# Corrosion rate study of aqueous 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) and its mixture with piperazine (PZ)

by

Zaki Saeed Ahmed Bahakim

Dissertation submitted in partial fulfillment of
the requirements for the Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2012

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# CERTIFICATION OF APPROVAL

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Approved by,

________________________

(AP Dr Mohamad Azmi Bustam)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2012

# CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

ZAKI SAEED AHMED BAHAKIM

# ABSTRACT

Carbon dioxide emission has been a worldwide concern around the globe due its greenhouse effect that leads to global warming. Current amine treating plant is used to remove $CO_2$ by absorption process using alkanolamines as an absorbent. Recently sterically hindered amines such as AHPD many others have grown interest in $CO_2$ absorption area due to its high $CO_2$ solubility (up to 1 mol $CO_2$/mol AHPD). Piperazine is a chemical derivative added to AHPD to enhance its absorption capacity to even more than 1 mol $CO_2$/mol AHPD. However, all amine solutions whether it is lean or saturated with $CO_2$ is corrosive. This has caused all plants that operate $CO_2$ absorption using amine solution encounter severe corrosion problems. The corrosion problem has a big impact on the plant's economy and also the safety of the workers around it.

This present study provides information on the corrosion rate of AHPD at different concentrations and also the effect of mixing ratio of AHPD/PZ blends. An electrochemical testing of Linear Polarization Method is used to evaluate the corrosion rate. The corrosion rate of AHPD solution is found to be increasing with increasing concentration of AHPD. For AHPD/PZ blends, it is found that when amount of PZ added to AHPD is increased, the rate of corrosion decreases which shows that PZ acts as a corrosion inhibitor when mixed with AHPD. Comparison among the AHPD solution with $CO_2$ loading and its fresh solution is also presented in this study.

# ACKNOWLEDGEMENT

This dissertation would not have been possible without the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study.

First and foremost I offer my sincerest gratitude to my supervisor, Associate Professor Dr Mohamad Azmi Bustam, who has supported me throughout my thesis with his patience and knowledge whilst allowing me the room to work in my own way.

I also would like to thank the research officers Ms Hasiah Binti Kamarudin and Ms Naimmatul Hani Binti Naina Mohd for their assistance and knowledge sharing during the period that I worked in the Ionic Liquids Laboratory. A special thanks goes to the Ionic Liquids Laboratory technician Mr Yusoff B Mohd for providing me with all the necessities and guide.

Not forgetting thanks to Final Year Project II coordinator, Dr Lukman b Ismail and all Chemical Engineering Department lecturers for the help and beneficial professional guidance to me.

Last but not least, thank you to my family for their love, support and encouragement.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background Studies

The rising level of carbon dioxide in the atmosphere in the past century has caused many concerns to environmentalist and green organizations due to its contribution to the green house effect and global warming. There are mainly seven sources of $CO_2$ emission: national-level combustion of solid, liquid, and gaseous fuels; flaring of gas from wells and industrial processes; cement production; oxidation of nonfuel hydrocarbons; and fuel from "international bunkers" used for shipping and air transport[1]. Carbon dioxide is widely recognized as a major greenhouse gas produced in large quantity worldwide by many important industries, including fossil-fuel electric power generation, synthetic ammonia industries, steel production and so on. With the current trend of the increasing level of $CO_2$, governments and international environment bodies have set strict rules and regulation on the amount of $CO_2$ emission from industries.

To reduce the emission of $CO_2$ to the atmosphere, acid gas absorption is used by most plants for many decades. There is currently great interest in Canada in capturing $CO_2$ from power-generating-station flue gases before the $CO_2$ gas is released into the atmosphere since this source discharged approximately 25% of the total $CO_2$ emissions [15]. Normally aqueous amine solutions is used as the solvent and the most common ones are alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and mthyldiethanolamine (MDEA). However, recently sterically hindered amine such as 2-amino-2-methyl-1-propanol (AMP) has become a competitor to the conventional alkanolamine due to its higher absorption and desorption capacity compared to the latter [2]. In the present, aqueous solutions of 2-amino-2-hydroxymethyl-1, 3-propanediol (AHPD), a primary sterically hindered amine, was examined as a potential $CO_2$

absorbent [3]. Another chemical called Piperazine (PZ) which is a derivative is also being used as an activator to enhance the absorption capacity of the amines by blending the two solutions together.

Historically, the $CO_2$ absorption process using aqueous amine solutions has faced corrosion problems in many plants [4]. According to Kohl and Nielson [5], the most severe operational problems in the $CO_2$ absorption process is corrosion. The corrosion problems causes a huge impact directly on the plant's economy since it causes unplanned downtime, production losses, reduced equipment life, and even injury or death [4]. The unplanned downtime of any typical plant can cost between $10,000 and $30,000 per day which is due to the production losses [6]. Besides that expenditure, other costs such as replacing the corroded system and treatments to mitigate the corrosion must be considered too. According to Gerus [7], millions of dollars are spent in $CO_2$ absorption plant that uses aqueous amine solutions to deal with the corrosion problem.

Table 1 below shows the absorption capacity and corrosion rate for different types of amines and their mixtures at concentration of 3 $kmol/m^3$ and 80 ˚C.

**Table 1. CO2 loading and corrosion rate for different types of amine***

| **Amine Type** | **Absorption capacity (mol/mol)** | **Corrosion Rate (mpy)** |
|---|---|---|
| MEA | 0.565 | 136.4 |
| DEA | 0.442 | 89.1 |
| MDEA | 0.243 | 67.6 |
| AMP | 0.554 | 125.9 |
| MEA/MDEA | 0.435 | 77.6 |
| DEA/MDEA | 0.365 | 72.4 |
| MEA/AMP | 0.561 | 127.3 |

**adapted from Veawab et al (1999)* [9]

Park et al [3] has made solubility of carbon dioxide study in aqueous AHPD for concentration of 10 & 20% measured at (313.15, 323.15 and 333.15) K and has found that the maximum $CO_2$ loading can reach up to 1.4 mol of $CO_2$ / mol of AHPD.
For Piperazine, Derk et al [8] has done a similar solubility studies for PZ concentration of 0.6M, and they found that the $CO_2$ loading increases with the partial pressure of $CO_2$. The maximum loading has reached up to 0.96 mol of $CO_2$/ mol of PZ.

## 1.2 Problem Statement

So far many works has been done to study the corrosion rate of amine solutions in order to find a better amine with the least corrosion problems. For sterically hindered amine, only AMP corrosion rate study has been carried out by Veawab et al [9]. For AHPD no such study has been made which led to the motivation in carrying out this study. For piperazine alone, corrosion rate study has been done by Quraishi et al [10]. But for AHPD-PZ blends, again nobody has done any work on the mixture corrosion rate study.

## 1.3 Objective

- To study the corrosion rate of aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD)
- To study effect of mixing ratio AHPD/Piperazine (PZ) blend on the corrosion rate

## 1.4 Scope of study

For corrosion rate study of this project, three different experimental techniques will be used. They are:-

- Linear Polarization Resistance method
- Tafel Extrapolation method

The corrosion behavior due to amine affected by the following process parameters, amine type, amine concentration, solution temperature, $CO_2$ loading and oxygen content [12]. For the present study, the scope is limited to the following:-

**Table 2. Parameters that will be tested in the experiment**

| **Parameter** | **Testing condition** |
|---|---|
| Amine type | • AHPD<br>• Mixture of AHPD and PZ (1:1 & 2:1)<br>at 20wt%, 30 °C and 2 hours of $CO_2$ loading |
| Amine concentration | • 10, 15 & 20 wt%<br>at 30 °C and 2 hours of $CO_2$ loading |

For the LPR and Tafel polarization, here we are accelerating the corrosion by applying some potential to the specimen. These two tests are not very long and hence it will be done 5 and 3 times respectively.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Corrosion Theory

Corrosion is mainly an electrochemical process where two reactions take place in equilibrium unless there is an external driving force. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species (often $O_2$ or $H^+$) is reduced, removing electrons from the metal. When these two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs [11].

For example when a metal (M) is immersed in water, the following half cell reactions will take place:-

$$\mathbf{M(s) \longrightarrow M^{n+}(aq) + ne^-} \qquad (1)$$

$$\mathbf{nH_2O + ne^- \longrightarrow H_2 + 2OH^-} \qquad (2)$$

The corrosion that is caused by amine is mainly due to the $CO_2$ that has been absorbed. After absorbing the $CO_2$ the amine will form a carbamate. In the presence of water, the carbamate will be hydrolysed and forms a bicarbonate ion. This ion is a corroding agent as it will dissolve the iron from the pipes or tanks to form iron carbonate [12].

$$\mathbf{2RNH_2 + CO_2 \longrightarrow RNHCOO^- + RNH_3^+} \qquad (3)$$

$$\mathbf{RNHCOO^- + H_2O \longrightarrow RNH_2 + HCO_3^-} \qquad (4)$$

$$\mathbf{Fe + HCO_3^- \longrightarrow FeCO_3 + H^+ + 2e^-} \qquad (5)$$

According to the reactions above, we can see that acid gas absorption by amine can cause the corrosion of iron or steel. Also the water helps to form the bicarbonate ion which will dissolve the iron. Therefore the higher the amount of the bicarbonate ion present, the higher the corrosion rate.

## 2.2 Alkanolamine Absorption

A wide variety of separation techniques involves the removal of vapor-phase impurities from gas stream including permeation through membrane, absorption into a liquid, condensation, chemical conversion to another compound and adsorption on a solid. One promising approach to remove $CO_2$ is via alkanolamines absorption. Alkanolamines absorption removes $CO_2$ from the gas stream by exothermic reaction of $CO_2$ with the amines. Credit for the development of alkanolamines as absorbents for acidic gases goes to R. R. Bottoms (1930). Triethanolamine (TEA) which was the first alkanolamine to become commercially available was used in the early gas-treating plants [5].

The amines that have proved to be of principal commercial interest for gas purification are primary amine whose members include monoethanolamine (MEA) and diglycolamine (DGA); secondary amine whose members include diethanolamine (DEA) and di-isopropylamine (DIPA); and tertiary amines whose members include triethanolamine (TEA) and methyldiethanolamine (MDEA) [5].

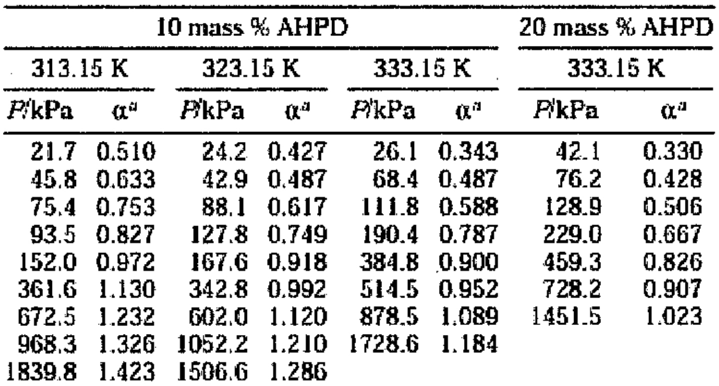
## 2.3 Sterically Hindered Amine

As mentioned above, recently sterically hindered amines received a great deal of attention because of its high thermodynamic capacity and fast absorption rates at high $CO_2$ loadings. According to Sartori et al (1983), the main reason for these great properties is mainly due to the steric hindrance that is introduced by substituting with a bulky group next to the amino group. By this way, it will lower the stability of the carbamate that is formed in reaction (3). This will increase the thermodynamic $CO_2$ loading to level more than the alkanolamines which have a stable carbamte. Low stability of the carbamate will also lead to the formation of free amine according to equation (4) which will therefore increase the concentration of the amine and hence increase the rate of absorption of the acid gas [2].

There are many different types of sterically hindered amines such as AMP, PE, AMPD, AEPD, AHPD etc. Currently many research has been done to study the solubility 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) because it was found that the $CO_2$ loading can reach upto 1 mol of $CO_2$ per mol of AHPD or even more.

Park et al (2002) has measured the solubilities of $CO_2$ in aqueous AHPD solutions at temperature of (313.15, 323.15 and 343.15) K over partial pressures of carbon dioxide ranging from 1 to 2000 kPa for 10 and 20 mass % of AHPD solutions. They found that the maximum $CO_2$ loading has reached upto 1.423 mol of $CO_2$ per mol of AHPD at 1839.8 kPa partial pressure of $CO_2$ and 313.15 K for 10 mass % of AHPD.

**Table 3. Solubility of $CO_2$ in aqueous AHPD solutions**



| 10 mass % AHPD | | | | | | 20 mass % AHPD | |
|---|---|---|---|---|---|---|---|
| 313.15 K | | 323.15 K | | 333.15 K | | 333.15 K | |
| $P$/kPa | $\alpha^a$ | $P$/kPa | $\alpha^a$ | $P$/kPa | $\alpha^a$ | $P$/kPa | $\alpha^a$ |
| 21.7 | 0.510 | 24.2 | 0.427 | 26.1 | 0.343 | 42.1 | 0.330 |
| 45.8 | 0.633 | 42.9 | 0.487 | 68.4 | 0.487 | 76.2 | 0.428 |
| 75.4 | 0.753 | 88.1 | 0.617 | 111.8 | 0.588 | 128.9 | 0.506 |
| 93.5 | 0.827 | 127.8 | 0.749 | 190.4 | 0.787 | 229.0 | 0.667 |
| 152.0 | 0.972 | 167.6 | 0.918 | 384.8 | 0.900 | 459.3 | 0.826 |
| 361.6 | 1.130 | 342.8 | 0.992 | 514.5 | 0.952 | 728.2 | 0.907 |
| 672.5 | 1.232 | 602.0 | 1.120 | 878.5 | 1.089 | 1451.5 | 1.023 |
| 968.3 | 1.326 | 1052.2 | 1.210 | 1728.6 | 1.184 | | |
| 1839.8 | 1.423 | 1506.6 | 1.286 | | | | |

** Adapted from Park et al (2002)*

As we can see from the table above, as the temperature increases the $CO_2$ loading decreases and as the partial pressure of $CO_2$ increases, the $CO_2$ loading increases.

