$_3^-$. However, the concentration range of HCO$_3^-$ in the bulk solution was much greater than that of H$_3$O$^+$ (i.e., the mole fraction of HCO$_3^-$ is in the range of $10^{-5}$, while the mole fraction of H$_3$O$^+$ is $10^{-13}$ – $10^{-12}$.). This suggests that both H$_3$O$^+$ and HCO$_3^-$ are oxidizing agents participating in the corrosion process, but HCO$_3^-$ could be a stronger oxidizing agent than H$_3$O$^+$ due to its quantity in the solution.
**Figure 4.1:** Effect of CO$_2$ loading on speciation in the bulk MEA solution (5.0 kmol/m$^3$ MEA; 40°C)
Figure 4.2: Effect of solution temperature on speciation in the bulk MEA solution (5.0 kmol/m³ MEA; 0.10 mol CO₂/mol MEA)
4.1.2.3 Effect of MEA concentration

The speciation was simulated for various MEA concentrations from 1 to 8 kmol/m$^3$ where the temperature and CO$_2$ loading were kept constant at 40°C and 0.10 mol CO$_2$/mol MEA, respectively. Figure 4.3 shows that the bulk concentrations of all chemical species, except MEA and MEAH$^+$, remained unchanged with the increasing MEA concentration. This implies that MEAH$^+$ might be another oxidizing agent participating in the corrosion process.

4.1.3 Speciation comparison with e-NRTL

The speciation results obtained from the K-E sub-model were compared to those from the e-NRTL model that were obtained from Veawab (2000). The comparison was made under a wide range of operating conditions, as listed in Table 4.2. For example, in Figures 4.4 - 4.5, for 2.0 kmol/m$^3$ MEA with 0.20 molCO$_2$/mol MEA, the K-E and the e-NRTL models generated different ranges of bulk concentrations of most chemical species, including H$_2$O (an oxidizing agent), except for H$_3$O$^+$ and HCO$_3^-$ (oxidizing agents). This is because the K-E sub-model was built based on the assumption of unity activity coefficients of all chemical species, whereas the e-NRTL model was based on the non-unity activity coefficients. Similar results were also obtained for other conditions as seen in the parity chart shown in Figures 4.6 - 4.7.
Figure 4.3: Effect of MEA concentration on speciation in the bulk MEA solution (40°C; 0.10 mol CO₂/mol MEA)
Table 4.2: List of conditions for species comparison between e-NRTL and K-E model

<table>
<thead>
<tr>
<th>MEA concentration (kmol/m³)</th>
<th>CO₂ loading (mol CO₂/mol MEA)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>80</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 4.4: Comparison of bulk concentrations of oxidizing agents determined from the K-E sub-model and the e-NRTL model (Veawab, 2000) (2 kmol/m³ MEA; 0.20 mol CO₂/mol MEA)
Figure 4.5: Comparison of bulk concentrations of non-oxidizing agents determined from the K-E sub-model and the e-NRTL model (Veawab, 2000) (2 kmol/m$^3$ MEA; 0.20 mol CO$_2$/mol MEA).
Figure 4.6: Comparison of bulk concentrations of oxidizing agents determined from the K-E sub-model and the e-NRTL model (Veawab, 2000)
Figure 4.7: Comparison of bulk concentrations of oxidizing agents determined from the K-E sub-model and the e-NRTL model (Veawab, 2000)
4.2 Simulation results of the developed corrosion model

4.2.1 Corrosion in base environment

4.2.1.1 Comparison with data from the literature

The developed corrosion model was used to simulate the corrosion process and predict corrosion rates of carbon steel in aqueous MEA-CO₂ environments. In this section, the focus of the model simulation is on the environments that induce no FeCO₃ film on the metal surface and contain no dissolved O₂ and no HSSs. The simulation results based on the K-E and e-NRTL models were compared with the experimental corrosion data obtained from the literature (Veawab, 2000 and Soosaiprakasam, 2007). All comparisons were made using polarization curves and electrode kinetic data, including corrosion current density (i_{corr}), corrosion potential (E_{corr}), and corrosion rate, as shown in Figures 4.8 to 4.13 and Table 4.3. The conditions for simulation were chosen from Veawab (2000) and were listed above in Table 4.2.

From Figures 4.8 - 4.13 and Table 4.3, most of the simulated polarization curves from both the K-E and e-NRTL models are governed by anodic and cathodic Tafel slopes similar to the experimental curves. However, the simulated curves shift slightly in the direction of greater current densities (i_{corr}) and greater corrosion potential (E_{corr}). This means the predicted corrosion rates are greater than the corrosion rates obtained from the experiments. The deviation of the simulated polarization curves might be due to the value of open circuit potential (E), which was regressed from Veawab (2000) and Soosaiprakasam and Veawab (2008) as a function of CO₂ loading. In the MEA-CO₂-H₂O system, E shows a slight dependence on temperature. When the multiple regression was performed to fit E as a function of CO₂ loading and temperature, the sum of errors (R²)
was as low as 0.76. Thus, in the developed corrosion model, $E$ was assumed to be independent of temperature, as it showed greater dependence on CO$_2$ loading where the R$^2$ value was approximately 0.98.

