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MODELLING THE ROLE OF ACIDIC SPECIES ON CO_2 CORROSION PREDICTION

MOHAMAD AZWAN BIN MOHD GHAZALI

Report submitted in partial fulfilment of the requirements for the award of Bachelor of Mechanical Engineering

Faculty of Mechanical Engineering UNIVERSITI MALAYSIA PAHANG

JUNE 2013

UNIVERSITI MALAYSIA PAHANG FACULTY OF MECHANICAL ENGINEERING

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I hereby declare that the work in this report is my own except for quotations and summaries which have been duly acknowledged. The report has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedicated to my father, Mr.Mohd Ghazali bin Md Noh, my beloved mother, Mrs.Che Gayah binti Md Arof, my broters and sisters, and last but not least to all my fellow friends

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ABSTRACT

The presence of acetic acid (HAc) in formation water of oil and gas reservoirs has long been suspected to contribute to the CO_2 corrosion rate. The prediction model has been developed based on mechanistic theories which is involved the fundamental of electrochemical reaction for partial cathodic and anodic process on the metal surface. By using this prediction model, the corrosion behaviour of carbon steel in the presence of HAc in combination with pH and temperature at simultaneously has been investigated. The corrosion prediction model was verified by comparing calculated corrosion rates with the corrosion data obtained from various literature sources and corrosion prediction software's and it's showed a good relationship in correlation and regression relationship and provided high precision in standard error estimation.From the findings, electrochemical measurements have shown that the presence of acetic acid affects predominantly the cathodic reaction and increased the rate of corrosion, which is agreed well with the general understanding of the CO_2 corrosion process.

ABSTRAK

Kehadiran asid asetik (HAc) dalam pembentukan air takungan minyak dan gas telah lama disyaki menyumbang kepada kadar hakisan CO_2 . Model ramalan telah dibangunkan berdasarkan teori mekanistik yang mana melibatkan asas tindak balas elektrokimia untuk proses separa katod dan anod pada permukaan logam. Dengan menggunakan model ramalan ini, kelakuan kakisan keluli karbon dengan kehadiran HAc dalam kombinasi dengan pH dan suhu pada masa yang sama telah disiasat. Model ramalan kakisan ini telah disahkan dengan membandingkan pengiraan kadar hakisan dengan data karat yang diperolehi daripada pelbagai sumber kesusasteraan dan perisian ramalan kakisan dan ia menunjukkan hubungan yang baik dalam hubungan regresi dan member ketepatan yang tinggi berdasarkan anggaran piawai ralat. Daripada hasil kajian, ukuran elektrokimia telah menunjukkan bahawa kehadiran asid asetik menjejaskan kebanyakannya tindak balas katod dan peningkatan kadar hakisan, yang mana telah bersetuju dengan pemahaman umum proses hakisan yang CO_2 .

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LIST OF SYMBOLS

α _c	Symmetry Factor
η	Overpotential
ΔH	Enthalpy of Activation
b	Tafel Slope
E _{corr}	Corrosion Potential
Erev	Reversible Potential
f	Flow Factor
F	Faraday Constant
<i>i</i> _a	Activation Current Density
<i>i</i> _{corr}	Corrosion Current Density
i _{lim}	Limiting Current Density
i _o	Exchange Current Density
i_o^{ref}	Reference Exchange Current
k_m	Mass Transfer Coefficient
k _r	Rate of Reaction Constant
r^2	Coefficient Determination
T _{ref}	Reference Temperature

LIST OF ABBREVIATIONS

aq	Aqueous Phase
CO_2	Carbon Dioxide
CR	Corrosion Rate
DW	De Waard
ECE	Electronic Corrosion Engineer
Fe	Iron
Fe ₃ C	Iron Carbide
FeCO ₃	Iron Carbonate
FeS	Iron Sulfide
g	Gas Phase
H_2	Hydrogen
HAc	Acetic Acid
mmpy	Millimeters per Year
PPM	Part per Million
R	Universal Gas Constant
S	Supersaturation
Т	Temperature

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In the formation water of oil and gas reservoirs the presence of organic acid species has long been suspected to contribute to the CO_2 corrosion rate. The effect has been considered to be secondary until new discoveries about the 80's and 90's the presence of acetic acid species showed the increased corrosion rate in CO_2 environment.

Model CO_2 corrosion prediction has been developed in many ways. These CO_2 corrosion prediction models can be divided into three categories that are empirical, semi-empirical and mechanistic models (Lee, 2004). Some recent models have been based on the underlying empirical CO_2 corrosion process. It has been done several studies on the empirical that occurs on carbon steel related to CO_2 corrosion. In the process of corrosion involves electrochemical, chemical processes and the processes transfer times occur simultaneously.

Prediction of corrosion behavior is an important concern in oil and gas industries. In design stage, corrosion prediction is used to select materials for construction and to maintain operations integrity. The prediction is also used to find better condition and improve the utilities. There are many CO_2 corrosion prediction models developed by industries. Such prediction models, basically, give accurate predictions. However, it has to be emphasized that those prediction model is valid only in certain conditions. It is not surprised when the same data will give different results. Thus, it is needed a further study of each model developed by industries to gain insight understanding of the model backgrounds (Yuli, 2010).

1.2 PROBLEM STATEMENT

The actual condition affecting CO_2 corrosion carries difficulty in the experiment and simulation to predict corrosion rate based on empirical method. By using empirical method, modeling interactions effects between the species and the operational conditions at the same time, require not only a large number of experiment but also lack in statistical analysis and graphical data that support the conclusion. Besides, there are limited corrosion prediction model in the literature to compute the mixed variables simultaneously and no expressions were previously developed to express the corrosion model in CO_2 environment.

Thus, mechanistic modeling and simulation should be prepared because extreme condition in actual situation make difficult to do experiments. For that reason, it is important to develop the CO_2 corrosion model that supported by either solid fundamental theory or supported analytical background which can express relationship among the operational conditions (temperature and pH) and reservoir species (HAc).

1.3 OBJECTIVES

The aim of this study is to enhance a better understanding of the influence of HAc on corrosion in CO_2 environment, and their roles in contributing to corrosion rate at the same time. The work that will be used to accomplish the following specific objectives:

- (i) Study the effects of acetic acid in combination with pH and temperature at the simultaneously steel corrosion in CO₂ environment.
- Modelling CO₂ corrosion within the presence of acetic acid based on mechanistic theories.

 (iii) Make comparison between model prediction and corrosion prediction software's available in industries, and experimental data.

1.4 SCOPES

The study investigated corrosion rate in CO₂simulated environmental containing HAc in several pH and temperature. Discussion of various parameters in the model related to the corrosion mechanism was based on the industrial corrosion software and available published experimental data. The scopes can be summarized as:

- (i) The range of HAc concentration used in this study is 0-200 ppm.
- (ii) The temperature and pH range tested in this study is $25 \ ^{0}C 85 \ ^{0}C$ and pH 4 pH 6.
- (iii) The corrosion model had been developed is based on mechanistic theories.
- (iv) The corrosion prediction has been verified with previous experimental data and corrosion prediction software's which are Freecorp, Cassandra, NORSOK and ECE.