In another work done by Iliuta et al [13], the solubility of carbon dioxide in aqueous AHPD, piperazine and mixed solvent solutions were measured at temperatures in the range of 283 to 342.15 K and a wide range of partial pressures of carbon dioxide. At 5 kPa partial pressures of $CO_2$ or higher, AHPD has a higher $CO_2$ solubility compared to AMPD and AEPD. It was found that the absorption capacity increases with the increase of piperazine concentration, proving that the piperazine is an effective promoter for the $CO_2$ absorption in AHPD solutions.

### 2.4 Corrosion Due To Amine

Veawab et al [12] have provided comprehensive information on the effects of process parameter variations on the corrosion behavior of carbon steel in $CO_2$ absorption system using aqueous amine solutions. The process parameters they worked on are amine type, amine concentration, solution temperature, $CO_2$ loading and oxygen content.

i) Amine type- The different amine that is used are MEA, DEA, MDEA, AMP and also mixture of MEA:DEA, DEA:MDEA and MEA:AMP in the ratio of 1:1. At 3 kmol/$m^3$ and 80 °C with $CO_2$ saturation. They found that different amine type gave different corrosion rate depending on their maximum $CO_2$ loading. The higher maximum loading will result in higher corrosion rate. For the mixture of amines, its corrosion rate is in between the individual amines.

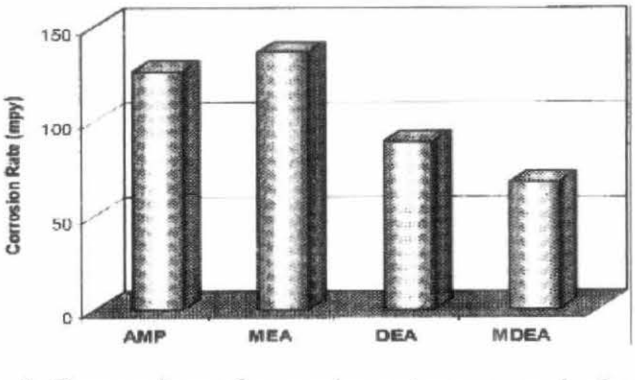


**Figure 1. Comparison of corrosion rates among single amines**

* *Adapted from Veawab et al (1999)*

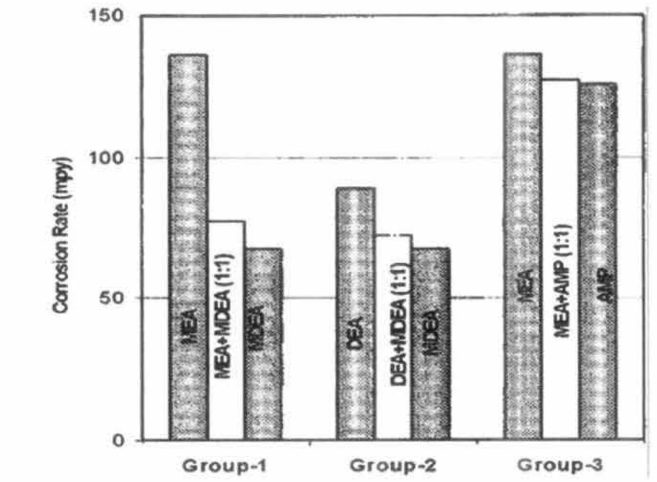


**Figure 2. Comparison of corrosion rates for mixed amine systems**

** Adapted from Veawab et al (1999)*

ii) Amine concentration – They found that the higher the amine concentration, the higher is the corrosion rate due to the reaction (3) & (4). However the corrosion rate seems to slow down gradually because the water is being used up in the hydrolysis of the carbamate. As the water diminishes, the rate of carbamate hydrolysis decreases and so does the corrosion rate.

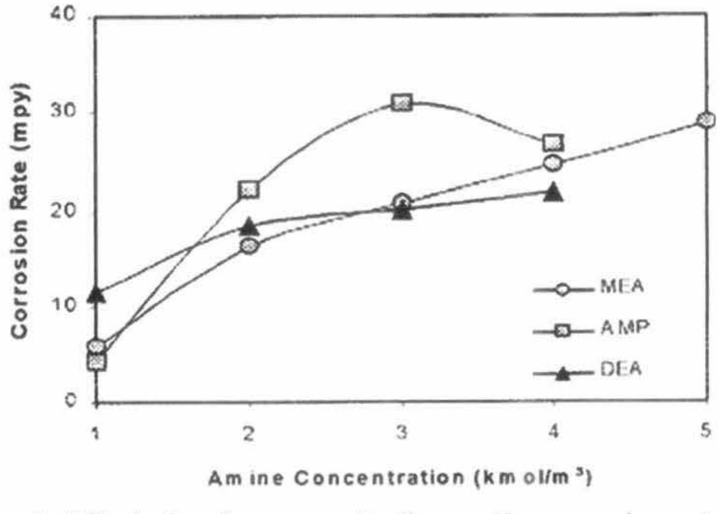


**Figure 3. Effect of amine concentration on the corrosion rate**

** Adapted from Veawab et al (1999)*

iii) Solution temperature – The corrosion rate increase with increasing solution temperature. As the equilibrium constant for the hydrolysis of the carbamate depends on temperature, therefore with increase in temperature, the forward rate of reaction increase which means more bicarbonate ion also increase leads to higher corrosion rate.

iv) $CO_2$ loading – Higher CO2 loading leads to higher corrosion rate. The reason is same as explained in part i).

v) Oxygen content – Higher Oxygen content leads to higher corrosion rate because:-

$$\mathbf{2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2} \tag{6}$$

$$\mathbf{2Fe(OH)_2 + 2H_2O + 0.5O_2 \rightarrow 2Fe(OH)_3} \tag{7}$$

Another work on corrosion rate study for a blended mixture of MEA-piperazine is done by Nainar et al (2009) [14]. According to them, MEA/PZ blends is proven to be a very good $CO_2$ capture solvent. Its absorption rate is 1.5-2.5 times greater than MEA alone. Since it has a very good absorption rate and capacity, they made a corrosion rate study for MEA:PZ in the ratio of 1:0, 1:1, 2:1 and 4:1 at 80 °C in the absence of oxygen content and 0.2 CO2 loading. The result they got is that as the amount of PZ in the blend is increased, the corrosion rate increases. According to them, since PZ is an oxidizing agent, as its amount is increased in the blend, it will result in greater oxidation and reduction reaction and hence corrosion takes place. They confirmed the reason from the polarization curve where it shows there is an increase in the cathodic current densities when the amount of PZ is increased. Higher cathodic current means higher oxidation reaction and thus leads to higher corrosion rate.

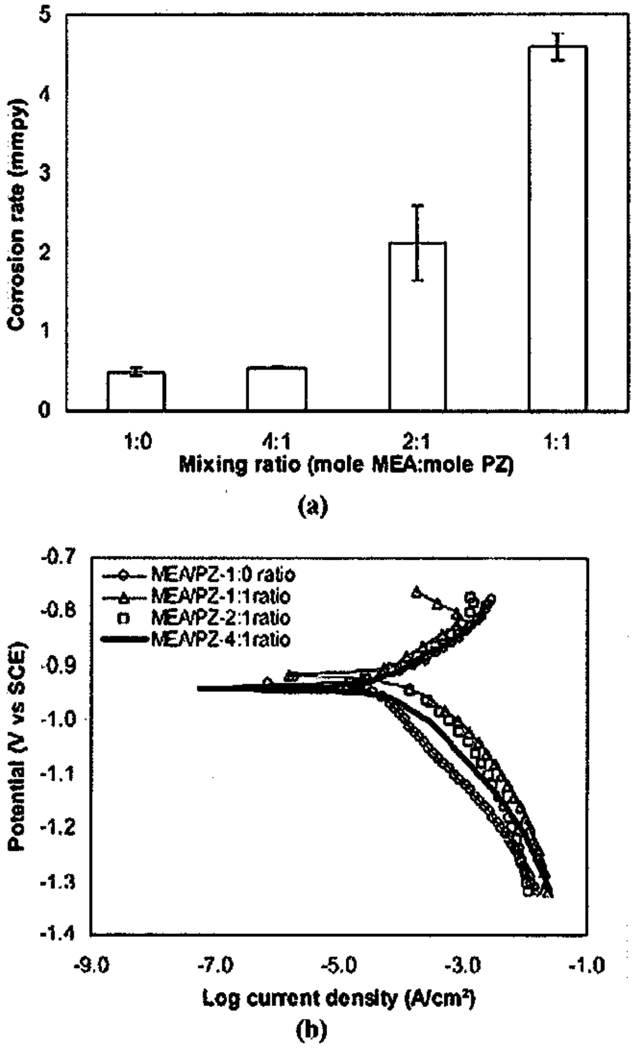


**Figure 4. Effect of mixing ratio of blended MEA/PZ solution (a) corrosion rate and (b) polarization behavior of carbon steel**

** Adapted from Nainar et al (2009)*

# CHAPTER 3

# METHODOLOGY

## 3.1 Project Activities

As mentioned above, two types of experiments will be conducted, Linear Polarization Resistance and Tafel Extrapolation.

### *3.1.1 Linear Polarization Resistance method*

In this LPR method, only small potential is applied which is around ±30mV to ensure the system we are testing remains linear. This is also a requirement so that the measurements are non-destructive and hence can be repeated a number of times on the same system. The polarization resistance (*R*p) defined as:

$$\mathbf{R_p = (dE/di)_{Ecorr}}$$

is determined as the slope of a polarization curve at *E*corr, where $i = 0$. Usually, potentiodynamic polarization curves collected in close vicinity of *E*corr are used for this purpose. ASTM G 59, "Standard Practice for Conducting Potentiodynamic Polarization-Resistance Measurements," deals with experimental procedures for determining *R*p according to the above equation [17].

Polarization resistance can be converted to $i_{corr}$ using the Stern-Geary equation [17]:

$$i\mathrm{corr} = B/R\mathrm{p}$$

where *B* is a parameter calculated using the Tafel slopes:

$$B = \beta a \beta c / 2.3(\beta a + \beta c)$$

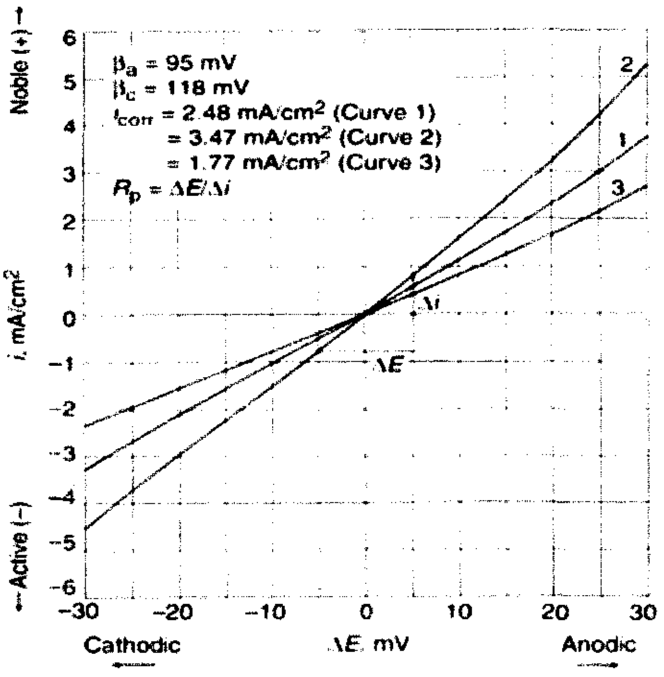


**Figure 5. Standard potentiodynamic polarization curves**

** Adapted from Mansfeld (2003)*

where β a and β c are the anodic and cathodic Tafel slopes, respectively. The corrosion rate, CR will be calculated using the following equation:-

$$\mathbf{CR = 0.1288 * (i_{corr} * EW/\rho)}$$

Where EW is the equivalent weight (dimensionless) and ρ is the density of the material(g/cm$^3$). CR is the corrosion rate (mpy) and lastly $i_{corr}$ is the corrosion current density (μA/cm$^2$).

### *3.1.2 Tafel Polarization*

In Tafel polarization, the potential applied is higher than LPR where it is in the range of ±300 mV. The procedure to use the potentiostat in this experiment is following the ASTM standard G5-94 Standard reference test method for making potentiostatic and potentiodynamic Anodic polarization measurements. Here we connect all the electrodes to the potentiostat and we measure the open circuit potential Eoc by letting it to stabilize for few minutes. After that we start to incrase the applied potential at a scan rate of 50mV every 5 min.