Figures 4.8 - 4.13 and Table 4.3 also show that the simulated corrosion data produced from the e-NRTL model are in a better agreement with the experimental results than the simulated data from the K-E model. The polarization curves produced from the e-NRTL-based model are closer to the experimental curves. They yield lower $i_{corr}$ and $E_{corr}$ and, in turn, lower predicted corrosion rates compared to the curves from the K-E-based model. The lower corrosion rates predicted from the e-NRTL-based model resulted from the activity coefficients used in the model. As mentioned previously, the e-NRTL model maps real behaviour of solution, meaning it takes into account the interaction among chemical species. This, thereby, causes the activity coefficients or the effective concentrations of chemical species, including oxidizing agents, to reduce to lower values than the K-E based model, which assumes ideal solution or unity activity coefficients for all chemical species.

4.2.1.2 Sensitivity analysis

A) Effect of solution temperature

Corrosion of carbon steel was simulated for 2.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA at three different temperatures (40, 60, and 80°C), and 5.0 kmol/m$^3$ MEA and 0.20 mol CO$_2$/mol MEA at two different temperatures (30 and 80°C). As illustrated in Figure 4.14 and Table 4.4, an increase in the solution temperature led to increases in $i_{corr}$ and corrosion rate, while the changes in $E_{corr}$, $\beta_a$, and $\beta_c$ were minimal.
Figure 4.8: Comparison of simulated and experimental (Veawab, 2000) polarization curves. (a) 1.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 80°C (b) 1.0 kmol/m³ MEA with 0.40 mol CO₂/mol MEA at 30°C
Figure 4.9: Comparison of simulated and experimental (Veawab, 2000) polarization curves. (a) 2.0 kmol/m$^3$ MEA with 0.10 mol CO$_2$/mol MEA at 30ºC (b) 2.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA at 30ºC (c) 2.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA at 40ºC (d) 2.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA at 60ºC (e) 2.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA at 80ºC (f) 2.0 kmol/m$^3$ MEA with 0.30 mol CO$_2$/mol MEA at 30ºC
Figure 4.10: Comparison of simulated and experimental (Veawab, 2000) polarization curves. (a) 2.0 kmol/m$^3$ MEA with 0.40 mol CO$_2$/mol MEA at 30ºC (b) 2.0 kmol/m$^3$ MEA with 0.40 mol CO$_2$/mol MEA at 60ºC
Figure 4.11: Comparison of simulated and experimental (Veawab, 2000) polarization curves. (a) 3.0 kmol/m³ MEA with 0.40 mol CO₂/mol MEA at 80°C (b) 3.0 kmol/m³ MEA with 0.40 mol CO₂/mol MEA at 30°C
Figure 4.12: Comparison of simulated and experimental (Veawab, 2000) polarization curves. (a) 4.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 30°C (b) 4.0 kmol/m³ MEA with 0.40 mol CO₂/mol MEA at 30°C
Figure 4.13: Comparison of simulated and experimental (Veawab, 2000 and Soosaiprakasam, 2007) polarization curves. (a) 5.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA at 30°C (b) 5.0 kmol/m$^3$ MEA with 0.40 mol CO$_2$/mol MEA at 30°C (b) 5.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA at 80°C
Table 4.3: Comparison of corrosion data from Kent-Eisenberg-based model and e-NRTL-based model with experimental data

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_{corr}$ (μA/cm$^2$)</td>
<td>$E_{corr}$ (V)</td>
<td>$CR$ (mmpy)</td>
</tr>
<tr>
<td>1 kmol/m$^3$ MEA, 80°C, 0.20 mol CO$_2$/mol MEA</td>
<td>5.3</td>
<td>0.062</td>
<td>80.0</td>
</tr>
<tr>
<td>1 kmol/m$^3$ MEA, 30°C, 0.40 mol CO$_2$/mol MEA</td>
<td>12.9</td>
<td>0.150</td>
<td>12.0</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 30°C, 0.10 mol CO$_2$/mol MEA</td>
<td>3.1</td>
<td>0.036</td>
<td>7.2</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 30°C, 0.20 mol CO$_2$/mol MEA</td>
<td>5.6</td>
<td>0.065</td>
<td>9.6</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 40°C, 0.20 mol CO$_2$/mol MEA</td>
<td>7.8</td>
<td>0.090</td>
<td>31.0</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 60°C, 0.20 mol CO$_2$/mol MEA</td>
<td>15.2</td>
<td>0.176</td>
<td>54.0</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 80°C, 0.20 mol CO$_2$/mol MEA</td>
<td>35.4</td>
<td>0.411</td>
<td>162.0</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 30°C, 0.30 mol CO$_2$/mol MEA</td>
<td>8.4</td>
<td>0.098</td>
<td>10.5</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 30°C, 0.40 mol CO$_2$/mol MEA</td>
<td>6.5</td>
<td>0.075</td>
<td>14.0</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 60°C, 0.40 mol CO$_2$/mol MEA</td>
<td>30.9</td>
<td>0.358</td>
<td>128.0</td>
</tr>
<tr>
<td>2 kmol/m$^3$ MEA, 80°C, 0.40 mol CO$_2$/mol MEA</td>
<td>52.6</td>
<td>0.610</td>
<td>195.0</td>
</tr>
<tr>
<td>3 kmol/m$^3$ MEA, 80°C, 0.20 mol CO$_2$/mol MEA</td>
<td>35.4</td>
<td>0.411</td>
<td>186.0</td>
</tr>
<tr>
<td>3 kmol/m$^3$ MEA, 30°C, 0.20 mol CO$_2$/mol MEA</td>
<td>5.5</td>
<td>0.064</td>
<td>16.0</td>
</tr>
<tr>
<td>4 kmol/m$^3$ MEA, 30°C, 0.20 mol CO$_2$/mol MEA</td>
<td>5.3</td>
<td>0.061</td>
<td>19.0</td>
</tr>
<tr>
<td>4 kmol/m$^3$ MEA, 30°C, 0.40 mol CO$_2$/mol MEA</td>
<td>4.7</td>
<td>0.054</td>
<td>21.0</td>
</tr>
<tr>
<td>5 kmol/m$^3$ MEA, 30°C, 0.20 mol CO$_2$/mol MEA</td>
<td>6.0</td>
<td>0.070</td>
<td>24.0</td>
</tr>
</tbody>
</table>