CHAPTER 2

LITERATURE REVIEW

2.1 CO₂**CORROSION**

In the oil and gas industry, carbon dioxide corrosion of carbon steel is a major problem. The presence of dry CO_2 gas or only oil is itself not corrosive. However, corrosion and subsequent failures cause by the contact of the surface of the metal with the aqueous phase. The work done in the past few decades have made the basic CO_2 corrosion reactions well understood and accepted (Nesic et al. 1995). The main chemical reactions include CO_2 dissolution and hydration to form carbonic acid,

$$\operatorname{CO}_2 g \Leftrightarrow \operatorname{CO}_2 (\operatorname{aq})$$
 (2.1)

$$CO_2(aq) + H_2O \Leftrightarrow H CO_3$$
 (2.2)

Carbonic acid dissociates to form bicarbonate which also dissociates to give carbonate and hydrogen ions.

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \tag{2.3}$$

$$HCO_3^{-} \Leftrightarrow H^+ + CO_3^{-2-} \tag{2.4}$$

The overall electrochemical reaction of CO₂ corrosion is given by:

$$Fe + CO_2 + H_2O \Leftrightarrow FeCO_3 + H_2 \tag{2.5}$$

Thus, CO_2 corrosion can form the formation of a corrosion product, $FeCO_3$ which when initiated can form a protective or a non-protective scale depending on

conditions of the environment. The electrochemical reactions at the steel surface include the anodic dissolution of iron:

$$Fe \to Fe^{2+} + 2e^{-} \tag{2.6}$$

and two chatodic reactions. The chatodic reactions are proton reduction reaction and the direct reduction of carbonic acid:

$$2H^+ + 2e^- \to H_2 \tag{2.7}$$

$$2H_2 CO_3 + 2e \rightarrow H_2 + 2HCO_3$$
(2.8)

Although more than three decades of tough research, it is still unknown which of the two reactions actually exist on the surface. Therefore, many have taken that the total currents of the two reactions is from the net cathodic current. It has been suggested that at higher pH the direct reduction of bicarbonate ion becomes important. Having outlined the mechanism, one can anticipate that there are many environmental factors such as solution chemistry, pressure, pH, flow velocity, temperature etc., and affect the uniform CO_2 corrosion rate of mild steel. The formation of the corrosion product scales due to the environmental conditions could also have a significant effect on the corrosion rate of the metal. Some of the important factors that the effect CO_2 corrosion in the oil and gas industry will be discussed the next subchapters.

2.2 FACTORS AFFECTING CO₂ CORROSION

2.2.1 The Effect of pH

In corrosion process, pH is one of the important parameters. Usually, corrosion rate will be lower at higher pH. The pH of a wet gas in CO₂ system is often assumed as equal to the saturation of FeCO₃ precipitation. The pH can also be calculated by involving the concentration of species such as CO₂, H₂CO₃, HCO₃⁻, CO₃²⁻, H₂S, HS⁻, S²⁻, H⁺, OH⁻, H₂O, Fe²⁺, CH₃COOH (acetic acid), CH₃COO⁻. Sometimes, pH calculation can be done by incorporating the FeCO₃ precipitation

kinetics. The pH is also influenced by H⁺ ions concentration, temperature, pressure, and ionic strength, thus pH in real conditions can be different from the calculated pH. Dissolved iron bicarbonate as the initial corrosion product will also contribute to increase the pH of solution.

An increase in pH will cause the film to become thicker, more dense and protective. Passivity of carbon steel is in the pH range of the carbonate/bicarbonate formation. Hoffmeister and Scheidacker (2004) recorded that at pH 5.8 the corrosion rate did not reduce significantly, which reflected a relatively porous, detached and unprotective scale. This may be related to fast formation of the scale.

pH of the fluid is calculated as initial pH of water and CO₂ only, which is expressed in the following:

$$pH_{CO_2} = 3.71 + 0.00417T - 0.5LOG(pCO_2)$$
(2.9)

The saturation pH is calculated as the smallest value according to the equation below:

$$pH_{ads} = 1.36 + 1307/T + 273 - 0.17 Log(fCO_2)$$
 (2.10)

2.2.2 The Effect of Temperature

Temperature will affects the conditions for formation of the protective carbonate layers and affects corrosion rate in a different manner. The solubility of FeCO₃ is high and the precipitation rate is slow at temperatures below than 60 °C, so that protective films will not form until the pH is increased more than solubility product (Hoffmeister and Scheidacker, 2004). Above 60 °C the solubility of FeCO₃ decreases and the protectiveness of the iron carbonate layer increases with temperature; thus, the corrosion rate is reduced.

Temperature affects corrosion rate in a different manner, at temperatures below 60 °C, hydrogen evolution acts as the rate determinating step. At temperatures

above 100 °C, there is a direct reaction between steel and water (Schikorr reaction) to produce dense and protective films (Schmitt and Horstemeier, 2006) but carbon steel will face problems with pitting and stress corrosion cracking (Halvorsen and Sontvedt, 2006) because, carbonate film is formed rapidly at 80 °C.

The protective film will form at the temperatures greater than 60 °C, called the scaling temperature. The temperature where corrosion rate reaches a maximum value is called scaling temperature. At this temperature, Fe concentration forms at the metal surface to produce protective film. The scaling temperature is affected by gas flow rate and pH, where higher flow rate and lower pH will produce higher scaling temperature. The correlation between scaling temperature and partial pressure of CO₂ is expressed as in Equation 2.24 below (Halvorsen and Sontvedt, 2006):

$$T_{\text{scale}} = 2400/(6.7 + 0.6 \text{Log}(\text{fCO}_2))$$
(2.11)

Where T_{scale} is scaling temperature, fCO₂ is a correction factor for T defined as:

$$F_{\text{scale}} = (2400/\text{T}) - 0.6 \text{Log}(\text{fCO}_2) - 6.7 \tag{2.12}$$

What is Fscale.

• F_{scale} is set to 1 if formation water is present or when a superficial gas velocity is above 20 m/s.

2.3 EFFECT OF ACETIC ACID

Since the 1980's, the influence of HAc on the corrosion rate of carbon steel in oilfield brines containing CO_2 is well documented in literature and has been the subject of many studies. As early as 1983, presence of acetic acid in the brine will increase the corrosion rate of carbon steel significantly have been reported by Crolet and Bonis (1983). The effect of HAc on CO_2 corrosion is to either increase or decrease corrosion strongly depending on pH and temperature. However, research on the effect of HAc in CO_2 system is still limited. In the literature, the effects of those factors are debatable and sometime contradictory. For that reason, it is important to

improve the understanding the effect $ofCO_2$ and Acetic Acid on carbon steel corrosion (Yuli, 2010).