An electrochemical reaction under kinetic control obeys the **Tafel Equation** [18]:-

$$I = I_0 \, e^{(2.3(E-E^{\circ})/\beta)}$$

In this equation,

| | |
|---|---|
| $I$ | is the current resulting from the reaction |
| $I_0$ | is a reaction dependent constant called the Exchange Current |
| $E$ | is the electrode potential |
| $E^{o}$ | is the equilibrium potential (constant for a given reaction) |
| $\beta$ | is the reaction's Tafel Constant (constant for a given reaction). Beta has units of volts/decade. |

The Tafel equation describes the behavior of one isolated reaction. In a corrosion system, we have two opposing reactions – anodic and cathodic. The Tafel equations for both the anodic and cathodic reactions in a corrosion system can be combined to generate the **Butler-Volmer Equation**:-

$$I = Ia + Ic = I_{corr}(e^{(2.3(E-Eoc)/\beta a)} - e^{(-2.3(E-Eoc)/\beta c)})$$

where

| | |
|---|---|
| $I$ | is the measured cell current in amps |
| $I_{corr}$ | is the corrosion current in amps |
| $E$ | is the electrode potential |
| $E_{oc}$ | is the corrosion potential in volts |
| $\beta_a$ | is the anodic Beta Tafel Constant in volts/decade |
| $\beta_c$ | is the cathodic Beta Tafel Constant in volts/decade |

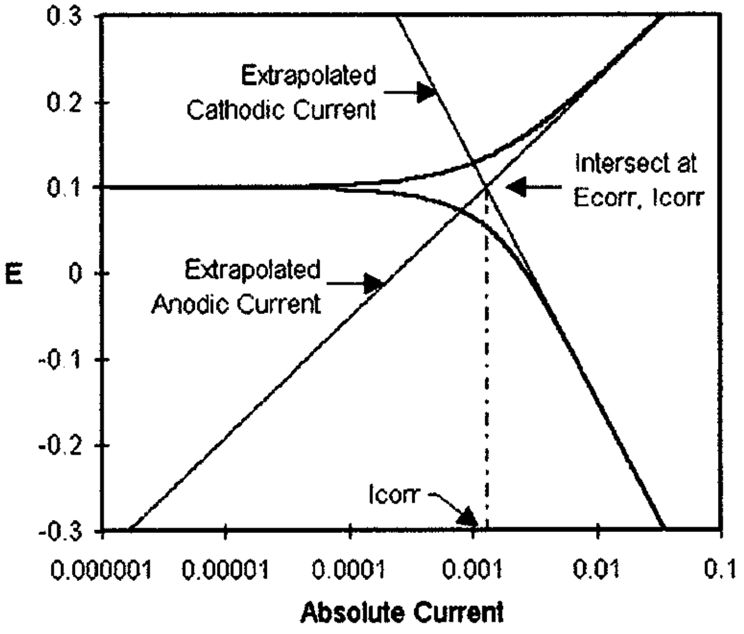


**Figure 6. Tafel plot**

* *Adapted from Scully (2000)*

$$CR = \frac{I_{corr} \cdot K \cdot EW}{dA}$$

| | |
|---|---|
| CR | The corrosion rate. Its units are given by the choice of K |
| $I_{corr}$ | The corrosion current in amps |
| K | A constant that defines the units for the corrosion rate |
| EW | The equivalent weight in grams/equivalent |
| d | Density in grams/cm$^3$ |
| A | Sample area in cm$^2$ |

### 3.2 Chemicals and Raw materials Used

- 2-amino-2-hydroxymethyl-1, 3-propanediol (AHPD) – ACROS ORGANICS
- Piperazine (PZ) - ACROS ORGANICS

- Deionized water (18.2 MΩ)
- $CO_2$ gas
- Ethanol solvent
- Epoxy resin - BUEHLER
- Diethylenetriamine (Hardener) - BUEHLER
- 1, 3 and 6 Pace Diamat (Polycrystalline Diamond Suspension) – Pace Technologies

### 3.3 Equipment/Instruments used

- Abrasive Cutter
- Grinder & Polisher – Metkon Forcipol
- Grinding Paper – Silicon Carbide 240, 320, 400, 600, 800, 1200 grit
- Potentiostat – WEIS 510 Multichannel EIS system
- Corrosion cell
- Heater – WiseStir MSH-20D
- Flowmeter - DWYER
- Computer (WEIS 1.7 data acquisition system)
- Working electrode – carbon steel
- Counter electrode – graphite
- Refernce electrode – Ag,AgCl/3M KCl electrode (MetroOHM)

### 3.4 Exprimental Procedure

Basically there are 3 different activities for this project namely solution preparation, specimen preparation and electrochemical corrosion testing.

### *3.4.1 Solution Preparation*

Required solutions:- **10 wt% AHPD aqueous solution**
**15 wt% AHPD aqueous solution**
**20 wt% AHPD aqueous solution**
**20 wt% PZ aqueous solution**

1- To prepare atleast 80 ml solution of 20 wt% of AHPD, it will need at least 80 ml solution of deionized water. Calculate the mass of the deionized water as:-

**Mass of deionized water = density * volume**
**= 1 g/ml * 80 ml**
**= 80 g**

The required amount of AHPD for 20 wt% solution is x g,

**x /( x + 80) = 0.2**

**x = 20 g of AHPD**

2- Weigh 20 g of AHPD solids in a beaker using the electronic weight balance.
3- Pour 80 ml of deionized water into the beaker using a pippette.
4- Stir the mixture using a glass rod until all the AHPD solid have dissolved.
5- Pour the solution into a Schott Duran bottle and close it until the time of experiment to be commenced.
6- Repeat step 1 to 5 but this time using 10 and 30 wt% of AHPD and 10 wt% of PZ.

### *3.4.2 Specimen Preparation*

i) Required specimen – Five 1x1 cm$^2$ bar shape ofcarbon steel with 0.3cm thickness

1- Draw 1 cm x 1 cm square on the main carbon steel bar.
2- Cut the drawn dimension using abrasive cutter to get 5 specimens.

ii) Mounting the specimen – chemicals reuired are epoxy resin, hardener and releasing agent

1- Prepare the mold using aluminium foil into a rectangular basket form.
2- Apply some release agent on the interior surface of the aluminium foil.
3- Connect a wire round the side of the specimen and hang it using a clamp so that the specimen is put inside the mold but ensuring that it does not touch the the aluminum surface of any side.
4- Mix 45 ml of the epoxy resin with 9 ml of the hardener (ratio 5:1) in a cup.
5- Stir and rotate the cup to ensure perfect mixing until the solution turns clear.
6- Pour the solution into the mold until it covers the specimen and the uninsulated part of the wire.
7- Keep it overnight to ensure complete solidifying of the epoxy resin.

iii) Grinding the specimen

1- Switch on the grinding machine and clean the grinding pad to remove all metal residues.
2- Place the grinding paper, silicon carbide 240 grit on the grinding pad and cover the the grinding paper ring and splash guard to hold the grinding paper.
3- Set the the rotating speed to 150 rpm.
4- Remove the emergency stop and switch on the power supply and press 'FWD' to start the rotaing pad.

5- Put the sample on the rotating silicon carbide paper and hold it firmly to avoid the surface becomes not balanced.
6- Shape the sample until it is as small as possible and only allowing one side of the metal to be exposed. The rest is still mounted with the epoxy resin.
7- Replace the Si.C 240 grit with 320 grit and grind the surface where the metal is exposed.
8- Repeat step 7 with SiC 400, 600, 800 and 1200 until the metal surface is smooth and shiny.

iv) Polishing the specimen

1- Place the 6 micron Pace Texpan polishing cloth on the polishing tab. Spray the polishing cloth with the polycrytalline diamond suspension of 6 um Diamat.
2- Do the rough polishing at 130 rpm for about 1 minute.
3- Repeat step 1 and 2 but this time using 3 micron Pace Texpan polishing cloth sprayed with 3um Dimat polycrytalline diamond suspension.
4- Then repeat step 1 and 2 but this time using 1 micron Pace Texpan polishing cloth sprayed with 1um Dimat polycrytalline diamond suspension.

v) Washing and Degreasing the specimen

1- Wash the specimen with deionized water and then dry it with a tissue paper.
2- Wash the specimen with ethanol, degrease it an then dry it with a tissue paper.
3- Place the specimen in a beaker and put it in the oven for 10 min to ensure complete dryness.
4- Place the specimen in an enclosed container filled with silica gel and then place it in a desicator until the experiment is about to begin.
5- Specimen preparation should be done maximum 1 hour prior to the experiment.

### *3.4.3 Corrosion Testing and Evaluation*

Setup the apparatus as shown below:-

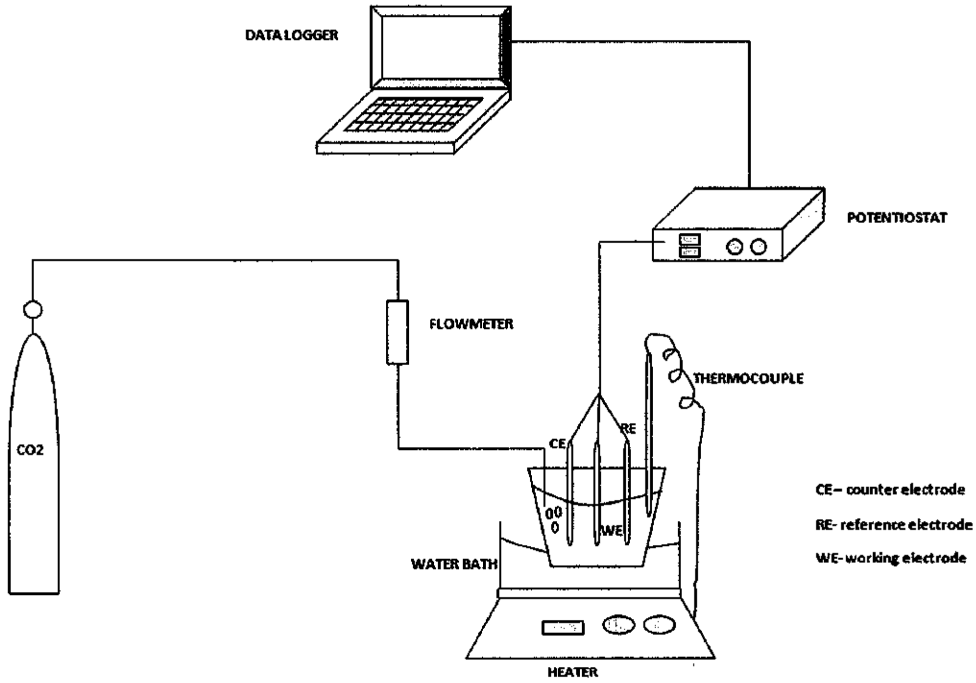


**Figure 7. Experiment setup for electrochemical testing.**

1. Pour 40 ml of the amine solution into the corrosion cell.

2. Purge CO2 gas into the solution for 1 hour at ambient temperature and pressure. (*Assume saturated after 1 hour)

3. Rinse the Reference Electrode (Ag/AgCl) with deionized water and then just lap with tissue paper to dry it before immersing it into the solution. Then immerse graphite Counter Electrode and finally the specimen of the carbon steel which is the working electrode.

4. Make sure that the exposed surface of the metal is facing the reference electrode and is placed as close as possible (1-2 mm) but not touching each other.

5. Connect the potentiostat wire connector to the respective electrode.

6. Start the software and set the parameters according to the type of testing to be run.

i) Linear Polarization Resistance

1- Set the potential as Eoc which is open circuit potential and the range is -30mV to +30mV.

2- Set the scan rate at 1mV/s.

3- Choose the channel that you need to apply the technique and start the experiment by saving the file name.

4- Run the experiment 3 times to ensure reproducibility of the data.

ii) Tafel Extrapolation

1- Set the potential as Eoc which is open circuit potential and the range is -300mV to +300mV.

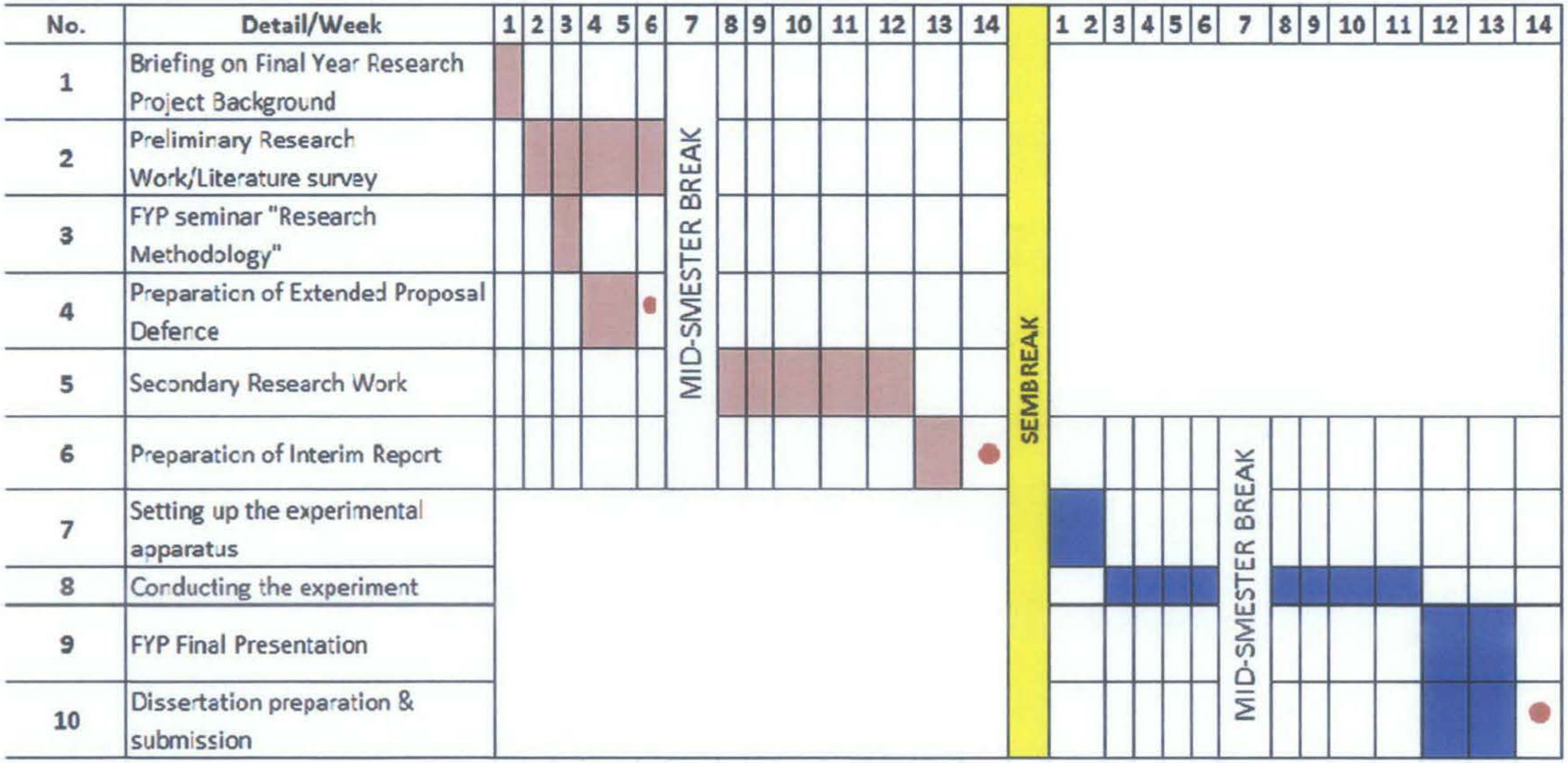
2- Set the scan rate at 1mV/s.