$CR = \text{Corrosion rate}$
The increasing $i_{corr}$ is due to the nature of corrosion kinetics, which can be seen in Table 4.5. That is, at higher temperatures, rates of corrosion reactions (both iron dissolution and reduction of oxidizing agents) are accelerated, resulting in the increasing $i_{corr}$ and corrosion rate. The negligible change in $\beta_a$ and $\beta_c$ implies that the corrosion mechanism does not change with the solution temperature.

To determine which oxidizing agents play an important role in corrosion in this aqueous MEA-CO$_2$ environment, the electrode kinetic parameters and the quantity of oxidizing agents in the bulk solution (Table 4.5 and Figures 4.15-4.16) were considered. It is apparent that H$_3$O$^+$ is the least influential in corrosion due to its low $i_0$ and small quantity in the bulk solution compared to HCO$_3^-$ and H$_2$O. Between HCO$_3^-$ and H$_2$O, HCO$_3^-$ is present in the bulk solution in a much smaller quantity than H$_2$O. Its $i_0$ increases significantly with the solution temperature while $i_0$ of H$_2$O decreases with the solution temperature (Figure 4.15). This demonstrates that H$_2$O and HCO$_3^-$ are the primary oxidizing agents. H$_2$O contributes less to the corrosion at higher temperature, whereas HCO$_3^-$ contributes more.

**B) Effect of CO$_2$ loading in solution**

Simulation was carried out for two solution conditions, *i.e.* 2 kmol/m$^3$ MEA at 80°C containing three different CO$_2$ loadings of 0.10, 0.20, and 0.30 mol CO$_2$/mol MEA; and 5 kmol/m$^3$ MEA at 30°C containing two different CO$_2$ loadings of 0.20 and 0.40 mol CO$_2$/mol MEA. Figure 4.17 and Table 4.4 shows that as the CO$_2$ loading increased, the anodic polarization curve did not shift, but the cathodic polarization curve shifted to the right where cathodic currents are greater, thereby increasing $i_{corr}$. The higher $i_{corr}$ is due to
Figure 4.14: Effect of solution temperature on simulated polarization curves from e-NRTL based model (a) 2.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA (b) 5.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA
Figure 4.15: Quantity (a) and $i_o$ value (b) of oxidizing agents (2.0 kmol/m$^3$ MEA with 0.20 mol CO$_2$/mol MEA)
Figure 4.16: Quantity (a) and \( i_o \) value (b) of oxidizing agents (5.0 kmol/m\(^3\) MEA with 0.20 mol CO\(_2\)/mol MEA)
**Table 4.4:** Simulated corrosion data obtained from sensitivity analysis

<table>
<thead>
<tr>
<th>Condition</th>
<th>$\beta_a$</th>
<th>$\beta_c$</th>
<th>$i_{corr}$ (μA/cm²)</th>
<th>$E_{corr}$ (V)</th>
<th>CR (mmpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 40°C</td>
<td>0.0414</td>
<td>0.1242</td>
<td>21</td>
<td>-0.616</td>
<td>0.242</td>
</tr>
<tr>
<td>2.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 60°C</td>
<td>0.0441</td>
<td>0.1322</td>
<td>41</td>
<td>-0.610</td>
<td>0.473</td>
</tr>
<tr>
<td>2.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 80°C</td>
<td>0.0467</td>
<td>0.1401</td>
<td>103</td>
<td>-0.618</td>
<td>1.187</td>
</tr>
<tr>
<td>5.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 30°C</td>
<td>0.0401</td>
<td>0.1203</td>
<td>8</td>
<td>-0.608</td>
<td>0.092</td>
</tr>
<tr>
<td>5.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 80°C</td>
<td>0.0467</td>
<td>0.1401</td>
<td>101</td>
<td>-0.620</td>
<td>1.164</td>
</tr>
<tr>
<td>2.0 kmol/m³ MEA with 0.10 mol CO₂/mol MEA at 80°C</td>
<td>0.0467</td>
<td>0.1401</td>
<td>7</td>
<td>-0.614</td>
<td>0.081</td>
</tr>
<tr>
<td>2.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 80°C</td>
<td>0.0467</td>
<td>0.1401</td>
<td>9</td>
<td>-0.606</td>
<td>0.104</td>
</tr>
<tr>
<td>2.0 kmol/m³ MEA with 0.30 mol CO₂/mol MEA at 80°C</td>
<td>0.0467</td>
<td>0.1401</td>
<td>12</td>
<td>-0.598</td>
<td>0.138</td>
</tr>
<tr>
<td>5.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 30°C</td>
<td>0.0401</td>
<td>0.1203</td>
<td>8</td>
<td>-0.608</td>
<td>0.092</td>
</tr>
<tr>
<td>5.0 kmol/m³ MEA with 0.40 mol CO₂/mol MEA at 30°C</td>
<td>0.0401</td>
<td>0.1203</td>
<td>14</td>
<td>-0.598</td>
<td>0.161</td>
</tr>
<tr>
<td>1.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 80°C</td>
<td>0.0467</td>
<td>0.1401</td>
<td>108</td>
<td>-0.616</td>
<td>1.245</td>
</tr>
<tr>
<td>3.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 80°C</td>
<td>0.0467</td>
<td>0.1401</td>
<td>130</td>
<td>-0.620</td>
<td>1.499</td>
</tr>
<tr>
<td>5.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA at 80°C</td>
<td>0.0467</td>
<td>0.1401</td>
<td>160</td>
<td>-0.624</td>
<td>1.844</td>
</tr>
<tr>
<td>1.0 kmol/m³ MEA with 0.40 mol CO₂/mol MEA at 30°C</td>
<td>0.0401</td>
<td>0.1203</td>
<td>9</td>
<td>-0.580</td>
<td>0.104</td>
</tr>
<tr>
<td>3.0 kmol/m³ MEA with 0.40 mol CO₂/mol MEA at 30°C</td>
<td>0.0401</td>
<td>0.1203</td>
<td>11</td>
<td>-0.576</td>
<td>0.127</td>
</tr>
<tr>
<td>5.0 kmol/m³ MEA with 0.40 mol CO₂/mol MEA at 30°C</td>
<td>0.0401</td>
<td>0.1203</td>
<td>14</td>
<td>-0.568</td>
<td>0.161</td>
</tr>
</tbody>
</table>
Table 4.5: Electrode kinetic parameters for temperature dependency