2.3.1 Chemistry of Acetic Acid

CH₃COOH is the structural formula for Acetic Acid (HAc). It is a weak acid that does not completely dissociate in aqueous solutions. It has been reported that free acetic acid could increase the corrosion rate (Martin, 2009). The mechanism of dissolved acetic acid in CO₂ corrosion can be correlated to the undissociated HAc concentration present in the brine (George and Nesic, 2004). Laboratory tests have validated that dissociated acid can alter the corrosion rate in CO₂ environment conducted by Garsany et al. (2004). The dissociation of HAc in water occurs according to the equations below (Nafday, 2004):

$$HAc_{(aq)} + H_2O \iff H_3O^+_{(aq)} + A^-_{(aq)}$$

$$(2.13)$$

Then the aqueous HAc partly dissociation into hydrogen and acetate ions:

$$HAc (aq) \iff H^{+}(aq) + Ac^{-}(aq)$$
(2.14)

$$\mathrm{H}^{+}(\mathrm{aq}) + \mathrm{e}^{-} \longrightarrow \frac{1}{2} \mathrm{H}_{2}(\mathrm{g}) \tag{2.15}$$

The equilibrium constant for HAc dissociation, K_{HAc} is:

$$K_{HAc} = \frac{\left[H^{+}\right]\left[Ac^{-}\right]}{\left[HAc\right]}$$
(2.16)

The overall corrosion reaction for carbon steel with the presence of acetic acid in the CO_2 environment is:

$$Fe + H_2CO_3 \longrightarrow FeCO_3 + H_2$$
(2.17)

 $Fe + 2HAc \rightarrow Fe(Ac)_2 + H_2$ (2.18)

The dependency of acetic acid equilibrium constant on temperature is expressed in the following formula (Nafday, 2004):

$$K_{\text{HAc}} = 10^{-(6.66104 - 0.0134916*Tk + 2.37856*10 - 5*Tk2)}$$
(2.19)

The rate of reaction involving CO_2 and acetic acid is believed to be limited by the preceding slow hydration of CO_2 (Nafday, 2004):

$$CO_2 + H_2O \rightarrow H_2CO_3 (aq) \tag{2.20}$$

The reaction mechanism and kinetics of the overall reactions are influenced by acetic acid concentration, CO₂ partial pressure, pH, and water contaminants.

2.3.2 Corrosion Mechanism of Acetic Acid

The effect of acetic acid on the corrosion of mild steel has been studied by several of researchers. Crolet et al. (1999) stated that CO_2 result of acidification also can cause the partial re-association of anions. Such weak acids will raise the limiting diffusion current for cathodic reduction then increase the oxidizing of H⁺. The presence of this acid also will tend to solubilise the dissolving iron ions.

The electrochemical behavior of carbon steel on the additions of HAc has shown that the presence of HAc in the solution decreases pH, increases the cathodic limiting current, and decreases E_{corr} . In this condition, the cathodic reaction will become the rate determining step. The limitation is due to diffusion of proton to the steel surface rather than electron transfer. In general, it has been agreed that HAc can increase the cathodic reaction rate (hydrogen evolution reaction) if the concentration is significant.

The study of the effect of acetate ions on the rates and mechanisms of corrosion by using a rotating disc electrode (RDE) on surfaces free film using voltametry, have been published by Garsany et al. (2002). They found a figure that can be attributed to reduction of HAc and hydrogen ion on steel surface. They argued

that as HAc dissociation can happen very quickly, it is not possible to differentiate the direct HAc reduction from reduction of hydrogen ions at the electrode surface. They argued that the increase rate of corrosion for HAc in CO_2 environment must be proportional to the undissociated acetic acid concentration in the brine. They emphasized that the electrochemistry of acetic acid at steel cannot be distinguishable from free proton because of its rapid dissociation. This conclusion was recorded after they used a rotating disk electrode to study the effect of Acetate ions on the rate of corrosion usingcyclic voltammetry.

The work of Crolet et al. (1999) suggested that the presence of HAc will inhibited the anodic (iron dissolution) reaction. Have conducted an experiment on low HAc concentrations (6 - 60 ppm). They found that the presence of HAc increased rate of corrosion due to an inversion in the bicarbonate/acetate ratio. At this inversion point, HAc is the main source of acidity since it is the predominant acid compared to carbonic acid.

2.3.3 Effects of Acetic Acid on Carbonate Film Formation

An investigation the role of HAc in corrosion rate on film formation was done by Crolet et al. (1999). The experiment succeeded in creating a film on the steel surface after exposing the specimen for three days at a temperature of 80 $^{\circ}$ C and high pH. He used LPR and EIS corrosion measurement methods to identify the effect of anodic reactions and HAc on the cathodic of CO₂ corrosion. He concluded that HAc affects the limiting current and do not affect the charge transfer mechanism of cathodic reaction. HAc acts as a source of hydrogen ions and HAc needs an activation time for its actionat room temperature (22 $^{\circ}$ C).

The role of acetic acid/ion can retard the time to reach scaling temperature have been observed by Vennesa et al. (2007). They related this effect as an increase in the corrosion area. This argument was supported by experimental observations which showed a reduction in corrosion rate in experiments without Acetate ion. There was proof that Acetate ion can attack existing iron carbonate films and make them thinner. The pitting corrosion will happen if the attack was localized, because of local film would be thinning. The results on the role of acetate in CO2 corrosion was by published Hedges and McVeigh (1999). Experiments was performed using rotating cylinder electrodes, both sodium acetate and HAc as a source of acetate ions in various media (two synthetic oilfield brines and 3% NaCl). Both sources of acetate ions shown to increase the corrosion rate, while sodium acetate increased the pH and acetic acid decreased it. The formation of thinner iron carbonate films will cause the increased corrosion rates since acetate ions have the ability to form iron acetate and remove iron away from the steel surface.

2.4 CORROSION PRODUCT FILM FORMATION

During the corrosion process, the types of corrosion product film formed on the surface of the metal will strongly effect the CO_2 corrosion of a metal. The protectiveness, stability, precipitation rate and the adherence of these films decide the result of (localized/ uniform) and the corrosion rate. Corrosion films can be divided into main elements that are Iron carbide (Fe₃C), Iron carbonate (FeCO₃) and Iron sulfide (FeS).

2.4.1 Iron Carbide (Fe₃C)

Iron carbide do not dissolved component of the mild steel, which is left behind from the corrosion process. It is conductive, very porous and non-protective. Iron carbide films can significantly affect the corrosion process by either decreasing the corrosion rate by acting as a diffusion barrier or increasing the corrosion due to galvanic coupling of the film to the metal, increase in the true specimen surface area and acidification of the solution inside the corrosion product film (Lee, 2004).

2.4.2 Iron Carbonate (FeCO₃)

The reaction for formation of solid iron carbonate is given by (Lee, 2004) :

$$\operatorname{Fe}^{2+} + \operatorname{CO}_3^{2-} \Leftrightarrow \operatorname{FeCO}_3(s)$$
 (2.21)

The precipitation of solid iron carbonate occurs when the product of concentrations of Fe^{2+} and CO_3^{2-} exceed a certain limit known as the solubility limit. However, the rate of precipitation of iron carbonate is so slow that most often the precipitation kinetics comes into consideration rather than the thermodynamics. The equation for the rate of precipitation of the iron carbonate (R _{FeCO3(S)}) is given as:

$$R_{FeCO3(S)} = \frac{A}{V} f(T). Ksp_{FeCO_3}. f(S_{FeCO_3})$$
(2.22)

Where Supersaturation S is defined as:

$$S_{FeCO_3} = \frac{c_{Fe^{2+}}c_{CO_3^{2-}}}{Ksp_{FeCO_3}}$$
(2.23)

With A/V = the surface area-to-volume ratio and Ksp_{FeCO_3} = solubility limit of FeCO₃ Since CO_3^{2-} ion concentration is dependent on the pH, it can be assumed that:

$$S = f (Fe^{2+}, pH)$$
 (2.24)

When steel surface precipitates by the iron carbonate, the corrosion rate decrease by presenting a diffusion wall for the species involved in the corrosion process and also blocking the steel portion and preventing electrochemical reactions from occurring.

The temperature and supersaturation is most important factors in disturbing the precipitation of iron carbonate.