3- Choose the channel that you need to apply the technique and start the experiment by saving the file name.

4- Run the experiment 1 time since this method uses high potential, which will destruct the surface of the metal through corrosion.

After the experiment has been carried out, the specimens needed to be grinded and polished again but starting fromm 800 grit SiC. For the graphs obtained, it can be analysed and obtain datas from the softwatre IVMAN 1.2.

### 3.5 Gant Chart



| No. | Detail/Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Briefing on Final Year Research Project Background | ■ |  |  |  |  |  | MID-SMESTER BREAK |  |  |  |  |  |  |  | SEMBREAK |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 2 | Preliminary Research Work/Literature survey |  | ■ | ■ | ■ | ■ | ■ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 3 | FYP seminar "Research Methodology" |  |  | ■ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 4 | Preparation of Extended Proposal Defence |  |  |  | ■ | ■ | ● |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 5 | Secondary Research Work |  |  |  |  |  |  |  | ■ | ■ | ■ | ■ | ■ |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 6 | Preparation of Interim Report |  |  |  |  |  |  |  |  |  |  |  |  | ■ | ● |  |  |  |  |  |  |  | MID-SMESTER BREAK |  |  |  |  |  |  |  |
| 7 | Setting up the experimental apparatus |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | ■ | ■ |  |  |  |  |  |  |  |  |  |  |  |  |
| 8 | Conducting the experiment |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | ■ | ■ | ■ | ■ |  | ■ | ■ | ■ | ■ |  |  |  |
| 9 | FYP Final Presentation |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | ■ | ■ |  |
| 10 | Dissertation preparation & submission |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | ■ | ■ | ● |

**- key milestone**

●

Figure 8. Gantt Chart for FYP

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Introduction

This chapter discusses the results and method that has been applied when evaluating the corrosion rate of the AHPD solution and its mixture with Piperazine using Linear Polarization Resistance method. As described in the previous chapter, in order to predict the corrosion rate, the polarization resistance value is needed from the experimental measurements of voltage versus current graphs. However, this is not easy to perform as other may think. Electrochemical testing method is one of the most sensitive experimental methods. Any amount of impurity present even if it is too small, it will have an adverse effect on the result and hence the accuracy will be too low. Moreover, once the sample is immersed in the solution, quick procedures must be taken before the sample corrodes naturally otherwise this will again reduce the accuracy.

## 4.2 Effect of purging $CO_2$ into 20wt% of AHPD on the corrosion rate

Two set of AHPD solutions with concentration of 20wt% were tested for corrosion on carbon steel sample. One solution is fresh AHPD solution and the second one is purged with $CO_2$ for 2 hours in an enclosed condition to allow the solution to absorb as much $CO_2$ as possible. The sample exposed surface area is $0.418cm^2$.

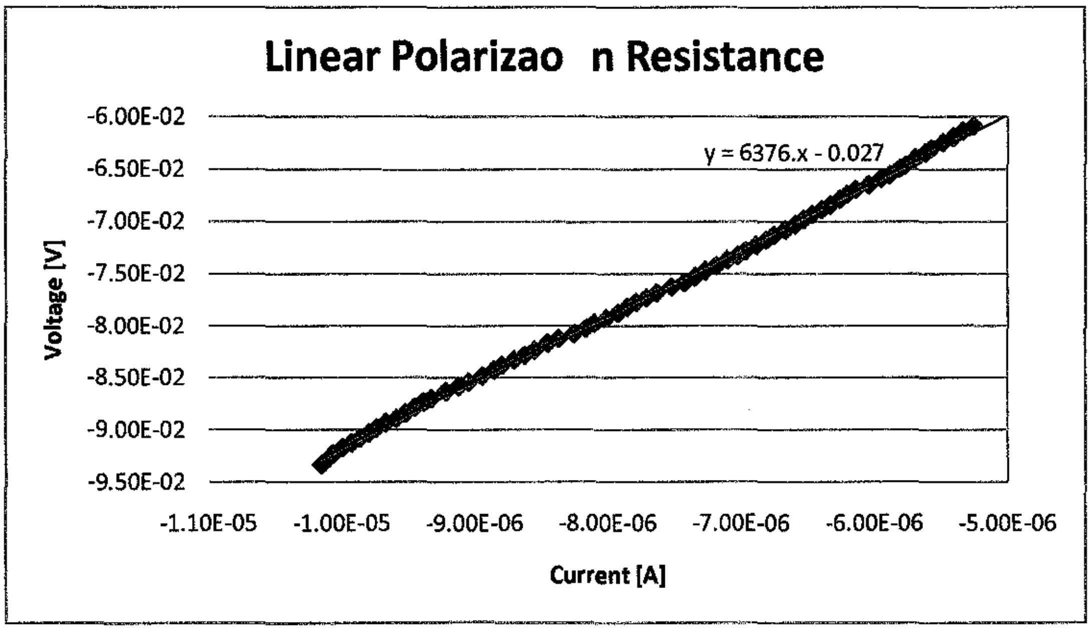


**Figure 9. Linear Polarization Resistance for fresh 20wt% AHPD**

The slope dE/dI is equivalent to the polarization resistance, **Rp** which is 6376 Ohm.

To calculate the corrosion rate we need to find the corrosion current $i_{corr}$ and corrosion current is calculated as follow:-

$$I_{corr} = B/R\mathrm{p}$$

where $B$ is a Stern-Geary constant calculated using the Tafel slopes:

$$B = \beta a \beta c / 2.3(\beta a + \beta c)$$

Substitue the anode and cathode tafel coefficient from above in the equation above:-

$$B = \frac{(1.2{*}e^{-1} \times 1.2{*}e^{-1})}{2.3(1.2{*}e^{-1} + 1.2{*}e^{-1})}$$

$$= 0.0261\ \mathrm{V}$$

$$\mathbf{I_{corr} = 0.0261 / 6376}$$

$$\mathbf{= 4.09 \text{ x } e^{-6} \text{ A}}$$

$$\mathbf{= 4.09\ \mu A}$$

The surface area, SA, of the metal specimen used in this experiment is **0.418 cm$^2$**.

$$\text{Corrosion current density, } \mathbf{i_{corr} = I_{corr} / SA}$$

$$\mathbf{= 4.09 / 0.418}$$

$$\mathbf{= 9.78\ \mu A/cm^2}$$

$$\mathbf{CR = 0.1288\ (i_{corr} * EW/\rho)}$$

The equivalent weight of carbon steel is **27.92** and its density is **7.87 g/cm$^3$**.

$$\mathbf{\text{Corrosion rate, } CR = 0.1288*(9.78 * 27.92 / 7.87)}$$

$$\mathbf{= 4.47 \text{ mpy}}$$

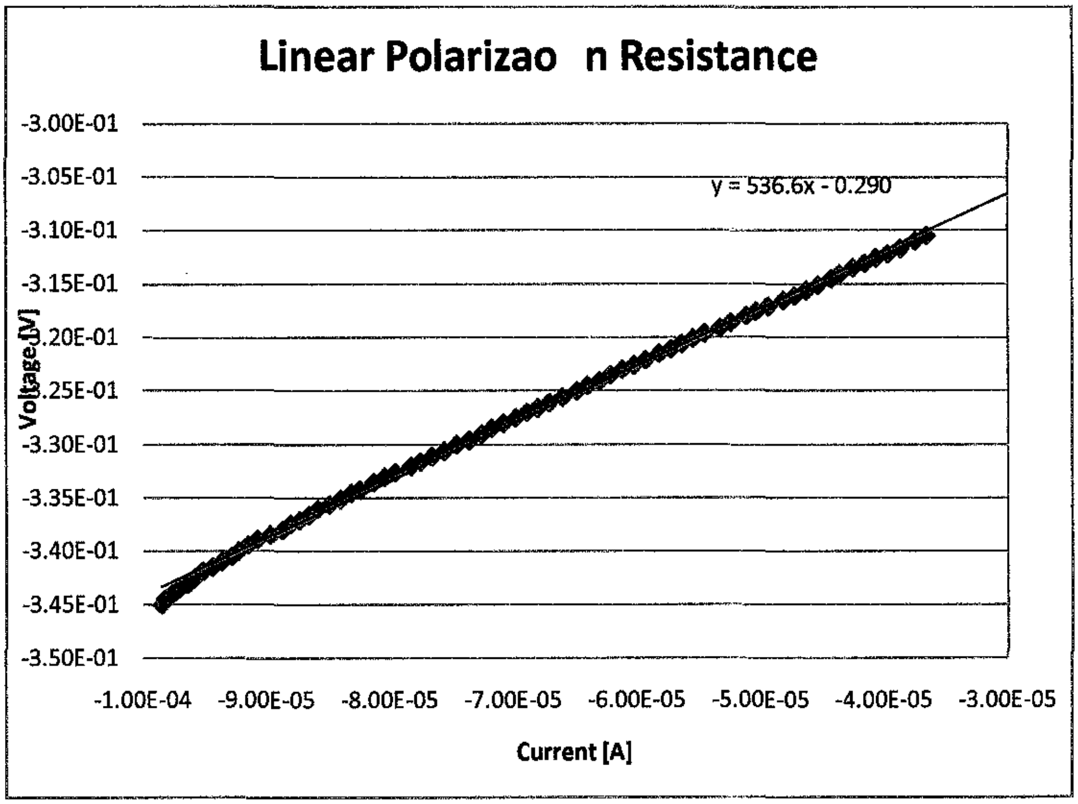


**Figure 10. Linear Polarization Resistance for 20wt% AHPD purged with $CO_2$**

The slope dE/dI is equivalent to the polarization resistance, **Rp** which is 536.6 Ohm.

To calculate the corrosion rate we need to find the corrosion current $i_{corr}$ and corrosion current is calculated as follow:-

$$I_{corr} = B/R\mathrm{p}$$

$$\mathbf{I_{corr} = 0.0261 / 536.6}$$

$$\mathbf{= 4.86 \times e^{-5}\ A}$$

$$\mathbf{= 48.6\ \mu A}$$

The surface area, SA, of the metal specimen used in this experiment is **0.418 $cm^2$**.

$$\text{Corrosion current density, } \mathbf{i_{corr} = I_{corr} / SA}$$
$$= \mathbf{48.6 / 0.418}$$
$$= \mathbf{116.27\ \mu A/cm^2}$$

$$\mathbf{CR = 0.1288\ (i_{corr} * EW/\rho)}$$

The equivalent weight of carbon steel is **27.92** and its density is **7.87 g/cm$^3$**.

$$\mathbf{\text{Corrosion rate, } CR = 0.1288 * (116.27 * 27.92 / 7.87)}$$
$$= \mathbf{53.13\ mpy}$$

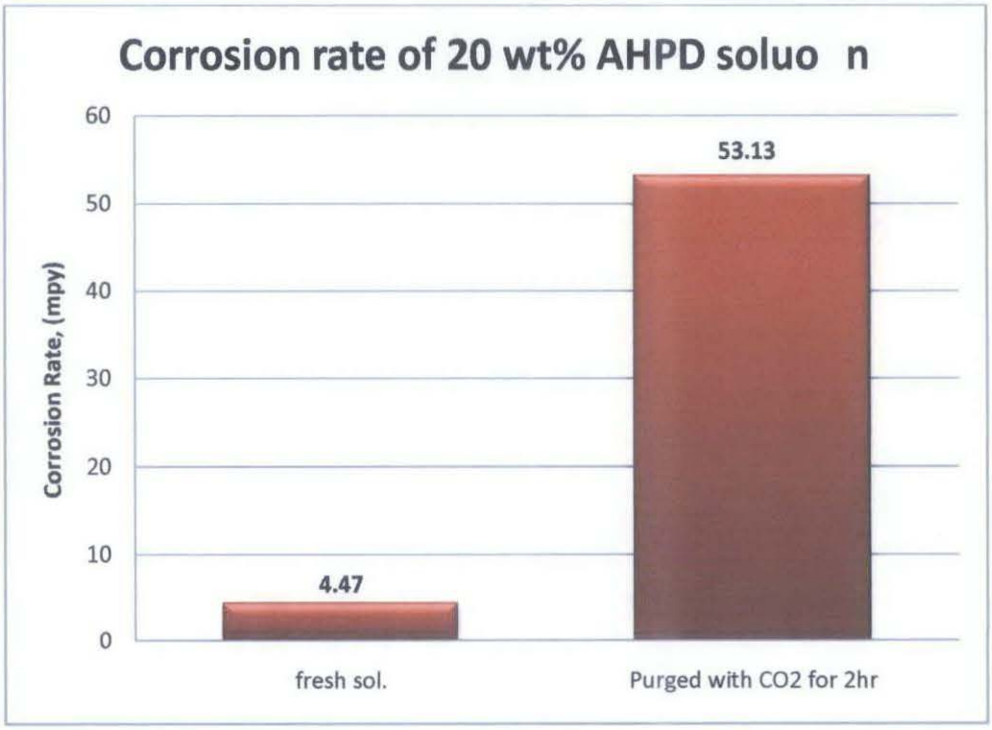


**Figure 11. Comparison of the corrosion rate between fresh AHPD solution and $CO_2$ loaded AHPD solution**

As can be seen from the above graph, the difference of the corrosion rate between the fresh AHPD solution and the $CO_2$ loaded AHPD solution is quite big. The corrosion rate of the fresh AHPD solution is 4.47 mpy which is considered low compared to the $CO_2$ loaded AHPD solution which is 53.13 mpy. This big difference in the corrosion rate can be explained by the reactions 3 to 5 that happen during the $CO_2$ absorption.

$$\mathbf{2RNH_2 + CO_2 \longrightarrow RNHCOO^- + RNH_3^+} \quad (3)$$

$$\mathbf{RNHCOO^- + H_2O \longrightarrow RNH_2 + HCO_3^-} \quad (4)$$

$$\mathbf{Fe + HCO_3^- \longrightarrow FeCO_3 + H^+ + 2e^-} \quad (5)$$

The first reaction is the formation of carbamate, $RNHCOO^-$ when $CO_2$ is loaded in the solution. In the presence of water, carbamate hydrolysis into bicarbonate ion takes place according to equation 4. Now this $HCO_3^-$ ion acts as a corroding agent in a typically aqueous solution containing dissolved $CO_2$. The corrosion reaction on the carbon steel takes place as equation 5. Whereas for fresh solution, since there is no $CO_2$ absorption, there will be no carbamate formation and hence no bicarbonate ion. Therefore corrosion is reduced to very small rate. From this we can conclude that it is the dissolved $CO_2$ in the AHPD solution that contributes to the corrosion on the carbon steel.