<table>
<thead>
<tr>
<th>Species</th>
<th>2.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA</th>
<th>5.0 kmol/m³ MEA with 0.20 mol CO₂/mol MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40°C</td>
<td>60°C</td>
</tr>
<tr>
<td>Species</td>
<td>Mole fraction</td>
<td>$E_{rev}$ (V)</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>1.151E-12</td>
<td>-0.771</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>5.039E-05</td>
<td>-0.665</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>9.595E-01</td>
<td>-0.561</td>
</tr>
<tr>
<td>Species</td>
<td>Mole fraction</td>
<td>$E_{rev}$ (V)</td>
</tr>
<tr>
<td>H$_3$O$^+$</td>
<td>4.710E-13</td>
<td>-0.797</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>3.196E-05</td>
<td>-0.661</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>8.796E-01</td>
<td>-0.544</td>
</tr>
</tbody>
</table>
the increasing concentration and \( i_0 \) of HCO\(_3^-\). As illustrated in Figures 4.18-4.19 and Table 4.6, H\(_2\)O does not contribute to the change in corrosion rate due to CO\(_2\) loading variation.

C) Effect of MEA concentration

The effect of MEA concentration on corrosion was simulated for three different MEA concentrations of 1, 3, and 5 kmol/m\(^3\) MEA containing 0.20 mol CO\(_2\)/mol MEA at 80°C and also for 1, 3, and 5 kmol/m\(^3\) MEA containing 0.40 mol CO\(_2\)/mol MEA at 30°C. As shown in Figure 4.20 and Table 4.4, when the MEA concentration increased, the polarization curves shifted slightly in the direction of greater current densities, reflecting a slight increase in \( i_{corr} \) (or corrosion rate). The slight increase in \( i_{corr} \) is due to the increases in HCO\(_3^-\) concentration and \( i_0 \) values of H\(_3\)O\(^+\), HCO\(_3^-\), and H\(_2\)O reduction. Note that these increases in HCO\(_3^-\) concentration and all values of \( i_0 \), as illustrated in Figures 4.21-4.22, are not apparent due to the scale of the figure.

4.2.2 Corrosion in the presence of dissolved O\(_2\)

The dissolved O\(_2\) was included in the developed corrosion model as an additional oxidizing agent, since it is typically contained in the flue gas produced from fuel combustion. In this section, the simulation results of the developed model were compared with the experimental data obtained from the literature (Soosaiprakasam, 2007 and Kittel et al., 2010). Figure 4.23 illustrates that the simulated polarization curves are in a similar range as the literature data. The simulated curves and Table 4.8 also show that the presence of dissolved O\(_2\) does not have a direct effect on corrosion.
Figure 4.17: Effect of CO₂ loading on simulated polarization curves from e-NRTL based model (a) 2.0 kmol/m³ MEA at 80°C (b) 5.0 kmol/m³ MEA at 30°C
Figure 4.18: Quantity (a) and $i_0$ value (b) of oxidizing agents (2.0 kmol/m$^3$ MEA at 80°C)
Figure 4.19: Quantity (a) and $i_0$ value (b) of oxidizing agents (5.0 kmol/m$^3$ MEA at 30°C)
Table 4.6: Electrode kinetic parameters for CO₂ loading dependency

### 2.0 kmol/m³ MEA at 80°C

<table>
<thead>
<tr>
<th>Species</th>
<th>0.10 mol CO₂/mol MEA</th>
<th>0.20 mol CO₂/mol MEA</th>
<th>0.30 mol CO₂/mol MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole fraction</td>
<td>$E_{rev}$ (V)</td>
<td>$i_0$ (μA/cm²)</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>6.134E-12</td>
<td>-0.827</td>
<td>0.005</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>7.075E-05</td>
<td>-0.690</td>
<td>7.619</td>
</tr>
<tr>
<td>H₂O</td>
<td>9.590E-01</td>
<td>-0.573</td>
<td>0.433</td>
</tr>
</tbody>
</table>