2.4.3 Iron Sulfide (FeS)

The formation of iron sulfide only occurs in the presence of H_2S . The reaction for formation of solid iron carbonate is given by (Lee, 2004):

$$\operatorname{Fe}^{2+} + \operatorname{S}^{2-} \Leftrightarrow \operatorname{FeS}(s)$$
 (2.25)

It has been assumed that the precipitation of solid iron sulfide occurs when the product of Fe^{2+} and S^{2-} concentrations go beyond the solubility limit of FeS. The equation for the rate of precipitation of the iron carbonate ($R_{FeS(S)}$) is given as:

$$R_{FeCO3(S)} = \frac{A}{V} f(T). Ksp_{FeS}. f(S)$$
(2.26)

Where Supersaturation S_{FeS} is defined as:

$$S_{FeS} = \frac{c_{Fe^{2}} + c_{S^{2}}}{K_{Sp_{FeS}}}$$
 (2.27)

With Ksp_{FeS} = solubility limit of FeS

It is assumed that iron sulfide affects the CO_2 corrosion in the same way as iron carbonate (by being a diffusion barrier and surface blockage). However, iron sulfide films are semi-conductive; in some cases it has been observed that the presence of iron sulfide may lead to localized corrosion and the cause is still not clear (Lee, 2004).

2.5 CORROSION PREDICTION MODELS

Models to calculate corrosion rate in CO_2 gas environments have many different approach. Each model predicts corrosion rate in different manner. They used parameters and formula based on literatures and their own experience. There are many equations that give certain predictions of corrosion rates for CO_2 environments. These include the de Waard and Milliam (1975) and it's many subsequent derivatives, Sun and Hong, (2002), Vera and Hernandez (2006) and Nesic et al. (2002). All of these were developed from different systems and assumptions.

During the last decade, the models were developed by involving limited variables. Recently, new variables are indicated having contributions in corrosion models. For examples, it has been demonstrated that flow can enhance the corrosion process. Based on that theory, the models tried to cover these factors de Waard et al (1995). The other factors, still in investigations, are effects of scaling product, effects of oil properties, inhibitors, and other species contaminants (H_2S , HAc, and naphthanic acid). The work done by de Waard and Milliam (1975) was carried out in stirred beakers at atmospheric conditions with carbon dioxide gas being bubbled through water. The equation they developed showed solely the effects of chemistry on the maximum corrosion rate and these give a reasonable estimate of the corrosion rate in a stagnant system with no corrosion product being present.

In subsequent considerations, many factors were added and de Waard et al. (2001) provided correction factors that which to account for the gas fugacity, the protective iron carbonate films formation, the effect of ferrous ions on the pH, the presence of oil, and the effect of condensing water.

2.6 COMMERCIAL CORROSION PREDICTION MODEL

2.6.1 ECE (Electronic Chemical Engineering)

ECE program software calculates corrosion rate based on the modified de Waard and Milliam (1975) method. **ECE** model includes oil wetting correlation based on field correlation. For low horizontal flow velocities < 1 m/s, the F_{oil} =1. ECE proposes a corrosion prediction expression as follows:

$$V_{cor} = \frac{1}{\frac{1}{V_r} + \frac{1}{V_m}}$$
(2.28)

Where, V_r is corrosion reaction and V_m is mass transfer effect. The corrosion reaction can be calculated using the following equation:

$$\log V_r = 4.84 - \frac{119}{t + 273} + 0.581\log(fCO_2) - 0.34(pH_{act} - pH_{CO_2})$$
(2.29)

And the mass transfer variable is defined as:

$$V_m = 2.8 \frac{U^{0.8}}{d^{0.2}} fCO_2$$
(2.30)

Where; T is temperature ($^{\circ}C$), pCO₂ is pressure (bar), fCO₂ is fugacity CO₂ (bar), pHCO₂ is the pure water pH saturated with CO₂ at prevailing pressure and temperature.

The fugacity of CO_2 is similar to its partial pressure, but corrected for nonideality of CO_2 at high pressure and temperature. The mass transfer represents the main part of the dependence on pipe diameter d and flow velocity U.

2.6.2 C Cassandra (DWM 93)

Cassandra is a model developed based on the experiences of de Waard and Milliam (1975). The input includes pH, CO_2 concentration, temperature, and water contaminant. This model does not consider scaling temperature. The user must set an assumption of the scaling temperature. The basic formula to calculate corrosion rate is expressed as in Equation 2.51 below:

$$\log(V_r) = 5.8 - 1710/T + 0.67\log(P_{CO_2})$$
(2.31)

This model has important aspects which influence rate of corrosion, namely corrosion inhibitor availability and corrosion risk categories. The model also accounts for the presence of acetate in water as acetic acid.

The major input to the model are: CO_2 mole %, temperature, total pressure, liquid velocity and water chemistry. Besides that, the model has secondary input, such as hydraulic diameter and glycol concentration, oil type (crude or condensate) and water type (condensed water or formation water). The effect of oil wetting in this model is not included.

2.6.3 NORSOK M-506 Model

The NORSOK standard is owned by Norwegian Oil Industry Association and Federation of Norwegian Manufacturing Industries. The model covers only calculation of corrosion rates where CO_2 is the corrosive agent. The corrosivity, e.g. contamination of O_2 , H_2S etc. is does not include. The model is an empirical model for CO_2 at different CO_2 fugacities, pH, temperatures, wall shear stresses, and temperatures from 20 to $160^{\circ}C$.

The model calculates pH and wall shear stress. The effect of acetic acid is not account for in this model, but it is still valid to predict corrosion rate if the concentration of acetic acid is less than 100 ppm. The corrosion rate is calculated as in the following equation:

$$CR_{t} = K_{t} fCO_{2}^{0.62} x (S/19)^{0.146+0.0324 \log(fCO_{2})} f(pH)t$$
(2.32)

Where CR is the corrosion rate in (mmpy), K_t is the constant for temperature, fCO_2 is the fugacity of CO₂ (bar), S is Wall shear stress (Pa), f(pH)t is the pH factor at temperature.

CHAPTER 3

RESEARCH METHODOLOGY



Figure 3.1: Flow chart methodology

The study can be divided to several steps. The first step is study literature review which is, the historical data variable was identified to find the trending of the CO_2 corrosion model. The second step is setting parameters used to calculate corrosion rate which consider the actual situation. Next step is developed model prediction based on mechanistic theories found in literatures. After that, the corrosion rate was calculated using developed model. In order to evaluate the model performance, the model prediction was verified with previous experimental data and corrosion prediction software's. The model performance was stated by the value of standard error estimation, coefficient determination and correlation that represents the accuracy and precision of the model compared to the data provided. Lastly, the results are analyzed and discussed before preparing the report. The steps are as shown in Figure 3.1 above.

3.1 MODEL DEVELOPEMENT

Corrosion model have been designed and developed in order to obtain the result that can be evaluated to predict corrosion rate after the factors that affecting CO_2 corrosion are identified. Variables involved are concentration of HAc, temperature, and pH. The model was developed base on mechanistic theories which is involved the fundamental of electrochemical reaction. From the open literature, parameters for the different equations, such as diffusion coefficients, reaction rate constants, and equilibrium constants are obtained.

In order to developed model that can predict corrosion rate, the character of the measured anodic and cathodic reactions must be found. The concentration HAc can influence the cathodic reaction in CO_2 corrosion according to at least two possible circumstances. The first is through dissociation, HAc acting as a source of hydrogen ions and the second is HAc being directly reduced on the metal surface. The current results as well as those recently presented by Sun et al. (2003) seem to agreed the first situation while some of following studies at high pressure and temperature as well as the work of Garsany et al. (2002) appear to agreed the second situation. Besides, electrochemical models relating both situations were made and successfully fitted to the data of experimental providing more evidence that it is very

difficult to differentiate the reduction of hydrogen ions from direct HAc reduction at the electrode surface. This is not surprising because the same dilemma related to the reduction of H_2CO_3 demanding a definitive answer since the mid-seventies.