### 4.3 Effect of increasing concentration of AHPD solution on the corrosion rate

As mentioned earlier, for concentration variable, three different concentration of AHPD will be tested for corrosion rate and that is 10wt%, 15wt% and 20wt%. This range is chosen because according to Park, J. et al. (2002), the $CO_2$ solubility is highest in this region and as we mentioned above that $CO_2$ loading is found to be a leading factor in the corrosiveness of the AHPD solution on the carbon steel. The exposed surface area of the specimen is 0.42 $cm^2$.

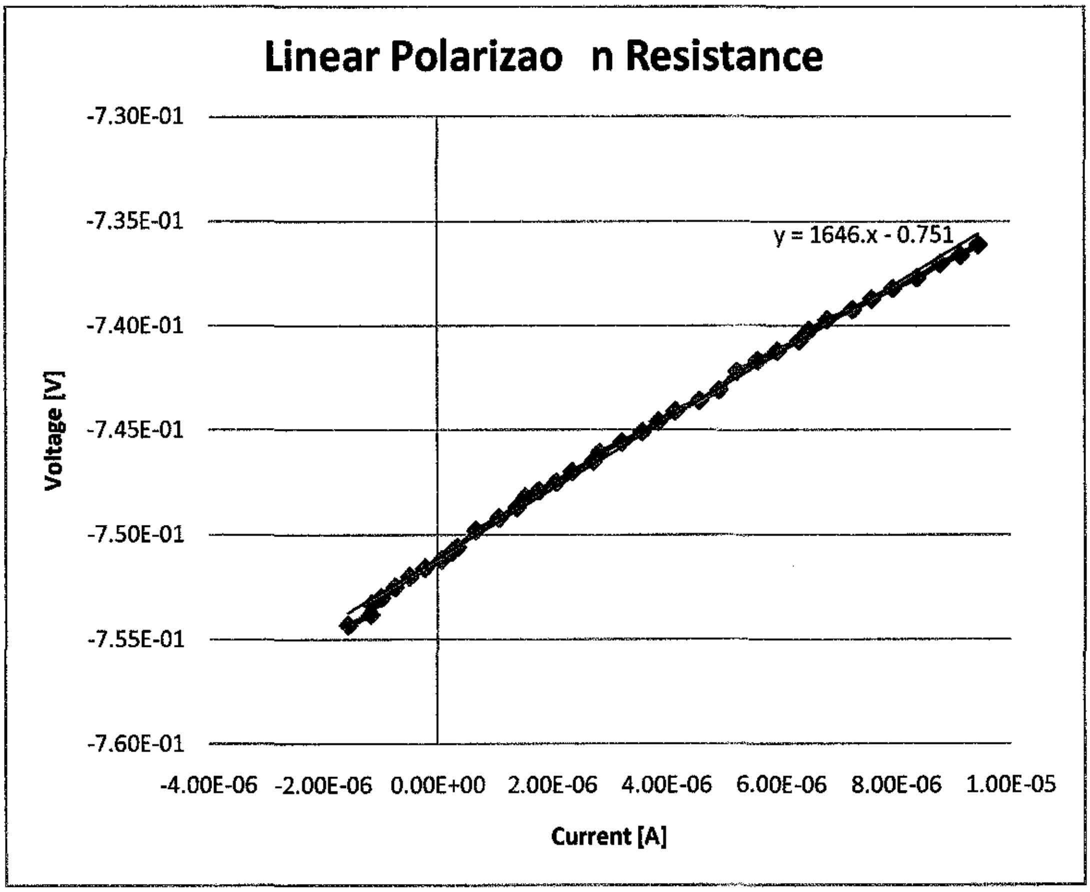


**Figure 12. Linear Polarization Resistance for 10wt% AHPD purged with $CO_2$**

The slope dE/dI is equivalent to the polarization resistance, **Rp** which is 1646 Ohm.

To calculate the corrosion rate we need to find the corrosion current $i_{corr}$ and corrosion current is calculated as follow:-

$$I_{corr} = B/R\text{p}$$

$$\mathbf{I_{corr} = 0.0261 / 1646}$$

$$\mathbf{= 1.59 \times e^{-5}\ A}$$

$$\mathbf{= 15.9\ \mu A}$$

The surface area, SA, of the metal specimen used in this experiment is **0.42 $\text{cm}^2$**.

$$\text{Corrosion current density, } \mathbf{i_{corr}} = \mathbf{I_{corr}} / \mathbf{SA}$$
$$= \mathbf{15.9 \ / \ 0.42}$$
$$= \mathbf{37.86\ \mu A/cm^2}$$

$$\mathbf{CR = 0.1288\ (i_{corr} * EW/\rho)}$$

The equivalent weight of carbon steel is **27.92** and its density is **7.87 $g/cm^3$**.

$$\mathbf{Corrosion\ rate,\ CR = 0.1288 * (37.86 * 27.92 / 7.87)}$$
$$\mathbf{= 17.30\ mpy}$$

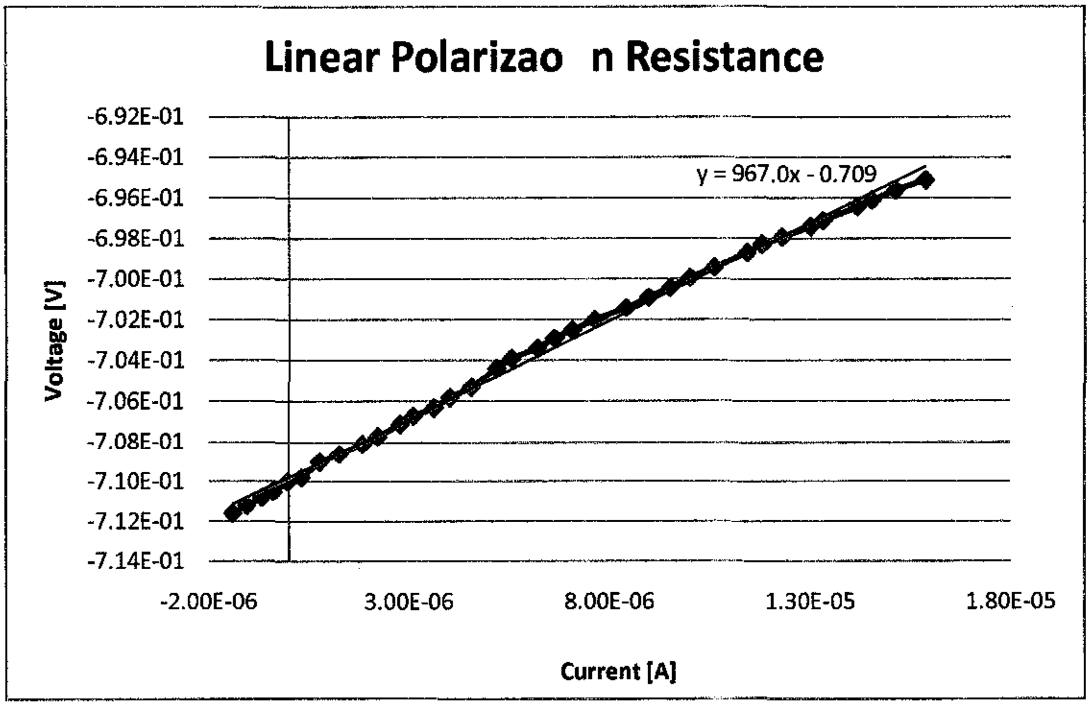


**Figure 13. Linear Polarization Resistance for 15wt% AHPD purged with $CO_2$**

The slope dE/dI is equivalent to the polarization resistance, **Rp** which is 967 Ohm.

To calculate the corrosion rate we need to find the corrosion current $i_{corr}$ and corrosion current is calculated as follow:-

$$I_{corr} = B/Rp$$

$$\mathbf{I_{corr} = 0.0261 / 967}$$
$$\mathbf{= 2.70 \times e^{-5}\ A}$$
$$\mathbf{= 27.0\ \mu A}$$

The surface area, SA, of the metal specimen used in this experiment is **0.42 cm$^2$**.

$$\text{Corrosion current density, } \mathbf{i_{corr} = I_{corr} / SA}$$
$$\mathbf{= 27.0 / 0.42}$$
$$\mathbf{= 64.29\ \mu A/cm^2}$$

$$\mathbf{CR = 0.1288\ (i_{corr}{*}EW/\rho)}$$

The equivalent weight of carbon steel is **27.92** and its density is **7.87 g/cm$^3$**.

$$\mathbf{Corrosion\ rate,\ CR = 0.1288{*}(64.29 * 27.92 / 7.87)}$$
$$\mathbf{= 29.38\ mpy}$$

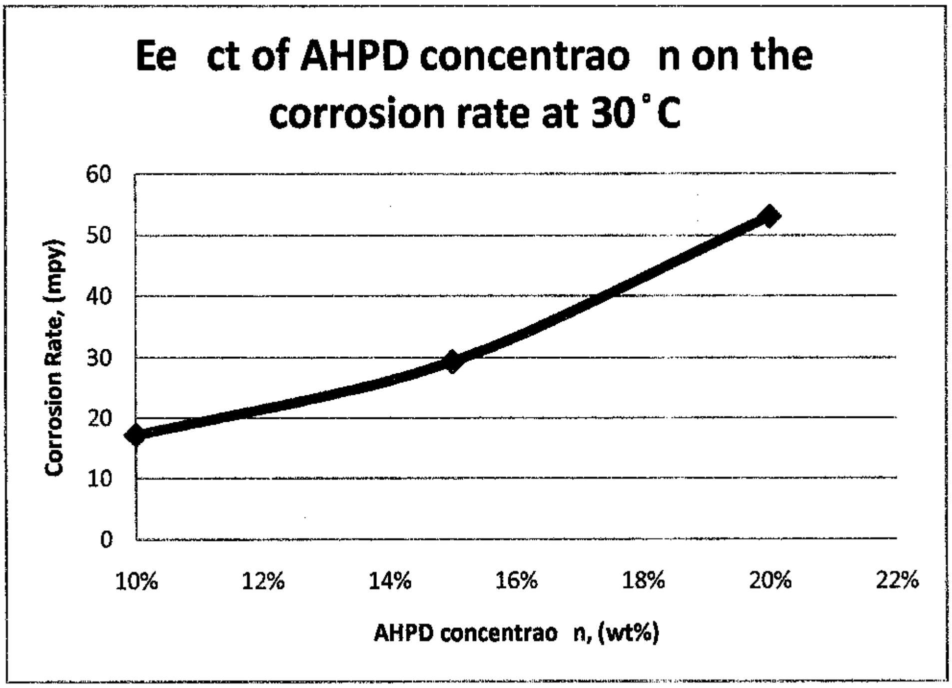


**Figure 14. Effect of AHPD concentration on the corrosion rate**

From the above graph, we can see that as the concentration of AHPD solution increases, the corrosion rate increases at constant $CO_2$ loading and temperature. This is because when we increase the amine concentration, this generally leads to an increase in the total amount of $CO_2$ molecule that is absorbed into the AHPD solution. This will result in higher amount of carbamate formation according to equation 3. And with the hydrolysis of the carbamate takes place, more $HCO_3^-$ ions will be formed which is as explained above, it is the corroding agent and corrodes carbon steel as stated in equation 5.

However, it is predicted that if the concentration is incresed further, the corrosion rate might will come to a point where it will start to decrease because as the AHPD concentration increases, the amount of water available in the solution tends to decrease. So the amount of the bicarbonate ion produced from the carbamate hydrolysis will be diminished and therefore reducing the amount of the corroding agent and hence corrosion rate starts to decrease.