### 5.0 kmol/m³ MEA at 30°C

<table>
<thead>
<tr>
<th>Species</th>
<th>0.20 mol CO₂/mol MEA</th>
<th>0.40 mol CO₂/mol MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole fraction</td>
<td>$E_{rev}$ (V)</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>4.710E-13</td>
<td>-0.746</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>3.196E-05</td>
<td>-0.610</td>
</tr>
<tr>
<td>H₂O</td>
<td>8.796E-01</td>
<td>-0.493</td>
</tr>
</tbody>
</table>
Figure 4.20: Effect of MEA concentration on simulated polarization curves from e-NRTL based model (a) 0.20 mol CO₂/mol MEA at 80°C (b) 0.40 mol CO₂/mol MEA at 30°C
Figure 4.21: Quantity (a) and $i_0$ value (b) of oxidizing agents (0.20 mol CO$_2$/mol MEA at 80°C)
Figure 4.22: Quantity (a) and $i_o$ value (b) of oxidizing agents (0.40 mol CO$_2$/mol MEA at 30°C)
Table 4.7: Electrode kinetic parameters for MEA concentration dependency

### 0.20 mol CO₂/mol MEA at 80°C

<table>
<thead>
<tr>
<th>Species</th>
<th>1.0 kmol/m³</th>
<th>3.0 kmol/m³</th>
<th>5.0 kmol/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole fraction</td>
<td>$E_{\text{rev}}$ (V)</td>
<td>$i_0$ (μA/cm²)</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>1.650E-11</td>
<td>-0.797</td>
<td>0.012</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1.816E-04</td>
<td>-0.661</td>
<td>18.880</td>
</tr>
<tr>
<td>H₂O</td>
<td>9.802E-01</td>
<td>-0.544</td>
<td>0.397</td>
</tr>
</tbody>
</table>

### 0.40 mol CO₂/mol MEA at 30°C

<table>
<thead>
<tr>
<th>Species</th>
<th>1.0 kmol/m³</th>
<th>3.0 kmol/m³</th>
<th>5.0 kmol/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole fraction</td>
<td>$E_{\text{rev}}$ (V)</td>
<td>$i_0$ (μA/cm²)</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>3.095E-12</td>
<td>-0.797</td>
<td>0.009</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1.941E-04</td>
<td>-0.661</td>
<td>14.160</td>
</tr>
<tr>
<td>H₂O</td>
<td>9.803E-01</td>
<td>-0.544</td>
<td>0.298</td>
</tr>
</tbody>
</table>
This is evidenced by the overlapping polarization curves of the MEA solutions with and without dissolved O\textsubscript{2}. These results are in good agreement with Kittel et al. (2010) but not in agreement with Soosaiprakasam (2007). Such negligible effects of the dissolved O\textsubscript{2} on corrosion were confirmed, however, by the simulated polarization curves at other operating conditions as presented in Figure 4.24.

The negligible effect of the dissolved O\textsubscript{2} can be explained by considering the individual polarization curves of four oxidizing agents present in the system (Figure 4.25). Firstly, the reversible potential for O\textsubscript{2} reduction is more positive than the oxidation of Fe to Fe\textsuperscript{2+}. As such, the O\textsubscript{2} reduction is a non-spontaneous process (Fontana, 2008). Secondly, when combining cathodic polarization curves of more than one reduction reaction, the reactions with \(i_0\) values that are 10 times less than the highest \(i_0\) value can be omitted from the mixed potential theory due to its negligible effect on the overall polarization curve (Fontana, 2008). This applies to the reduction of dissolved O\textsubscript{2} of which the \(i_0\) value is at least \(10^3\) times less than those of major reduction reactions of H\textsubscript{2}O and HCO\textsubscript{3}\textsuperscript{-} (Figure 4.22). From the polarization curves, it can be concluded that dissolved O\textsubscript{2} does not influence the corrosion rate by electrochemical reaction but it may influence the corrosion by accelerating the oxidative degradation of MEA and by forming degradation products which in turn affect the corrosion rate.

4.2.3 Corrosion in the presence of FeCO\textsubscript{3} film

A layer of the FeCO\textsubscript{3} film on the metal surface was added into the model. Its effect on corrosion rate in an aqueous MEA-CO\textsubscript{2} environment was studied. As shown in Figures 4.26-4.30 and Table 4.9, the presence of FeCO\textsubscript{3} film shifts the polarization
Figure 4.23: Comparison of simulated polarization curves with experimental results

(a) Soosaiprakasam, 2007 (5 kmol/m$^3$ MEA, 80°C, 0.20 mol CO$_2$/mol MEA) (b) Kittel et al., 2010 (5 kmol/m$^3$ MEA, 80°C, 0.50 mol CO$_2$/mol MEA)
Figure 4.24: Effect of dissolved oxygen on the polarization curve (e-NRTL based model)