In the following subchapters it will be assumed that HAc acts only as a source of hydrogen ions and therefore, only a slight modification needs to be made to the hydrogen ion reduction equation related to the calculation of the limiting current, compared to the electrochemical model of Nesic et al. (1996). In anodic reaction only one reaction is assumed to be present, which is the dissolution of iron.

3.1.1 Hydrogen Ion Reduction

In order to find the effect of mass transfer and charge transfer on hydrogen ion reduction, the rate equation for the cathodic part is used (West, 1964):

$$i_{(H)} = i_{o(H)} \left(\frac{\left[H^+ \right]_s}{\left[H^+ \right]_p} \exp \left(\frac{\alpha_c F}{RT} \eta \right) \right)$$
(3.1)

Where $i_0(H^+)$ represent the exchange current density in A/m², $[H^+]_s$ and $[H^+]_b$ represent the hydrogen ions concentrations at the metal surface and bulk, both in mol/m³, α_c represent the symmetry factor, and η represent the overpotential from the reversible potential in V. The difference between the applied potential and the reversible potential is the overpotential. (E_{rev}) the reversible potential for hydrogen reduction is given by:

$$E_{rev(H^+)} = -\frac{2.303RT}{F} pH - \frac{2.303RT}{2F} \log P_{H_2}$$
(3.2)

Where P_{H_2} represent the partial pressure of hydrogen in atm. In the experiments, the partial pressure of hydrogen was assumed to be zero. From the mass transfer equation, the concentration of surface hydrogen ion can be found as:

$$i_{(H^+)} = k_m F([H^+]_{b} - [H^+]_{s})$$
(3.3)

Where k_m represent the hydrogen mass transfer coefficient in m/s. The final current density vs voltage equation for H⁺ reduction can be found from substitution of Equation (3.3) into (3.1) and solving for $[H^+]_s$ yields:

$$\frac{1}{i_{(H^+)}} = \frac{1}{i_{a(H^+)}} + \frac{1}{i_{\lim(H^+)}^d}$$
(3.4)

Where $i_{a(H^+)}$ represent the activation current density in A/m² and $i_{lim(H^+)}^{d}$ represent the diffusion limiting current density in A/m². The activation current density is found as:

$$i_{a(H^+)} = i_{o(H^+)} \times 10^{-\frac{\eta}{b_c}}$$
(3.5)

Where $i_{0(H^+)}$ represent the exchange current density in A/m² and b_c is the cathodic Tafel slope in V/dec. The exchange current density and temperature dependence of the cathodic Tafel slope is found as:

$$\dot{i}_{o} = \dot{i}_{oref} \left(\frac{c_{H^{+}}}{c_{H^{+}ref}}\right)^{a_{1}} \left(\frac{c_{CO_{2}}}{c_{CO_{2}ref}}\right)^{a_{2}} \left(\frac{c_{H_{2}CO_{3}}}{c_{H_{2}CO_{3}ref}}\right)^{a_{3}} \cdot e^{\frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}$$
(3.6)

	i _{oref}	a_1	$C_{H^+ ref}$	<i>a</i> ₂	C _{CO2} ref	<i>a</i> ₃	C _{H2} CO3ref	ΔH	T _{ref}	E _{rev}	b_c
	$\frac{A}{m^2}$		molar		molar		molar	kJ mol	°C	V	V
$2H^+ + 2e^- \to H_2$	0.05	0.5	10 ⁻⁴	0	N/A	0	N/A	30	25	$-\frac{2.3RT}{F}pH$	$\frac{2.3RT}{2F}$
$2H_2 CO_3 + 2e^- \rightarrow$ $H_2 + 2HCO_3^-$	0.06	-0.5	10 ⁻⁵	0	N/A	1	10 ⁻⁴	50	20	$-\frac{2.3RT}{F}pH$	$\frac{2.3RT}{2F}$
$Fe \rightarrow Fe^{2+} + 2e^{-}$	1	1 for $p_{CO_2} < 1$ bar 0 for p_{CO_2} 1 bar	10 ⁻⁴	2 for pH<4 1 for 4 <ph<5 0 for pH>5</ph<5 	0.0366	0	N/A	37.5	25	-0.488	0.03 for pH<4 0.08 for 4 <ph<5 0.12 for pH>5</ph<5

Table 3.1: Parameters in electrochemical for the reactions included in the model which fit the general rate Equation (3.16)

The exchange current density for the temperature dependence is given by:

$$\frac{i_o}{i_o^{ref}} = e^{-\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}$$
(3.7)

Where i_o^{ref} represent the reference exchange current measured at some reference temperature, T_{ref} and ΔH represent the enthalpy of activation in kJ/mol.

3.1.2 Limiting Current for H⁺ reduction

Equation (3.4), the mass transfer limiting current density is calculated by:

$$i_{\lim(H^+)}^d = k_m F \left[H^+ \right]_b \tag{3.8}$$

Where, in static state the mass transfer coefficient, k_m is 1×10^{-4} .

3.1.3 Limiting Current Arising from the Presence of HAc

The chemical reactions could affect limiting currents if a slow chemical reaction precedes the hydrogen ion reduction reaction (Vetter, 1976). He termed this limiting current a "chemical reaction" limiting current. By using HAc as the example, He then derived equations to predict the chemical reaction limiting currents produced in stagnant weak acid solutions. By using the example of carbonic acid as the weak acid, Nesic et al. (1995) have expanded the equations to flowing systems. In case of flowing systems in the presence of HAc, to predict the limiting currents, Vetter's/Nesic's derivation will need to be re-derived with flow taken into account. To predict the reaction limiting current, the final equation is given by:

$$i_{\lim(H^+)} = Fc_b \sqrt{Dk_r [Ac^-]} f$$
(3.9)

Where k_r represents the rate of reaction constant from the dissociation HAc reaction and *f* represent the flow factor, which is given:

$$f = \frac{1 + e^{-2\delta_m/\delta_r}}{1 - e^{-2\delta_m/\delta_r}}$$
(3.10)

Where δ_r and δ_m represent the reaction and mass transfer layer thicknesses, respectively, and are given by:

$$\delta_r = \sqrt{\frac{Dc_b}{v_0}} = \sqrt{\frac{Dc_b}{kc_b}} = \sqrt{\frac{D}{k_r [Ac^-]}}$$
(3.11)

$$\delta_r = \frac{B}{k_m} \tag{3.12}$$

Where v_0 represent the rate of hydrogen production at equilibrium and *D* represent the diffusivity of hydrogen ions in m²/s. HAc could be mass transfer limiting since the HAc limiting currents are not chemical reaction limiting. The mass transfer limiting current density has the similar form as the limiting current density for the hydrogen ion and is found as:

$$i_{\lim(HAc)}^{d} = k_m F[HAc]_{b}$$
(3.13)

Where k_m represent the HAc mass transfer coefficient in m/s and $[HAc]_b$ represent the bulk concentration of HAc.