## 4.4 Effect of mixing ratio of blended AHPD/PZ on the corrosion rate

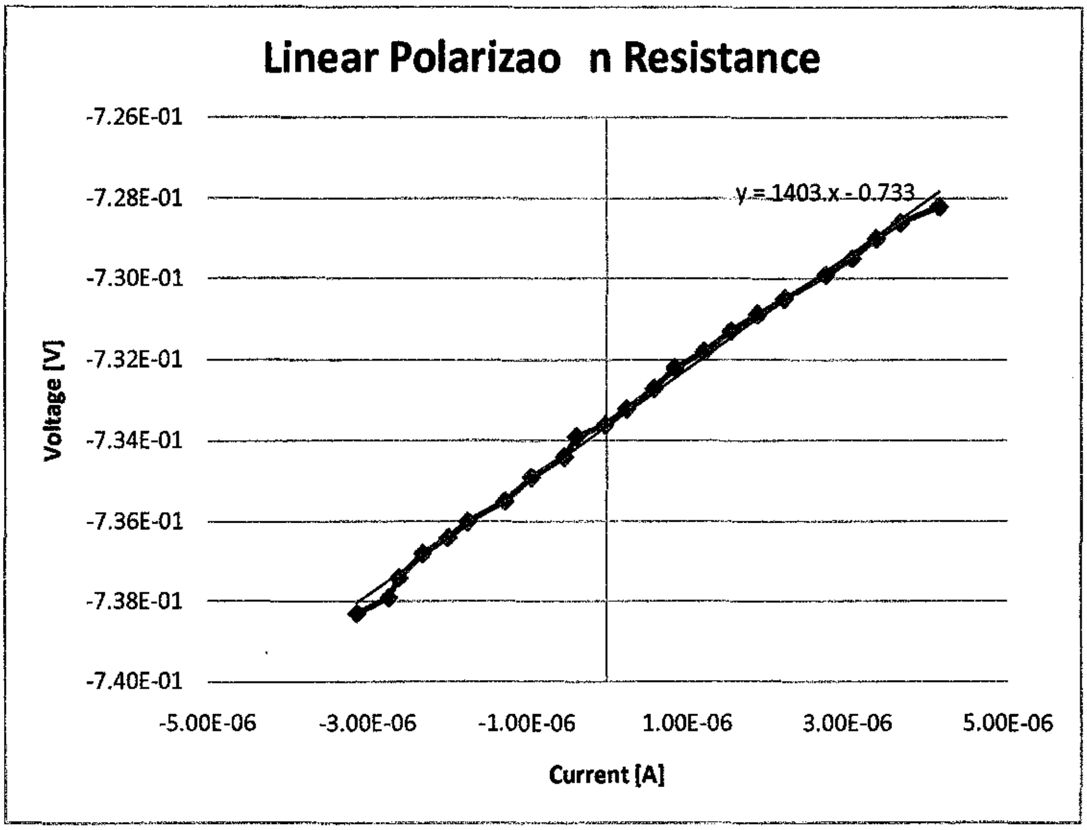


**Figure 15. Linear Polarization Resistance for 20wt% of AHPD/PZ blend (2:1) purged with $CO_2$**

The slope dE/dI is equivalent to the polarization resistance, **Rp** which is 1403 Ohm.

To calculate the corrosion rate we need to find the corrosion current $i_{corr}$ and corrosion current is calculated as follow:-

$$I_{corr} = B/Rp$$

$$\begin{aligned} I_{corr} &= 0.0261 / 1403 \\ &= 1.86 \times e^{-5} \text{ A} \\ &= 18.6 \ \mu\text{A} \end{aligned}$$

The surface area, SA, of the metal specimen used in this experiment is **0.42 cm$^2$**.

$$\text{Corrosion current density, } \mathbf{i_{corr} = I_{corr} / SA}$$
$$\mathbf{= 18.6 / 0.42}$$
$$\mathbf{= 44.29\ \mu A/cm^2}$$

$$\mathbf{CR = 0.1288\ (i_{corr}*EW/\rho)}$$

The equivalent weight of carbon steel is **27.92** and its density is **7.87 g/cm$^3$**.

$$\mathbf{Corrosion\ rate,\ CR = 0.1288*(44.29 * 27.92 / 7.87)}$$
$$\mathbf{= 20.24\ mpy}$$

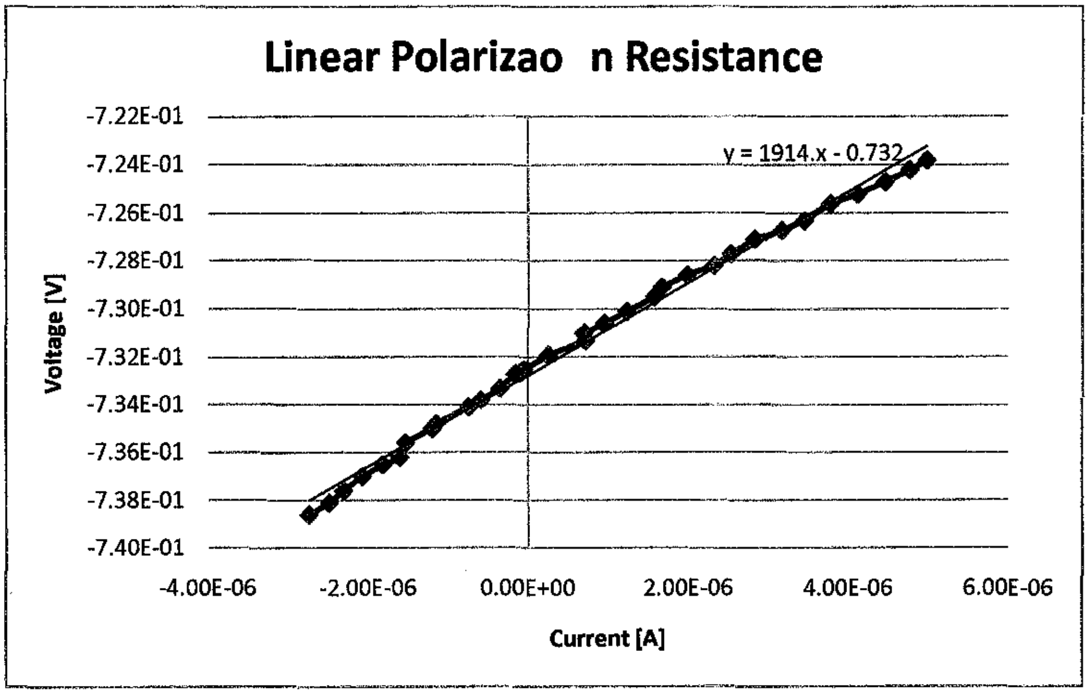


**Figure 16. Linear Polarization Resistance for 20wt% of AHPD/PZ blend (1:1) purged with $CO_2$**

The slope dE/dI is equivalent to the polarization resistance, **Rp** which is 1914 Ohm.

To calculate the corrosion current we need to find the corrosion current $i_{corr}$ and corrosion current is calculated as follow:-

$$I_{corr} = B/R\text{p}$$

$$\begin{aligned} \mathbf{I_{corr}} &= \mathbf{0.0261 / 1914} \\ &= \mathbf{1.36 \text{ x } e^{-5} \text{ A}} \\ &= \mathbf{13.6\ \mu A} \end{aligned}$$

The surface area, SA, of the metal specimen used in this experiment is **0.42 cm$^2$**.

$$\begin{aligned} \text{Corrosion current density, } \mathbf{i_{corr}} &= \mathbf{I_{corr} / SA} \\ &= \mathbf{13.6 / 0.42} \\ &= \mathbf{32.38\ \mu A/cm^2} \end{aligned}$$

$$\mathbf{CR = 0.1288\ (i_{corr} * EW/\rho)}$$

The equivalent weight of carbon steel is **27.92** and its density is **7.87 g/cm$^3$**.

$$\begin{aligned} \textbf{Corrosion rate, CR} &= \mathbf{0.1288 * (32.38 * 27.92 / 7.87)} \\ &= \mathbf{14.80 \text{ mpy}} \end{aligned}$$

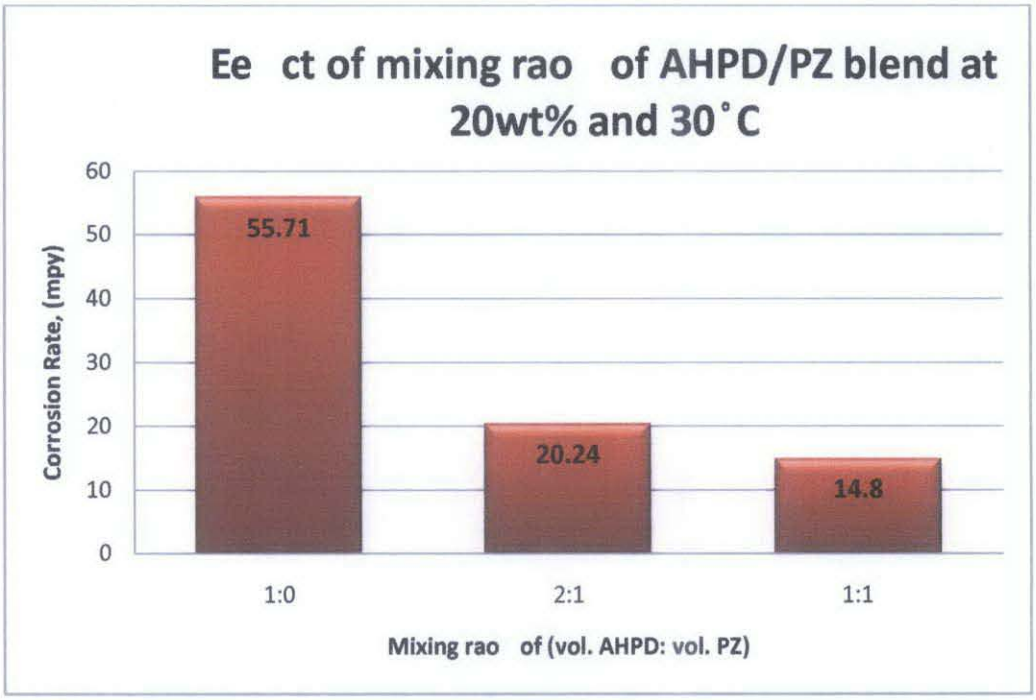


**Figure 17. Effect of mixing ratio of AHPD/PZ blend**

As can be seen from the above graph, as the amount PZ mixed with AHPD increased, the corrosion rate drops substantially. This is quite an unexpected result yet interesting as we have mentioned earlier that PZ acts as absorption enhancer. And now we can see from the result above that it inhibits the corrosion rate when it is added to AHPD. This is probably because the piperazine forms a barrier between the metal and the corrosive environment by its interaction with the metal molecules. Hence we can conclude that piperazine acts as a corrosion inhibitor [10].

## 4.5 Tafel extrapolation method

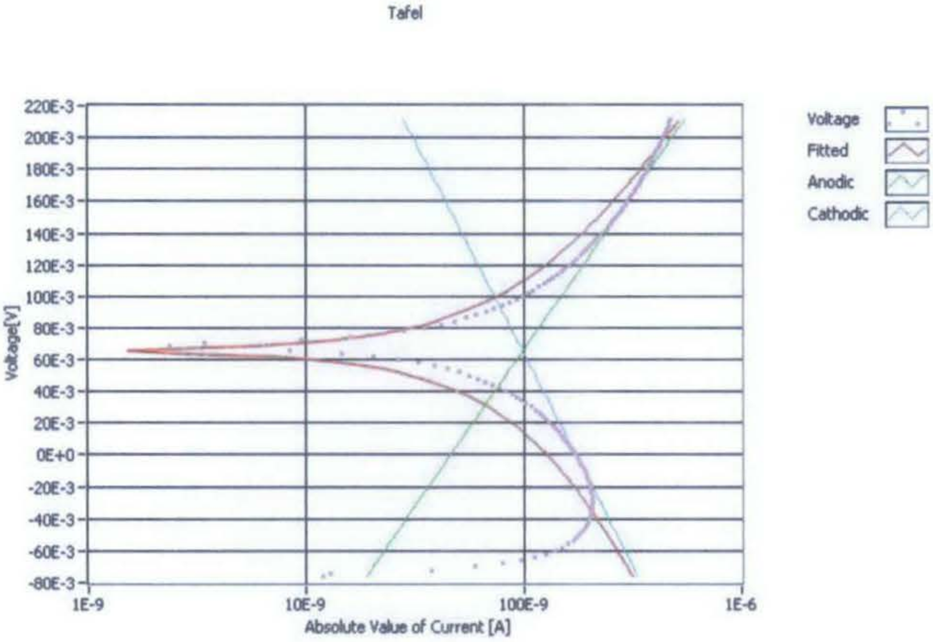


**Figure 18. Tafel Plot for 20wt% of AHPD solution at 30°C**

From the extrapolation of the Tafel slopes, the point of their intersection will be the point of corrosion current. From the graph we obtain this value as **100 x $e^{-9}$ A**.
The surface area of the metal specimen used in this experiment is **0.461cm$^2$**.

Therefore the corrosion current density = **100 x $e^{-9}$ / 0.461**
= **2.169 x $e^{-7}$ A/cm$^2$**
= **0.2169 μA/cm$^2$**

**CR = 0.1288 * ($i_{corr}$*EW/ρ)**

The equivalent weight of carbon steel is **27.92** and its density is **7.87 g/cm$^3$**.

**Corrosion rate, CR = 0.1288 * (0.2169 * 27.92 / 7.87)**
**= 0.099 mpy**

The corrosion rate obtained from linear polarization resistance is around 4.47 mpy which is quite logicaal when compared to the other amines. However the data gathered from from the Tafel extrapolation gave a different value and almost neligible corrosion which is around 0.099 mpy. This result is definitely wrong as it is impossible to have this much low corrosion from amine solution. Beside that it does not match the linear polarization resistance method.

This experiment has been run for 10 times under the same conditions that is 20 wt% of AHPD fresh solution at room temperature. However all the results for both test obtained are almost the same which gives the reproducibility and reliabilty of the data.

Regarding the error from the Tafel plot, it most probably due to high resistance in the solution as the corrosion current can be seen too low at the magnitude of $e^{-7}$ A. This small value of the corrosion current indicates that there is less cathodic and anodic reaction going on the surface of the metal. Like it is said that it might be due to solution resistance which leads to potential error. This is maybe because the working electrode is not placed as near as possible to the reference electrode and hence there will be a film of the solution in between that acts as a solution resistance. When this happens, the metal is said to be undergone passivation.

Another possible reason why the Tafel plot gave low corrosion current is perhaps due to too high or too low scan rate. The experiment was carried out at 1mV/s scan rate. High scan rate will give higher current and hence low polarization resistance and this will cause overestimation of the corrosion rate and vice versa.