(a) 1 kmol/m³ MEA, 80°C, 0.20 mol CO₂/mol MEA (b) 3 kmol/m³ MEA, 80°C, 0.20 mol CO₂/mol MEA (c) 5 kmol/m³ MEA, 80°C, 0.20 mol CO₂/mol MEA
Figure 4.25: Simulated anodic and cathodic polarization curves for 5 kmol/m$^3$ MEA containing 0.20 mol CO$_2$/mol MEA at 80°C (all polarization curves start at coordinate $i_0$, $E_{rev}$)
Table 4.8: Simulated corrosion data of MEA system with and without dissolved oxygen (e-NRTL-based model)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Without dissolved oxygen</th>
<th>With dissolved oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_{\text{corr}}$ ($\mu A/cm^2$)</td>
<td>$E_{\text{corr}}$ (V)</td>
</tr>
<tr>
<td>1 kmol/m$^3$ MEA, 80$^\circ$C, 0.20 mol CO$_2$/mol MEA</td>
<td>108</td>
<td>-0.616</td>
</tr>
<tr>
<td>3 kmol/m$^3$ MEA, 80$^\circ$C, 0.20 mol CO$_2$/mol MEA</td>
<td>130</td>
<td>-0.620</td>
</tr>
<tr>
<td>5 kmol/m$^3$ MEA, 80$^\circ$C, 0.20 mol CO$_2$/mol MEA</td>
<td>160</td>
<td>-0.624</td>
</tr>
<tr>
<td>5 kmol/m$^3$ MEA, 80$^\circ$C, 0.50 mol CO$_2$/mol MEA</td>
<td>280</td>
<td>-0.638</td>
</tr>
</tbody>
</table>
curves (particularly the reduction curve) to the left, where the current density is less when compared to the system without FeCO\(_3\) films. This directly indicates lower \(i_{corr}\) and, in turn, a lower corrosion rate in the presence of FeCO\(_3\) films. The FeCO\(_3\) film increases the resistance to the diffusion of the chemical species (including the oxidizing agents) from the bulk solution to the metal-solution interface and vice versa. As a result, lower concentrations of oxidizing agent are available at the metal-solution interface for corrosion reactions. This translates to a lower corrosion rate.

The effect of the resistance to species diffusion due to the presence of FeCO\(_3\) films is more predominant at elevated temperature (\(i.e., 120^\circ\text{C}\)). This is because the thickness of the film is increased with temperature, inducing higher resistance to diffusion. It should also be noted that the resistance to the diffusion due to the film is not sensitive to the changes in MEA concentration and CO\(_2\) loading, as evidenced in Figures 4.26 to 4.28 and Table 4.9. The corrosion current densities of the system with and without the film are similar even though the CO\(_2\) loading is varied from 0.15 to 0.25 mol CO\(_2\)/mol MEA and MEA concentration is varied from 1.0 to 5.0 kmol/m\(^3\). The speciation details of the oxidizing agents are shown in Table 4.10. The concentrations of the other chemical species are not shown in Table 4.10 since, at infinite time, the concentrations of non-oxidizing agents in the bulk solution and at the metal-solution interface are equal. They do not take part in any reduction reactions at the metal surface.

4.2.4 Corrosion in the presence of heat-stable salts

To simulate corrosion in the presence of HSSs, acetic acid was chosen as the representative of the HSSs in the MEA-based CO\(_2\) absorption process due to the
Figure 4.26: Comparison of simulated polarization curve from K-E based model with and without FeCO₃ film at 120°C and 1.0 kmol/m³ MEA at different CO₂ loadings.

(a) 0.15 mol CO₂/mol MEA (b) 0.20 mol CO₂/mol MEA (c) 0.25 mol CO₂/mol MEA
Figure 4.27: Comparison of simulated polarization curve from K-E based model with and without FeCO$_3$ film at 120°C and 3.0 kmol/m$^3$ MEA at different CO$_2$ loadings. (a) 0.15 mol CO$_2$/mol MEA (b) 0.20 mol CO$_2$/mol MEA (c) 0.25 mol CO$_2$/mol MEA
Figure 4.28: Comparison of simulated polarization curve from K-E based model with and without FeCO$_3$ film at 120°C and 5.0 kmol/m$^3$ MEA at different CO$_2$ loadings. (a) 0.15 mol CO$_2$/mol MEA (b) 0.20 mol CO$_2$/mol MEA (c) 0.25 mol CO$_2$/mol MEA
Figure 4.29: Comparison of simulated polarization curves from K-E based model with and without FeCO$_3$ film with 5.0 kmol/m$^3$ MEA and 0.15 mol CO$_2$/mol MEA at different solution temperatures (a) 90°C, (b) 100°C, (c) 110°C, (d) 120°C
Figure 4.30: Comparison of simulated polarization curves from K-E based model with and without FeCO$_3$ film with 5.0 kmol/m$^3$ MEA and 0.25 mol CO$_2$/mol MEA at different solution temperatures (a) 90°C, (b) 100°C, (c) 110°C, (d) 120°C
Table 4.9: Simulated corrosion data from K-E-based model with and without FeCO$_3$ films

<table>
<thead>
<tr>
<th>Condition</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (µA/cm$^2$)</th>
<th>CR (mmpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With FeCO$_3$</td>
<td>Without FeCO$_3$ film</td>
<td></td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.15 mol CO$_2$/mol MEA, 90°C</td>
<td>-0.658</td>
<td>-0.652</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>-0.638</td>
<td>-0.636</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>-0.662</td>
<td>-0.658</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>-0.640</td>
<td>-0.638</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>-0.640</td>
<td>-0.638</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>-0.656</td>
<td>-0.648</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>-0.648</td>
<td>-0.640</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>-0.636</td>
<td>-0.630</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>-0.658</td>
<td>-0.652</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>-0.646</td>
<td>-0.638</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>-0.646</td>
<td>-0.628</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>-0.646</td>
<td>-0.648</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>-0.652</td>
<td>-0.638</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>-0.633</td>
<td>-0.627</td>
<td>260</td>
</tr>
</tbody>
</table>
Table 4.10: Comparison of speciation details (mole fraction) of the oxidizing agents from K-E-based model with and without FeCO$_3$ films