As it has been discussed above that HAc acting solely as a source of hydrogen ions, then it is only increases the limiting current and not involved in a separate cathodic reaction at the metal surface. For that reason, the limiting current for hydrogen ion reduction, must be corrected to account for HAc transport to the metal surface by modifying Equation (3.4):

$$\frac{1}{i_{(H^+)}} = \frac{1}{i_{a(H^+)}} + \frac{1}{i_{\lim(H^+)}^d + i_{\lim(HAc)}^d}$$
(3.14)

Where the HAc limiting current density is given by the Equation (3.13).

3.1.4 Limiting Current Arising from the Presence of CO₂

Since carbonic acid is also a weak acid like HAc, it would be consistent to assume that it too, would only act as a source of hydrogen ions and add to the limiting current. With this modification, the Equation (3.14) now has the final form:

$$\frac{1}{i_{(H^+)}} = \frac{1}{i_{a(H^+)}} + \frac{1}{i_{\lim(H^+)}^d + i_{\lim(HAc)}^d + i_{\lim(H_2CO_3)}^r}$$
(3.15)

3.1.5 Chemical Reactions

The list of the chemical reactions included in the current version of the model and their equilibrium constants shown Table 3.2. The coefficient of equilibrium reaction rates for reactions accounted in the model shown in Table 3.3.

Table 3.2: Chemical reactions accounted for in the model and their equilibrium constants

	Reaction	Equilibrium constant
Dissolution of	$CO_{2}(g) \rightarrowtail CO_{2}$	$K_{sol} = c_{CO_2} / p_{CO_2}$
carbon dioxide		
Water dissociation	$H_2 0 \stackrel{k_{f,wa}}{\longleftrightarrow} H^+ + OH^-$	$K_{wa} = c_{H^+} c_{OH^-}$
	$k_{b,wa}$	
Carbon dioxide	$CO + HO \rightleftharpoons HCO$	$K_{hy} = c_{H_2CO_2} / c_{CO_2}$
Hydration	$k_{b,hy}$	~ 2 5 2

Table 3.2 continued

Carbonic acid	$H_2CO_3 \stackrel{k_{f,ca}}{\underset{k}{\longrightarrow}} H^+ + HCO_3^-$	$K_{ca} = c_{H^+} c_{HCO_3^-} / c_{H_2CO_3}$
Dissociation	K _{b,ca}	
Bicarbonate anion	$HCO_2^{-} \stackrel{k_{f,bi}}{\longleftrightarrow} H^+ + CO_2^{2-}$	$K_{bi} = c_{H^+} c_{CO_2^{2-}} / c_{HCO_2^{2-}}$
Dissociation	$k_{b,bi}$	
Acetic acid	k _{f,ac}	K = c c / c
dissociation	$HAc \underset{k_{b,ac}}{\longleftrightarrow} HAc^+ + Ac^-$	$H_{HAc} = C_{H^+} C_{Ac^-} + C_{HAc}$

Table 3.3: Equilibrium reactions rate coefficients

Constant	Sources
$K = -\frac{14.5}{10^{-(2.27+5.65\times10^{-3}T_f - 8.06\times10^{-6}T_f^2 + 0.075I)}}$	(Oddo and
$R_{sol} = 1.00258^{-10}$	Tomson, 1982)
$K_{wa} = 10^{-(293,868-0.0737549T_{K}+7.4788 \times 10^{-5} \times T_{K}^{2})}$	(Kharaka et al.,
	1988)
$K_{hy} = 2.58 \times 10^{-3}$	(Palmer and Van
	Eldik, 1983)
$K_{eq} = 387.6 \times 10^{-(6.41 - 1.594 \times 10^{-3} T_f + 8.52 \times 10^{-6} T_f^2 - 3.07 \times 10^{-5} p - 0.0477 \mathcal{U}^{1/2} + 0.118 \mathcal{U})}$	(Oddo and
ca	Tomson, 1982)
$K_{f} = 10^{-(10.61 - 4.97 \times 10^{-3} T_f + 1.33 \times 10^{-5} T_f^2 - 2.624 \times 10^{-5} p - 1.166 t^{1/2} + 0.3466 t)}$	(Oddo and
	Tomson, 1982)
$K_{HA_{R}} = 10^{-(6.66104 - 0.0134916T_{K} + 2.3785610^{-5} \times T_{K}^{2})}$	(Kharaka et al.,
	1988)

Note: in the table above T_c represent the temperature in degrees Celsius, T_f represent the temperature in degrees Fahrenheit, T_K represent the absolute temperature in Kelvin, p is the pressure in psi and I is ionic strength in molar

3.1.6 Anode Reaction

The dissolution of iron in the region of the corrosion potential was assumed to be hence pure Tafel behavior and under activation control.

$$i_{(Fe)} = i_{o,(Fe)} x 10^{\frac{\eta}{b_a}}$$
(3.16)

3.1.7 Implementation of the Model

After implemented the model requires inputs the HAc concentration, pH, and temperature so that the current density for every reaction can be calculated. The potentiodynamic sweep can be predicted by solving for the difference between the total of the cathodic reactions from the anodic reactions once the corrosion potential is known. From the anodic current at the corrosion potential, the corrosion current or rate is can be found.

3.3 MODEL VERIFICATION

Verification is important in order to evaluate the model performance. The results from the prediction model were verified with the previous experimental data found in literature sources and corrosion prediction software's. The corrosion model prediction software that has been used consists of Freecorp, Cassandra, NORSOK and ECE. Models to calculate corrosion rate in CO_2 gas environments have many different approach. Each model predicts corrosion rate in different manner.

3.3.1 Model Validation

Model validation is used to calculate data which referred to proven data. The accuracy and precision of the model is represented as (Yuli, 2010):

(i) Coefficient determination:

Coefficient determination is used to measure of how well observed outcomes are replicated by the model. Coefficient determination (r^2) is defined as:

$$r^{2} = \frac{ss_{regression}}{ss_{total}} = \frac{\sum \left(\stackrel{\wedge}{y} - \stackrel{-}{y_{i}} \right)}{\sum \left(y_{i} - \stackrel{-}{y_{i}} \right)}$$
(3.17)

Where $\bar{y}_i = i^{\text{th}}$ observed response value, $\hat{y}_i =$ mean response and SS = sum of square.

The coefficient of determination or r^2 (goodness-of-fit) and F statistic (statistical significance) can be obtained after scalars SS_r, SS_e, in the matrix form are calculated as follow:

$$SS_{r} = b^{T}X^{T}Y - (1/n)(Y^{T}UU^{T}Y)$$
(3.18)

$$SS_e = Y^T Y - b^T X^T Y$$
(3.19)

$$SS_{total} = Y^{T}Y^{T} - (1/n)(Y^{T}UU^{T}Y)$$
(3.20)

$$r^2 = SS_r / SS_{total}$$
(3.21)

$$F = (SS_r/k)/(SS_e/(n-k-1))$$
(3.22)

(ii) Correlation:

To determine if there is a possible linear relationship between two variables measured on the same subject researchers can use the correlation coefficient. The correlation coefficient for the predicted response is calculated by:

$$S_{xy} = \sum xy - \frac{(\sum x)(\sum y)}{n}$$
(3.23)

(iii) Standard error estimation:

The standard error used to measure the accuracy of predictions. The standard error for the predicted response is calculated by:

$$S_{y(x)} = s\sqrt{x^{(m)'}(x'x)^{-1}x^{(m)}}$$
(3.24)

The variable s is standard deviation of the response while x is the orthogonal matrix and x^{m} is the particular location of response.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 INTRODUCTION

This chapter presents the results and discussions of the effect of acetic acid, temperature, and pH on corrosion in CO_2 environment. The studies carried out in this work included developed the corrosion prediction model based on mechanistic theory. To evaluate the accuracy and precision, the model were compared against literature data from published papers and corrosion model calculated by industrial corrosion software.