Another possibility for this error is because in standard electrochemical terting methods, usually a 1 litre corrosion cell is used where as in in this project, a 40mL mini cell is used. Small volume with low AHPD concentration such as 20wt% means that only small amount of AHPD molecules is present and hence with TAFEL experiment where we use destructive method of high potential method, it is possible that the solution is decomposed before even the potential sweep is completed. This will lead to an error to the result as there will be less electrons moving in the circuit and therefore the corrosion current will be too small like what is observed in the above graph around e-7 A.

Therefore for TAFEL extrapolation method in this project is not considered as a reliable method for calculating the corrosion rate of AHPD solution.

# CHAPTER 5

# CONCLUSION & RECOMMENDATION

## 5.1 Conclusion

The corrosion rate of aqeuous AHPD with and without $CO_2$ loading was measured using Linear Polarization Resistance method and it was found that with $CO_2$ loading, the corrosion rate is much higher than the fresh solution. This is due to the carbamate formation that leads to more bicarbonate ions which is the corroding agent. The effect of different concentration of AHPD on the corrosion rate was also measured and it was found that as the concentration of AHPD is increased, the corrosion rate also increases. This is because that higher concentration of amine means more amine molecules which will absorb more $CO_2$ molecules and hence higher carbamate formation that will again produce bicarbonate ions which is the corroding agent by hydrolysis. Lastly the effect of mixing ratio of AHPD/PZ blend on the corrosion rate was beyond expectation where the as the amount of PZ in the blend is increased, the corrosion rate decreases. Therefore Piperazine is found to be acting as a corrosion inhibitor in the AHPD/PZ mixture. Both objectives were achieved but however a lot of recommendation needs to done.

## 5.2 Recommendations

- To determine the exact $CO_2$ loading for the 2 hours purging for fair result because everytime the prging is done, it might not achieve the same $CO_2$ loading as the previous one and this will adversely affect the result.

- The amount of Piperazine was limited and hence the tests for mixing ration of AHPD/PZ blends was done once only. To increase the reliability of the data above, reproducibility needs to be done.

- Linear Polarization Resistance method is a method to measure the corrosion rate by accelrating the rate. However the corrosion rate in the natural phenomena might not be the same. In order to find out, a simple immersion test should be conducted which will take 3 months to 1 year to obtain the natural corrosion rate. Then we can compare the results.

- To verify the corrosion rate obtained from LPR method, TAFEL extrapolation method should be used. But as can be seen above, it did not give reliable result. To get a good result from TAFEL extrapolation method, we need to conduct the experiment using the standard method where 1 litre corrosion cell should be used.

### 5.3 Future Work

In addition to the recommendations that has been mentioned above, we can carry on this project to more deeper level by conducting the experiment in the real condition that will be used in the amine treating plant. In order to that we will have many different new variable which might affect the corrosion rate such as temperature, $CO_2$ loading, oxygen concentration etc. By doing so, if the experiments shows promising result, then this amine can be taken into consideration to be commercialised and proposed to PETRONAS to be used in their plants.

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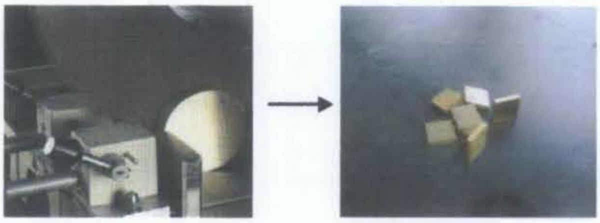
# APPENDICES

## 1- Sample Preparation

i) Cutting

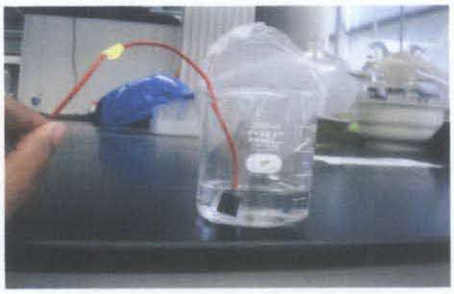


ii) Mounting

iii) Grinding

iv) Polishing

v) Degreasing



vi) Drying

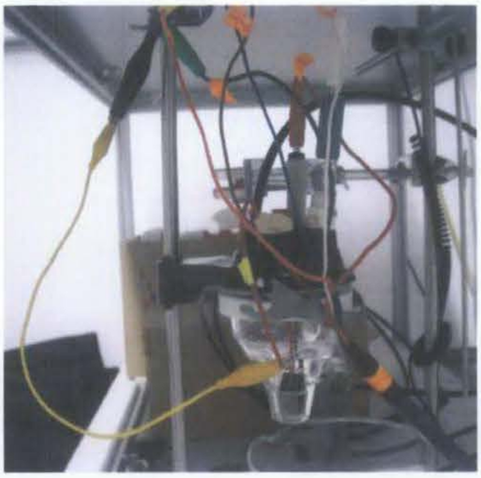
## 2- Solution Preparation

-Weighing

- Dissolving

- $CO_2$ Purging

## 3- Experimental Setup



## 4- Data Result for 10wt% AHPD solution

| Time[s] | Current[A] | Voltage[V] | LinPol |
|---|---|---|---|
| 21.5 | -1.57E-06 | -7.54E-01 | -7.53E-01 |
| 22 | -1.18E-06 | -7.54E-01 | -7.53E-01 |
| 22.5 | -1.17E-06 | -7.53E-01 | -7.53E-01 |
| 23 | -9.92E-07 | -7.53E-01 | -7.52E-01 |
| 23.5 | -7.57E-07 | -7.53E-01 | -7.52E-01 |
| 24 | -4.99E-07 | -7.52E-01 | -7.52E-01 |
| 24.5 | -2.34E-07 | -7.52E-01 | -7.51E-01 |
| 25 | 5.59E-08 | -7.51E-01 | -7.51E-01 |
| 25.5 | 2.45E-07 | -7.51E-01 | -7.50E-01 |
| 26 | 3.40E-07 | -7.51E-01 | -7.50E-01 |
| 26.5 | 6.62E-07 | -7.50E-01 | -7.50E-01 |
| 27 | 1.07E-06 | -7.49E-01 | -7.49E-01 |
| 27.5 | 1.38E-06 | -7.49E-01 | -7.49E-01 |
| 28 | 1.53E-06 | -7.48E-01 | -7.48E-01 |
| 28.5 | 1.77E-06 | -7.48E-01 | -7.48E-01 |
| 29 | 2.07E-06 | -7.48E-01 | -7.47E-01 |
| 29.5 | 2.35E-06 | -7.47E-01 | -7.47E-01 |
| 30 | 2.72E-06 | -7.47E-01 | -7.46E-01 |
| 30.5 | 2.83E-06 | -7.46E-01 | -7.46E-01 |
| 31 | 3.21E-06 | -7.46E-01 | -7.46E-01 |
| 31.5 | 3.57E-06 | -7.45E-01 | -7.45E-01 |
| 32 | 3.85E-06 | -7.45E-01 | -7.45E-01 |
| 32.5 | 4.14E-06 | -7.44E-01 | -7.44E-01 |
| 33 | 4.57E-06 | -7.44E-01 | -7.44E-01 |
| 33.5 | 4.92E-06 | -7.43E-01 | -7.43E-01 |
| 34 | 5.22E-06 | -7.42E-01 | -7.42E-01 |
| 34.5 | 5.58E-06 | -7.42E-01 | -7.42E-01 |
| 35 | 5.93E-06 | -7.41E-01 | -7.41E-01 |
| 35.5 | 6.31E-06 | -7.41E-01 | -7.41E-01 |
| 36 | 6.48E-06 | -7.40E-01 | -7.40E-01 |
| 36.5 | 6.80E-06 | -7.40E-01 | -7.40E-01 |
| 37 | 7.24E-06 | -7.39E-01 | -7.39E-01 |
| 37.5 | 7.58E-06 | -7.39E-01 | -7.39E-01 |
| 38 | 7.95E-06 | -7.38E-01 | -7.38E-01 |
| 38.5 | 8.37E-06 | -7.38E-01 | -7.38E-01 |
| 39 | 8.77E-06 | -7.37E-01 | -7.37E-01 |
| 39.5 | 9.13E-06 | -7.37E-01 | -7.36E-01 |
| 40 | 9.44E-06 | -7.36E-01 | -7.36E-01 |

## 5- Data Result for 15wt% AHPD solution

| Time[s] | Current[A] | Voltage[V] | LinPol |
|---|---|---|---|
| 23 | -1.41E-06 | -7.12E-01 | -7.10E-01 |
| 23.5 | -1.05E-06 | -7.11E-01 | -7.10E-01 |
| 24 | -6.83E-07 | -7.11E-01 | -7.09E-01 |
| 24.5 | -3.98E-07 | -7.11E-01 | -7.09E-01 |
| 25 | -3.26E-08 | -7.10E-01 | -7.09E-01 |
| 25.5 | 3.10E-07 | -7.10E-01 | -7.08E-01 |
| 26 | 7.69E-07 | -7.09E-01 | -7.08E-01 |
| 26.5 | 1.26E-06 | -7.09E-01 | -7.08E-01 |
| 27 | 1.84E-06 | -7.08E-01 | -7.07E-01 |
| 27.5 | 2.22E-06 | -7.08E-01 | -7.07E-01 |
| 28 | 2.78E-06 | -7.07E-01 | -7.06E-01 |
| 28.5 | 3.11E-06 | -7.07E-01 | -7.06E-01 |
| 29 | 3.63E-06 | -7.06E-01 | -7.06E-01 |
| 29.5 | 4.02E-06 | -7.06E-01 | -7.05E-01 |
| 30 | 4.55E-06 | -7.05E-01 | -7.05E-01 |
| 30.5 | 5.17E-06 | -7.04E-01 | -7.04E-01 |
| 31 | 5.54E-06 | -7.04E-01 | -7.04E-01 |
| 31.5 | 6.20E-06 | -7.03E-01 | -7.03E-01 |
| 32 | 6.62E-06 | -7.03E-01 | -7.03E-01 |
| 32.5 | 7.06E-06 | -7.03E-01 | -7.03E-01 |
| 33 | 7.62E-06 | -7.02E-01 | -7.02E-01 |
| 33.5 | 8.41E-06 | -7.01E-01 | -7.01E-01 |
| 34 | 8.97E-06 | -7.01E-01 | -7.01E-01 |
| 34.5 | 9.51E-06 | -7.00E-01 | -7.00E-01 |
| 35 | 1.00E-05 | -7.00E-01 | -7.00E-01 |
| 35.5 | 1.06E-05 | -6.99E-01 | -6.99E-01 |
| 36 | 1.14E-05 | -6.99E-01 | -6.99E-01 |
| 36.5 | 1.18E-05 | -6.98E-01 | -6.98E-01 |
| 37 | 1.23E-05 | -6.98E-01 | -6.98E-01 |
| 37.5 | 1.30E-05 | -6.97E-01 | -6.97E-01 |
| 38 | 1.33E-05 | -6.97E-01 | -6.97E-01 |
| 38.5 | 1.42E-05 | -6.96E-01 | -6.96E-01 |
| 39 | 1.45E-05 | -6.96E-01 | -6.96E-01 |
| 39.5 | 1.51E-05 | -6.96E-01 | -6.96E-01 |
| 40 | 1.59E-05 | -6.95E-01 | -6.95E-01 |

### 6- Data Result for 20wt% fresh AHPD solution

| Time[s] | Current[A] | Voltage[V] | LinPol |
|---|---|---|---|
| 7.5 | -1.02E-05 | -9.33E-02 | -9.26E-02 |
| 8 | -1.01E-05 | -9.27E-02 | -9.23E-02 |
| 8.5 | -1.01E-05 | -9.22E-02 | -9.21E-02 |
| 9 | -1.00E-05 | -9.17E-02 | -9.16E-02 |
| 9.5 | -9.93E-06 | -9.12E-02 | -9.12E-02 |
| 10 | -9.87E-06 | -9.08E-02 | -9.08E-02 |
| 10.5 | -9.80E-06 | -9.03E-02 | -9.04E-02 |
| 11 | -9.74E-06 | -8.98E-02 | -9.00E-02 |
| 11.5 | -9.67E-06 | -8.93E-02 | -8.96E-02 |
| 12 | -9.59E-06 | -8.89E-02 | -8.91E-02 |
| 12.5 | -9.53E-06 | -8.84E-02 | -8.86E-02 |
| 13 | -9.45E-06 | -8.78E-02 | -8.82E-02 |
| 13.5 | -9.39E-06 | -8.73E-02 | -8.78E-02 |
| 14 | -9.33E-06 | -8.69E-02 | -8.74E-02 |
| 14.5 | -9.22E-06 | -8.63E-02 | -8.67E-02 |
| 15 | -9.12E-06 | -8.58E-02 | -8.61E-02 |
| 15.5 | -9.05E-06 | -8.54E-02 | -8.56E-02 |
| 16 | -8.95E-06 | -8.48E-02 | -8.50E-02 |
| 16.5 | -8.86E-06 | -8.43E-02 | -8.44E-02 |
| 17 | -8.80E-06 | -8.38E-02 | -8.41E-02 |
| 17.5 | -8.70E-06 | -8.33E-02 | -8.35E-02 |
| 18 | -8.63E-06 | -8.28E-02 | -8.30E-02 |
| 18.5 | -8.55E-06 | -8.23E-02 | -8.25E-02 |
| 19 | -8.45E-06 | -8.17E-02 | -8.19E-02 |
| 19.5 | -8.37E-06 | -8.12E-02 | -8.14E-02 |
| 20 | -8.25E-06 | -8.08E-02 | -8.06E-02 |
| 20.5 | -8.17E-06 | -8.02E-02 | -8.01E-02 |
| 21 | -8.10E-06 | -7.97E-02 | -7.97E-02 |
| 21.5 | -8.02E-06 | -7.92E-02 | -7.91E-02 |
| 22 | -7.93E-06 | -7.87E-02 | -7.86E-02 |
| 22.5 | -7.86E-06 | -7.82E-02 | -7.82E-02 |
| 23 | -7.79E-06 | -7.77E-02 | -7.77E-02 |
| 23.5 | -7.71E-06 | -7.73E-02 | -7.72E-02 |
| 24 | -7.64E-06 | -7.68E-02 | -7.68E-02 |
| 24.5 | -7.53E-06 | -7.62E-02 | -7.61E-02 |
| 25 | -7.43E-06 | -7.58E-02 | -7.55E-02 |
| 25.5 | -7.35E-06 | -7.53E-02 | -7.50E-02 |
| 26 | -7.27E-06 | -7.47E-02 | -7.45E-02 |