<table>
<thead>
<tr>
<th>Condition</th>
<th>H$_2$O$^+$</th>
<th>HCO$_3^-$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without</td>
<td>With</td>
<td>Without</td>
<td>With</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>FeCO$_3$</td>
<td>FeCO$_3$</td>
<td>FeCO$_3$</td>
</tr>
<tr>
<td></td>
<td>film</td>
<td>film</td>
<td>film</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.15 mol CO$_2$/mol MEA, 90°C</td>
<td>1.66E-11</td>
<td>1.57E-11</td>
<td>1.50E-04</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.25 mol CO$_2$/mol MEA, 90°C</td>
<td>3.84E-11</td>
<td>3.65E-11</td>
<td>3.48E-04</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.15 mol CO$_2$/mol MEA, 100°C</td>
<td>2.81E-11</td>
<td>2.58E-11</td>
<td>1.96E-04</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.25 mol CO$_2$/mol MEA, 100°C</td>
<td>6.50E-11</td>
<td>5.98E-11</td>
<td>4.52E-04</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.15 mol CO$_2$/mol MEA, 110°C</td>
<td>4.61E-11</td>
<td>4.15E-11</td>
<td>2.51E-04</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.25 mol CO$_2$/mol MEA, 110°C</td>
<td>1.07E-10</td>
<td>9.59E-11</td>
<td>5.78E-04</td>
</tr>
<tr>
<td>1.0 kmol/m$^3$ MEA, 0.15 mol CO$_2$/mol MEA, 120°C</td>
<td>8.06E-11</td>
<td>6.04E-11</td>
<td>3.16E-04</td>
</tr>
<tr>
<td>1.0 kmol/m$^3$ MEA, 0.20 mol CO$_2$/mol MEA, 120°C</td>
<td>1.23E-10</td>
<td>9.22E-11</td>
<td>4.76E-04</td>
</tr>
<tr>
<td>1.0 kmol/m$^3$ MEA, 0.25 mol CO$_2$/mol MEA, 120°C</td>
<td>1.78E-10</td>
<td>1.34E-10</td>
<td>6.78E-04</td>
</tr>
<tr>
<td>3.0 kmol/m$^3$ MEA, 0.15 mol CO$_2$/mol MEA, 120°C</td>
<td>7.79E-11</td>
<td>5.84E-11</td>
<td>3.31E-04</td>
</tr>
<tr>
<td>3.0 kmol/m$^3$ MEA, 0.20 mol CO$_2$/mol MEA, 120°C</td>
<td>1.20E-10</td>
<td>9.03E-11</td>
<td>5.09E-04</td>
</tr>
<tr>
<td>3.0 kmol/m$^3$ MEA, 0.25 mol CO$_2$/mol MEA, 120°C</td>
<td>1.78E-10</td>
<td>1.33E-10</td>
<td>7.50E-04</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.15 mol CO$_2$/mol MEA, 120°C</td>
<td>7.34E-11</td>
<td>6.24E-11</td>
<td>3.18E-04</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.20 mol CO$_2$/mol MEA, 120°C</td>
<td>1.13E-10</td>
<td>8.52E-11</td>
<td>4.90E-04</td>
</tr>
<tr>
<td>5.0 kmol/m$^3$ MEA, 0.25 mol CO$_2$/mol MEA, 120°C</td>
<td>1.69E-10</td>
<td>1.44E-10</td>
<td>7.29E-04</td>
</tr>
</tbody>
</table>
availability of the electrochemical data required for model development. The simulation results from Figure 4.28 show that the presence of acetic acid has no apparent effect on the polarization curves and, thus, has a negligible effect on $i_{corr}$ (Table 4.12). The negligible change in $i_{corr}$ is attributed to the negligible changes in the concentrations of all oxidizing agents ($\text{H}_3\text{O}^+$, $\text{HCO}_3^-$, and $\text{H}_2\text{O}$) (Table 4.11).
Figure 4.31: Comparison of simulated polarization curves from e-NRTL based model containing 0.20 mol CO₂/mol MEA at 80°C with different concentrations MEA and acetic acid (a) 1.0 kmol/m³ MEA (b) 3.0 kmol/m³ MEA (c) 5.0 kmol/m³ MEA
Table 4.11: Comparison of simulated corrosion data with and without acetic acid from e-NRTL-based model

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$i_{corr} (\mu A/cm^2)$</th>
<th>$E_{corr} (V)$</th>
<th>$CR (mmpy)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetic acid concentration (ppm)</td>
<td>Acetic acid concentration (ppm)</td>
<td>Acetic acid concentration (ppm)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>1 kmol/m³ MEA</td>
<td>108.00</td>
<td>108.02</td>
<td>108.09</td>
</tr>
<tr>
<td>3 kmol/m³ MEA</td>
<td>130.00</td>
<td>130.04</td>
<td>130.18</td>
</tr>
<tr>
<td>5 kmol/m³ MEA</td>
<td>160.00</td>
<td>160.09</td>
<td>160.29</td>
</tr>
</tbody>
</table>
Table 4.12: Speciation of aqueous MEA-CO$_2$ solution (80°C with 0.20 mol CO$_2$/mol MEA)

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>1.0 kmol/m$^3$ MEA</th>
<th>3.0 kmol/m$^3$ MEA</th>
<th>5.0 kmol/m$^3$ MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetic acid concentration (ppm)</td>
<td>Acetic acid concentration (ppm)</td>
<td>Acetic acid concentration (ppm)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>MEA</td>
<td>2.46E-02</td>
<td>2.46E-02</td>
<td>2.44E-02</td>
</tr>
<tr>
<td>MEAH$^+$</td>
<td>8.16E-03</td>
<td>8.15E-03</td>
<td>8.08E-03</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>1.59E-11</td>
<td>1.59E-11</td>
<td>1.59E-11</td>
</tr>
<tr>
<td>MEACOO$^-$</td>
<td>7.94E-03</td>
<td>7.93E-03</td>
<td>7.86E-03</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>1.88E-04</td>
<td>1.88E-04</td>
<td>1.88E-04</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.76E-07</td>
<td>3.76E-07</td>
<td>3.75E-07</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>4.68E-06</td>
<td>4.68E-06</td>
<td>4.68E-06</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>1.54E-05</td>
<td>1.54E-05</td>
<td>1.54E-05</td>
</tr>
</tbody>
</table>
5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