4.2 INITIAL IDENTIFICATION OF CORROSION RATE MODEL

Corrosion process can be constructed mathematically from mechanistic theory by using fundamental concepts of electrochemical reactions. The mathematical formulas for describing corrosion process are formed based on several assumptions as described in Chapter 3; the resulting graphs as presented from Figure 4.1 to Figure 4.3. Based on these graphs of corrosion model, the corrosion rate can be predicted due to the difference in concentration of HAc, temperature, and pH.



Figure 4.1: Tafel slope at various concentrations of HAc

Figure 4.1 show the relationship between potential and current density in difference concentration of HAc. The range of HAc concentration is from 0 ppm until 200 ppm. Other conditions that represent the graph is an environment at pH 4, and 25 $^{\circ}$ C in stagnant. From the graph, it is observed that corrosion current (i_{corr}) directly proportional with the concentration of HAc.



Figure 4.2: Tafel slope at different temperature

Figure 4.2 show the relationship between potential and current density in difference of temperature. The range of temperatures is from 25 $^{\circ}$ C to 85 $^{\circ}$ C. Other conditions that represent the graph are an environment at pH 4in stagnant. From the graph, it is observed that corrosion current (i_{corr}) directly proportional with temperature.



Figure 4.3: Tafel slope at varying pH

Figure 4.3 show the relationship between potential and current density in difference of pH. The range of pH is from pH 4 to pH 6. Other conditions that represent the graph are an environment at temperature 25 $^{\circ}$ C in stagnant. From the graph, it is observed that corrosion current (i_{corr}) inversely proportional with pH.

4.3 VERIFICATION WITH EXPERIMENT DATA

The comparison of the model with Hedge's (1999), Che Ismail's (2005) and Nesic's (2007) experimental data are shown in Figure 4.4, Figure 4.5 and Figure 4.6, respectively.



Figure 4.4: Comparison between model and Hedge's experiment data at various concentrations of HAc



Figure 4.5: Comparison between model and Che Ismail's experiment data at various temperatures



Figure 4.6: Comparison between model and Nesic's experiment data at varying pH

Based on this corrosion prediction model, all figures show good agreement between calculated and experimental data. Comparing to Hedge's experiments at 60 $^{\circ}$ C in stagnant condition, the model has coefficient determination (R²) of 94 %, correlation of 97 % and standard error estimation deviation of 0.11. Comparing to Nesic's experiment data at 20 °C and stagnant condition, the model has coefficient determination of 65 %, correlation of 81 % and standard error estimation deviation of 0.26. In comparison to Che Ismail's experimental data at pH 5.5 and stagnant condition, the model shows a relationship with R² of 96 %, correlation of 98 %, and standard error deviation of 0.01.

Che Ismail's experiment showed a good relationship in correlation and regression relationship and provided high precision (0.01) in standard error estimation. Both HAc concentration and temperature show a similar trend on corrosion rate where corrosion rate will increased as either HAc concentration or temperature was increased. Meanwhile, for pH corrosion rate will decrease as pH increase.

4.4 VERIFICATION WITH CORROSION PREDICTION SOFTWARE'S

The results from the model also has been comparing with several corrosion prediction software that available in industries. The comparisons of the model with corrosion prediction software are importance to known the accuracy and precision of the model by calculating the coefficient determination (\mathbb{R}^2), correlation and standard error estimation. The corrosion prediction software's that has been used for the verification are Freecorp, NORSOK, ECE and Cassandra. The comparisons are made based on different of HAc concentration, temperature, and pH.

4.4.1 Effect of HAc



Figure 4.7: Comparison corrosion rate between model with ECE and Freecorp software

Graph above shows that the comparison of corrosion rate between model and corrosion prediction software's at varying of HAc concentrations. In comparison to ECE, the model shows a relationship with coefficient determination of 99.7 %, correlation of 99.8 %, and standard error deviation of 0.05.

The model showed a good relationship with ECE software in correlation and regression relationship and provided high precision in standard error estimation compared to NORSOK software at various temperatures. Both model and ECE show a similar trend on corrosion rate where corrosion rate increased as HAc concentration was increased but for Freecorp, its shows the constant graph.

4.4.2 Effect of Temperature

Comparison between model and ECE, Freecorp, NORSOK and Cassandra are shown in Figure 4.8, Figure 4.9, Figure 4.10, and Figure 4.11, respectively. The corrosion rates are calculated at CO^2 pressure 1 bar, pH 4, temperature from 25 °C to 85 °C, and stagnant condition.



Figure 4.8: Comparison between model and ECE at various temperatures



Figure 4.9: Comparison between model and Freecorp at various temperatures



Figure 4.10: Comparison between model and NORSOK at various temperatures



Figure 4.11: Comparison between model and Cassandra at various temperatures

Graph above shows that the comparison of corrosion rate between model and corrosion prediction software's at various temperatures. Comparing to ECE, the model has coefficient determination of 92 %, correlation of 96 % and standard error estimation deviation of 0.05. In comparison to Freecorp, the model shows a relationship with coefficient determination of 84 %, correlation of 91 %, and standard error deviation of 0.07. A comparison between the model and NORSOK, it shows a coefficient determination of 62 %, correlation 0f 78 %, and standard error estimation 0f 0.1. Meanwhile, for comparison between model and Cassandra, the model has coefficient determination of 79 %, correlation of 89 % and standard error estimation deviation of 0.08.

The model showed a good relationship with ECE software in correlation and regression relationship and provided high precision in standard error estimation compared to others corrosion prediction software's at various temperatures.

The model graph is similar to the NORSOK calculation. The similarity was that there was a decrease trend of corrosion rate after reaching certain temperature. While the other models software corrosion data calculated corrosion rate in increasing trend continuously.

4.4.3 Effect of pH

Comparison between model and ECE, Freecorp, NORSOK and Cassandra are shown in Figure 4.12. The corrosion rates are calculated at CO^2 pressure 1 bar, temperature from 25°C, pH 4 to pH 6.5, and stagnant condition.



Figure 4.12: Comparison corrosion rate between model with NORSOK and Cassandra software's at varying pH

Graph above shows that the comparison of corrosion rate between model and corrosion prediction software's at varying pH. Comparing to NORSOK, the model

has coefficient determination of 92 %, correlation of 96 % and standard error estimation deviation of 0.12. In comparison to Cassandra, the model shows a relationship with coefficient determination of 98 %, correlation of 99 %, and standard error deviation of 0.06.

The model showed a good relationship with Cassandra software in correlation and regression relationship and provided high precision in standard error estimation compared to NORSOK software at various temperatures. All graphs show the same trend where corrosion rate decreased when pH increased.

4.5 EFFECTS OF HAC CONCENTRATION AND TEMPERATURE

The combined effects of HAc concentration with temperature on corrosion rate is presented in Figure 4.13. The figure shows that the corrosion rate will increase when concentration of HAc and temperature is increased. The effects of temperature on contributing corrosion rate seemed to be slower than effects HAc concentration. In the range from 25 $^{\circ}$ C to 75 $^{\circ}$ C, the maximum corrosion rate increase is 1.15 mmpy in HAc concentration of 200 ppm. Meanwhile, in the range of HAc concentration from 0ppm to 200ppm, the maximum corrosion rate increase is 2.66 mmpy in temperature of 45 $^{\circ}$ C.