| | | | |
|---|---|---|---|
| 26.5 | -7.19E-06 | -7.42E-02 | -7.39E-02 |
| 27 | -7.11E-06 | -7.37E-02 | -7.34E-02 |
| 27.5 | -7.03E-06 | -7.33E-02 | -7.29E-02 |
| 28 | -6.97E-06 | -7.28E-02 | -7.25E-02 |
| 28.5 | -6.89E-06 | -7.23E-02 | -7.21E-02 |
| 29 | -6.81E-06 | -7.17E-02 | -7.16E-02 |
| 29.5 | -6.76E-06 | -7.13E-02 | -7.12E-02 |
| 30 | -6.67E-06 | -7.08E-02 | -7.07E-02 |
| 30.5 | -6.60E-06 | -7.03E-02 | -7.02E-02 |
| 31 | -6.53E-06 | -6.98E-02 | -6.98E-02 |
| 31.5 | -6.47E-06 | -6.93E-02 | -6.94E-02 |
| 32 | -6.40E-06 | -6.88E-02 | -6.90E-02 |
| 32.5 | -6.33E-06 | -6.84E-02 | -6.86E-02 |
| 33 | -6.26E-06 | -6.79E-02 | -6.81E-02 |
| 33.5 | -6.20E-06 | -6.74E-02 | -6.77E-02 |
| 34 | -6.14E-06 | -6.69E-02 | -6.73E-02 |
| 34.5 | -6.04E-06 | -6.65E-02 | -6.67E-02 |
| 35 | -5.95E-06 | -6.59E-02 | -6.61E-02 |
| 35.5 | -5.88E-06 | -6.56E-02 | -6.57E-02 |
| 36 | -5.81E-06 | -6.49E-02 | -6.53E-02 |
| 36.5 | -5.77E-06 | -6.46E-02 | -6.50E-02 |
| 37 | -5.70E-06 | -6.40E-02 | -6.46E-02 |
| 37.5 | -5.62E-06 | -6.34E-02 | -6.41E-02 |
| 38 | -5.58E-06 | -6.30E-02 | -6.38E-02 |
| 38.5 | -5.49E-06 | -6.24E-02 | -6.33E-02 |
| 39 | -5.41E-06 | -6.19E-02 | -6.28E-02 |
| 39.5 | -5.34E-06 | -6.13E-02 | -6.23E-02 |
| 40 | -5.26E-06 | -6.08E-02 | -6.18E-02 |

## 7- Data Result for 20wt% AHPD solution after purged with $CO_2$

| Time[s] | Current[A] | Voltage[V] | LinPol |
|---|---|---|---|
| 5.5 | -9.85E-05 | -3.45E-01 | -3.42E-01 |
| 6 | -9.83E-05 | -3.45E-01 | -3.42E-01 |
| 6.5 | -9.77E-05 | -3.44E-01 | -3.42E-01 |
| 7 | -9.71E-05 | -3.44E-01 | -3.42E-01 |
| 7.5 | -9.64E-05 | -3.43E-01 | -3.41E-01 |
| 8 | -9.58E-05 | -3.43E-01 | -3.41E-01 |
| 8.5 | -9.52E-05 | -3.42E-01 | -3.41E-01 |
| 9 | -9.44E-05 | -3.42E-01 | -3.40E-01 |
| 9.5 | -9.36E-05 | -3.41E-01 | -3.40E-01 |
| 10 | -9.29E-05 | -3.41E-01 | -3.39E-01 |
| 10.5 | -9.23E-05 | -3.40E-01 | -3.39E-01 |
| 11 | -9.15E-05 | -3.39E-01 | -3.39E-01 |
| 11.5 | -9.07E-05 | -3.39E-01 | -3.38E-01 |
| 12 | -8.98E-05 | -3.39E-01 | -3.38E-01 |
| 12.5 | -8.87E-05 | -3.38E-01 | -3.37E-01 |
| 13 | -8.81E-05 | -3.37E-01 | -3.37E-01 |
| 13.5 | -8.73E-05 | -3.37E-01 | -3.37E-01 |
| 14 | -8.66E-05 | -3.37E-01 | -3.36E-01 |
| 14.5 | -8.59E-05 | -3.36E-01 | -3.36E-01 |
| 15 | -8.49E-05 | -3.36E-01 | -3.35E-01 |
| 15.5 | -8.40E-05 | -3.35E-01 | -3.35E-01 |
| 16 | -8.32E-05 | -3.35E-01 | -3.34E-01 |
| 16.5 | -8.24E-05 | -3.34E-01 | -3.34E-01 |
| 17 | -8.13E-05 | -3.34E-01 | -3.33E-01 |
| 17.5 | -8.05E-05 | -3.33E-01 | -3.33E-01 |
| 18 | -7.96E-05 | -3.33E-01 | -3.33E-01 |
| 18.5 | -7.83E-05 | -3.32E-01 | -3.32E-01 |
| 19 | -7.75E-05 | -3.32E-01 | -3.32E-01 |
| 19.5 | -7.66E-05 | -3.31E-01 | -3.31E-01 |
| 20 | -7.56E-05 | -3.31E-01 | -3.31E-01 |
| 20.5 | -7.46E-05 | -3.30E-01 | -3.30E-01 |
| 21 | -7.36E-05 | -3.30E-01 | -3.29E-01 |
| 21.5 | -7.26E-05 | -3.29E-01 | -3.29E-01 |
| 22 | -7.18E-05 | -3.29E-01 | -3.29E-01 |
| 22.5 | -7.08E-05 | -3.28E-01 | -3.28E-01 |
| 23 | -6.98E-05 | -3.28E-01 | -3.28E-01 |
| 23.5 | -6.89E-05 | -3.27E-01 | -3.27E-01 |
| 24 | -6.80E-05 | -3.27E-01 | -3.27E-01 |

| | | | |
|---|---|---|---|
| 24.5 | -6.71E-05 | -3.26E-01 | -3.26E-01 |
| 25 | -6.60E-05 | -3.26E-01 | -3.26E-01 |
| 25.5 | -6.49E-05 | -3.25E-01 | -3.25E-01 |
| 26 | -6.40E-05 | -3.25E-01 | -3.25E-01 |
| 26.5 | -6.31E-05 | -3.24E-01 | -3.24E-01 |
| 27 | -6.21E-05 | -3.24E-01 | -3.24E-01 |
| 27.5 | -6.12E-05 | -3.23E-01 | -3.23E-01 |
| 28 | -6.02E-05 | -3.23E-01 | -3.23E-01 |
| 28.5 | -5.93E-05 | -3.22E-01 | -3.22E-01 |
| 29 | -5.82E-05 | -3.22E-01 | -3.22E-01 |
| 29.5 | -5.72E-05 | -3.21E-01 | -3.21E-01 |
| 30 | -5.64E-05 | -3.21E-01 | -3.21E-01 |
| 30.5 | -5.55E-05 | -3.20E-01 | -3.20E-01 |
| 31 | -5.45E-05 | -3.20E-01 | -3.20E-01 |
| 31.5 | -5.32E-05 | -3.19E-01 | -3.19E-01 |
| 32 | -5.24E-05 | -3.19E-01 | -3.19E-01 |
| 32.5 | -5.12E-05 | -3.18E-01 | -3.18E-01 |
| 33 | -5.03E-05 | -3.18E-01 | -3.18E-01 |
| 33.5 | -4.94E-05 | -3.17E-01 | -3.17E-01 |
| 34 | -4.81E-05 | -3.17E-01 | -3.16E-01 |
| 34.5 | -4.72E-05 | -3.16E-01 | -3.16E-01 |
| 35 | -4.63E-05 | -3.16E-01 | -3.16E-01 |
| 35.5 | -4.53E-05 | -3.15E-01 | -3.15E-01 |
| 36 | -4.42E-05 | -3.15E-01 | -3.15E-01 |
| 36.5 | -4.36E-05 | -3.14E-01 | -3.14E-01 |
| 37 | -4.25E-05 | -3.14E-01 | -3.14E-01 |
| 37.5 | -4.16E-05 | -3.13E-01 | -3.13E-01 |
| 38 | -4.06E-05 | -3.13E-01 | -3.13E-01 |
| 38.5 | -3.97E-05 | -3.12E-01 | -3.12E-01 |
| 39 | -3.87E-05 | -3.12E-01 | -3.12E-01 |
| 39.5 | -3.75E-05 | -3.11E-01 | -3.11E-01 |
| 40 | -3.66E-05 | -3.11E-01 | -3.11E-01 |

## 8- Data Result for 20wt% AHPD/PZ blend (1:1)

| Time[s] | Current[A] | Voltage[V] | LinPol |
|---|---|---|---|
| 26 | -2.74E-06 | -7.39E-01 | -7.37E-01 |
| 26.5 | -2.49E-06 | -7.38E-01 | -7.37E-01 |
| 27 | -2.31E-06 | -7.38E-01 | -7.36E-01 |
| 27.5 | -2.08E-06 | -7.37E-01 | -7.36E-01 |
| 28 | -1.82E-06 | -7.37E-01 | -7.35E-01 |
| 28.5 | -1.61E-06 | -7.36E-01 | -7.35E-01 |
| 29 | -1.54E-06 | -7.36E-01 | -7.35E-01 |
| 29.5 | -1.20E-06 | -7.35E-01 | -7.34E-01 |
| 30 | -1.15E-06 | -7.35E-01 | -7.34E-01 |
| 30.5 | -7.44E-07 | -7.34E-01 | -7.34E-01 |
| 31 | -5.90E-07 | -7.34E-01 | -7.33E-01 |
| 31.5 | -3.56E-07 | -7.33E-01 | -7.33E-01 |
| 32 | -1.62E-07 | -7.33E-01 | -7.33E-01 |
| 32.5 | -5.54E-08 | -7.33E-01 | -7.32E-01 |
| 33 | 2.53E-07 | -7.32E-01 | -7.32E-01 |
| 33.5 | 7.19E-07 | -7.31E-01 | -7.31E-01 |
| 34 | 6.98E-07 | -7.31E-01 | -7.31E-01 |
| 34.5 | 9.49E-07 | -7.31E-01 | -7.31E-01 |
| 35 | 1.23E-06 | -7.30E-01 | -7.30E-01 |
| 35.5 | 1.57E-06 | -7.30E-01 | -7.30E-01 |
| 36 | 1.67E-06 | -7.29E-01 | -7.29E-01 |
| 36.5 | 1.98E-06 | -7.29E-01 | -7.29E-01 |
| 37 | 2.31E-06 | -7.28E-01 | -7.28E-01 |
| 37.5 | 2.53E-06 | -7.28E-01 | -7.28E-01 |
| 38 | 2.82E-06 | -7.27E-01 | -7.27E-01 |
| 38.5 | 3.16E-06 | -7.27E-01 | -7.27E-01 |
| 39 | 3.45E-06 | -7.26E-01 | -7.26E-01 |
| 39.5 | 3.77E-06 | -7.26E-01 | -7.26E-01 |
| 40 | 4.11E-06 | -7.25E-01 | -7.25E-01 |
| 40.5 | 4.46E-06 | -7.25E-01 | -7.24E-01 |
| 41 | 4.76E-06 | -7.24E-01 | -7.24E-01 |
| 41.5 | 4.98E-06 | -7.24E-01 | -7.24E-01 |

## 8- Data Result for 20wt% AHPD/PZ blend (2:1)

| Time[s] | Current[A] | Voltage[V] | LinPol |
|---|---|---|---|
| 20.5 | -3.13E-06 | -7.38E-01 | -7.37E-01 |
| 21 | -2.74E-06 | -7.38E-01 | -7.37E-01 |
| 21.5 | -2.61E-06 | -7.37E-01 | -7.37E-01 |
| 22 | -2.31E-06 | -7.37E-01 | -7.36E-01 |
| 22.5 | -2.00E-06 | -7.36E-01 | -7.36E-01 |
| 23 | -1.75E-06 | -7.36E-01 | -7.36E-01 |
| 23.5 | -1.28E-06 | -7.36E-01 | -7.35E-01 |
| 24 | -9.51E-07 | -7.35E-01 | -7.35E-01 |
| 24.5 | -5.35E-07 | -7.34E-01 | -7.34E-01 |
| 25 | -3.86E-07 | -7.34E-01 | -7.34E-01 |
| 25.5 | -2.50E-08 | -7.34E-01 | -7.33E-01 |
| 26 | 2.45E-07 | -7.33E-01 | -7.33E-01 |
| 26.5 | 5.88E-07 | -7.33E-01 | -7.33E-01 |
| 27 | 8.48E-07 | -7.32E-01 | -7.32E-01 |
| 27.5 | 1.21E-06 | -7.32E-01 | -7.32E-01 |
| 28 | 1.55E-06 | -7.31E-01 | -7.31E-01 |
| 28.5 | 1.88E-06 | -7.31E-01 | -7.31E-01 |
| 29 | 2.21E-06 | -7.31E-01 | -7.31E-01 |
| 29.5 | 2.72E-06 | -7.30E-01 | -7.30E-01 |
| 30 | 3.05E-06 | -7.30E-01 | -7.30E-01 |
| 30.5 | 3.36E-06 | -7.29E-01 | -7.29E-01 |
| 31 | 3.65E-06 | -7.29E-01 | -7.29E-01 |
| 31.5 | 4.14E-06 | -7.28E-01 | -7.28E-01 |