A mechanistic corrosion model for carbon steel in the MEA-based CO₂ absorption process was successfully developed. The developed model was verified with the corrosion data obtained from various literature sources. Its predictive capacity was greater than the previous mechanistic corrosion model in that the developed model has the capacity to predict corrosion rates in aqueous MEA-CO₂ environments that contain dissolved O₂ and heat-stable salts and with the presence of FeCO₃ film on the metal surface. The developed model was proven to have the capacity to predict changes in corrosion behaviour due to changes in operating conditions of the CO₂ absorption process. The following are important findings obtained from the model simulations in this thesis:

- The use of the vapour-liquid equilibrium e-NRTL sub-model in the developed corrosion model yields higher accuracy for corrosion prediction compared to the use of the Kent-Eisenberg sub-model.
- H₃O⁺ contributes the least to the corrosion in aqueous MEA-CO₂ environments compared to other tested oxidizing agents, including H₂O and HCO₃⁻.
- Variations in solution temperature alter kinetics of both types of corrosion reactions (i.e., iron dissolution and reduction of oxidizing agents) with no changes in corrosion mechanism. HCO₃⁻ contributes the most to the changes in corrosion kinetics at higher temperatures, while H₂O contributes the most at lower temperatures.
Variations in CO$_2$ loading alter kinetics of the reduction of oxidizing agents but not that of iron dissolution. HCO$_3^-$ contributes the most to the changes in corrosion kinetics compared to the other tested oxidizing agents.

Variations in MEA concentration affect corrosion in lower magnitudes than the variations in temperature and CO$_2$ loading. The MEA concentration effects can result from all of the tested oxidizing agents.

The presence of dissolved O$_2$ and acetic acid (tested as the HSSs) in aqueous MEA-CO$_2$ environments do not affect corrosion of carbon steel due to their quantity and electrode kinetics characteristics.

5.2 Recommendations for future work

Corrosion in aqueous MEA-CO$_2$ systems is a wide area of study in which there is scope for further research. The present work can be expanded as suggested below:

- Inclusion of protonated amines as oxidizing agents and studying their effect on the corrosion rate.

- This model has been developed for MEA-based operations, but it can be extended to any alkanolamine, provided all the vapour-liquid equilibrium data are available.

- In this work, a few electrochemical parameters were regressed from the literature, but fundamental studies of kinetics of the electrochemical reactions could help to achieve more accurate results.

- Inclusion of other types of heat-stable salts (such as oxalate and formate) needs to be studied if the kinetics data for the reduction of these salts are available.
REFERENCES


APPENDIX A

REGRESSION RESULTS FOR DETERMINING OPEN CIRCUIT POTENTIAL (E)

The value of open circuit potential (E) was regressed from data obtained from Veawab (2000) and Soosaiprakasam and Veawab (2008). ‘E’ showed dependence on both CO₂ loading and temperature but whereas the dependence on the CO₂ loading was higher (Refer Table A.1). So the value of E was regressed as a function of CO₂ loading (shown in Figure A.1) and the equation obtained is shown below (Equation A.1).

\[ E = 0.116 \times \alpha_{CO_2} - 0.6506 \]  \hspace{1cm} (A.1)

When multiple linear regression was done to fit the data as a function of both temperature and CO₂ loading, the sum of errors (R²) was 0.76. The equation obtained with multiple linear regression is shown below (Equation A.2).

\[ E = -0.67 + 0.129 \times \alpha_{CO_2} + 0.000212 \times t \]  \hspace{1cm} (A.2)

Therefore, in the developed corrosion model, E was assumed to be independent of temperature, as it showed greater dependence on CO₂ loading where the R² value was approximately 0.98.
Table A.1: Open circuit potential (E) at various CO$_2$ loading and two different temperatures

<table>
<thead>
<tr>
<th>CO$_2$ loading (mol CO$_2$/mol MEA)</th>
<th>Temperature (°C)</th>
<th>Open circuit potential – $E$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80</td>
<td>-0.649</td>
</tr>
<tr>
<td>0.1</td>
<td>80</td>
<td>-0.639</td>
</tr>
<tr>
<td>0.2</td>
<td>80</td>
<td>-0.629</td>
</tr>
<tr>
<td>0.3</td>
<td>80</td>
<td>-0.619</td>
</tr>
<tr>
<td>0.4</td>
<td>80</td>
<td>-0.599</td>
</tr>
<tr>
<td>0</td>
<td>30</td>
<td>-0.674</td>
</tr>
<tr>
<td>0.1</td>
<td>30</td>
<td>-0.637</td>
</tr>
<tr>
<td>0.2</td>
<td>30</td>
<td>-0.639</td>
</tr>
<tr>
<td>0.3</td>
<td>30</td>
<td>-0.629</td>
</tr>
<tr>
<td>0.4</td>
<td>30</td>
<td>-0.609</td>
</tr>
</tbody>
</table>
Figure A.1: Regression of open circuit potential (E) as a function of CO$_2$ loading

$$E = 0.116 \times \alpha_{CO_2} - 0.6506$$