Figure 4.13: Combined effect of HAc concentration and temperature

4.6 EFFECTS OF HAC CONCENTRATION AND pH

Figure 4.14 shows the result of corrosion rate predicted by model at various pH and concentration of HAc. These calculations were performed at pH from pH 4 to pH 6, HAc concentration from 0 ppm to 200 ppm, temperature 25 °C and in stagnant condition. The figure shows that the corrosion rate will increase when concentration of HAc increased but decrease when pH is increased. In this graph, the maximum corrosion rate is at pH 4 and 200 ppm which is 2.66 mmpy.



Figure 4.14: Combined effect of HAc concentration and pH

4.7 EFFECTS OF TEMPERATURE AND pH

The combined effects of temperature with pH on corrosion rate calculated by model prediction are presented in Figure 4.15. These calculations were performed at pH from pH 4 to pH 6, temperature from 25 °C to 80 °C, 0 ppm of HAc concentration and in stagnant condition. From the figure, it is seen that corrosion rate increase when either temperature increase or pH decrease. In this graph, the maximum corrosion rate is at pH 4 and temperature 75 °C which is 1.35 mmpy.



Figure 4.15: Combined effect of temperature and pH

4.8 **DISCUSSION**

4.8.1 EFFECTS OF HAC CONCENTRATION

The effects of HAc concentration on corrosion, as calculated by model prediction in CO₂ corrosion is presented in Figure 4.7 at temperature 25 °C and Figure 4.13 at various temperatures. The figures show that the increase in HAc concentration leads in increasing corrosion rate. According to George and Nesic (2007) the increase in corrosion rate caused by acetic acid is related to the role of acetic acid in providing protons and adding a new cathodic reaction via the direct reduction of undissociated HAc. Nafday (2004) adds that the mechanism of dissolved HAc in CO₂ corrosion can also be attributed to the concentration of undissociated HAc present in the solution. Previously, Crolet et al. (1999) has proposed HAc effects in low concentrations (6 - 60 ppm). They argued that the presence of HAc, at this concentration, inhibited the anodic (iron dissolution). They concluded that the increase in the rate of corrosion was due to an inversion in the bicarbonate/acetate ratio. At this inversion point, HAc is the predominant acid compared to carbonic acid, and becomes the main source of acidity. Several researchers Che Ismail (2005), James (2004), and Nesic (2007) who have conducted experiments involving HAc confirmed that the presence of HAc causes higher corrosion rate compared to without HAc.

Observation by George and Nesic (2007) related to the electrochemical behavior of carbon steel on the additions of HAc has shown that the presence of HAc in the solution caused several results which is decreasing pH, and increasing cathodic limiting current. In addition, he argued that the cathodic reaction will become the rate determining step and the limitation was due to diffusion of proton to the steel surface rather than electron transfer. There is a proof that HAc can increase the cathodic reaction rate by hydrogen evolution reaction process if the concentration is significant.

As calculated by model prediction in Figure 4.14, the corrosion rate at pH 4 is higher than at pH 5 and pH 6. The effect is proportional to the amount of HAc added. At pH 5 and pH 6, the corrosion rate also increases when HAc concentration was increased. However, the average corrosion rate at pH 5 and pH 6 is lower than the average corrosion rate at pH 4. These observations suggest that H⁺ ions are the predominant factor that contributes to corrosion rate.

4.8.2 EFFECTS OF TEMPERATURE

Effects of temperature on CO_2 corrosion can be seen in Figure 4.5 and Figure 4.8. From the observation, figures shows that corrosion rate increases proportionally with increasing temperature and there was a decrease trend of corrosion rate after reaching certain temperature. It happened because the effect of scaling temperature. Based on the literature reviews Che Ismail's (2005), Heuer (1998), it is known that the effect of temperature is to increase corrosion rate until the temperature reaches a maximum value called scaling temperature. Beyond this temperature, the corrosion rate will decrease or becomes constant. Factors affecting the scaling temperature are pH, HAc concentration and rotation speed. Schmitt and Rothman (1978) found that the kinetics of CO_2 corrosion changed substantially in the proximity of 60 °C. de Warrd and Lozt (1993) also reported that the temperature range from 60°C to 100 °C was a transition region for CO_2 corrosion.

Temperature also can increase or decrease corrosion rate depending on films properties produced during corrosion reactions. An increase of the corrosion rate can be related to the degree of solubility of the species in solution. Song et al. (2004) said that higher solubility of FeCO₃ slows down the formation of the protective film. He also stated that, at temperatures below 60 °C, hydrogen evolution took part as a rate determining step and carbonate scale did not form well. The film was detached and porous, which gave little protection and cannot be detected. In this condition, the kinetics of film formation was faster and corrosion rate was under charge-transfer control. Above 60 °C, the protectiveness of the iron carbonate layer increases with temperature as the solubility of iron carbonate decreases. Thus, the corrosion rate is reduced. However, at higher temperatures, there is a direct reaction between steel and water to produce dense and protective films, as stated by Heuer, (1998). Therefore, in this condition corrosion rate may be cause by film formation.

4.8.3 EFFECTS OF pH

The effects of pH on corrosion rate as calculated by model prediction are presented in Figure 4.12, Figure 4.14 and Figure 4.15. At low pH, corrosion rate increases sharply. According to Garsany et al. (2002), in relating to HAc, the increase of corrosion rate will increase proportionally to the concentration of undissociated acetic acid in the brine solution. Johnson and Tomson (1991) also examined the effect of pH on corrosion rate in synthetic seawater solution with HAc. They found a localized corrosion when 600 ppm HAc was added.

According to Nafday (2004), In CO_2 environments, pH is influenced by changing the H⁺ ions concentration, temperature, pressure, and ionic strength. pH is affected by dissolved iron bicarbonate which is pH will increase when there is an increase of ion bicarbonate. The increased in pH leads to reduction in corrosion rate can be explained by the properties of the protective film. At higher pH, the carbonate film becomes thicker, more dense and protective. Thus, Cui et al. (1998) conclude that the passivity of carbon steel lies within the pH range of the carbonate/bicarbonate.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 INTRODUCTION

This chapter will conclude the project and briefly discussed about the recommendation that can be applied in the future work. The conclusion obtained according to the result from chapter 4. In order to modelling the role of acidic species on CO_2 corrosion prediction based on mechanistic theories, other aspects of future work also will be discussed.

5.2 CONCLUSION

A mechanistic corrosion prediction model for CO_2 environment successfully developed. The developed model was proven to have the capacity to predict corrosion behaviour due to changes in concentration of HAc, temperature and pH. The corrosion prediction model was verified by comparing calculated corrosion rates with the corrosion data obtained from various literature sources and corrosion prediction software's which are ECE, NORSOK, Cassandra, Freecorp and its showed a good relationship in correlation and regression relationship and provided high precision in standard error estimation. In general, the use of the model has the benefit to calculate the corrosion rate in extreme conditions such as high temperatures, which can reduce the dependency on experiment.

5.3 **RECOMMENDATION**

The model considers pH, and temperature in combination with acetic acid concentration to predict corrosion. However, in field conditions, there are other variable such as oxygen, sodium chloride and other species that affect corrosion. Therefore it is recommended that further study to be conducted by using the same technique but including other variables such as O_2 , inhibitor, NaCl, and any other species that promote corrosion.

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