

**A Study of Corrosion Behaviour for Steels Precipitated with Paraffin
Wax Precipitation**

Dissertation

by

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Bachelor of Engineering (Hons)
(Mechanical)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Mechanical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
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Approved by,

(DR. KEE KOK ENG)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JAN 2016

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 people.

(ARVIN KUMAR A/L A SIARAMU)

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ABSTRACT

Paraffin wax and CO₂ corrosion have caused many problems in oil and gas industry. These problems mainly caused in the transportation and utilities where the pipelines are severely corroded. Adding to this situation paraffin wax deposition causing blockage which results flow assurance. Many experiments have been conducted individually on finding the factors that cause corrosion and factors causing wax precipitation. Only a few research relating both the problems together. In this research, the objective is to design and develop apparatus to produce wax onto a steel surface in laboratory environment and to determine the effect of paraffin wax precipitation on the corrosion of steel. In order to complete these objective, wax appearance temperature (WAT) was determine in order to precipitate 1.5mm thick 10% and 30% paraffin wax on the APL 5L X65 steel. Modified cold spot test was designed in order to precipitate paraffin wax on 24°C X65 steel for 24 hours. Before conducting the *Linear Polarization Resistance (LPR)* experiment for the precipitated samples, a baseline test was conducted using three electrode system in a glass cell to identify the corrosion rate of X65 carbon steel in the 3% NaCl purged with CO₂ under room temperature without any precipitation. The 10% and 30% paraffin wax precipitation samples were placed in the same experiment under similar condition for 24 hours. The corrosion rate which is taken from all three LPR test to comparison analysis. Based on the analysis, it has been found that as the composition of the paraffin wax increases the corrosion rate decrease. This proves that paraffin wax precipitated on the steel act as a protective layer to inhibit corrosion.

Key Words: *Paraffin Wax; Carbon Steel (API 5L X65); CO₂ Corrosion; Paraffin Wax precipitation Experiment; Wax Appearance Temperature (WAT); Linear Polarization Resistance (LPR); Glass Cell; Modified Cold Spot Test*

CHAPTER 1:INTRODUCTION

1.1 Background of study

Paraffin deposition is one of long standing problem in the oil industry,' Crude oils often contain paraffins which precipitate and adhere to the liner, tubing, sucker rods and surface equipment as the temperature of the producing stream decreases in the normal course of flowing, gas lifting or pumping. Heavy paraffin deposits are undesirable because they reduce the effective size of the flow conduits and restrict the production rate from the well [1]. Where severe paraffin deposition occurs, removal of the deposits by mechanical, thermal or other means is require, resulting in costly down time and increased operating costs.

Significant operating costs are incurred from treatments designed to remove waxy deposits from production tubing or squeeze treatments designed to inhibit wax deposition [1]. The costs are increased further by formation damage and loss of production that may result from these treatments.

Paraffin deposits collect in wellbores, production tubing, and flowlines. Under certain conditions, paraffin deposition may occur also in the producing formation. The problems caused by these deposits are related to restricted flow as shown in Figure 1, which leads to increased flowline pressure, decreased production, and mechanical problems [2].

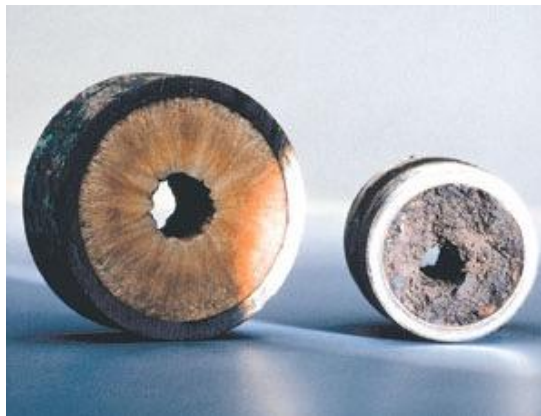


Figure 1: A cross-section of paraffin and scale blocked flowlines [2]

Another problem that is face by the oil and gas industry is that the corrosion in steel pipelines. This is a common problem face by the industry due to presence of water and microbiological species which cause corrosion. The usage of corrosion resistant alloys (CRAs) has to be excluded because of high cost. On the other hand, Carbon steel are widely used in the industry because of minimal effort, simple manufacturing and conveniences in using [2]. However, the pipelines lifespan is reduced due to internal corrosion. In 2008, A study conducted by Matthew R. Simmons (NACE International) which has estimated that the total cost of corrosion in the oil and gas industry is \$1.327 billion annually which includes \$589 million of direct cost in the surface pipeline and facility cost [3].

In that, great portion is due to internal corrosion in transportation utilities. Thus, in order to diminish the loss brought on by internal corrosion, it is important to study the occurrences of internal pipeline corrosion more intense and reduce the aspects that induce it.

1.2 Problem Statement

As stated in the background study, internal corrosion in the pipeline has cost billions of U.S dollars for treatments and replacing the current steel pipeline with CRAs will only increase the cost even more. There is an additional layer of paraffin wax forms naturally within these steel pipelines during crude oil transportation. Many experiments have been conducted individually on finding the factors that cause corrosion and factors causing wax precipitation. Depending on the paraffin concentration in oil, the effect on corrosion changes. For example if the paraffin wax content in the crude oil is high, it forms a protective layer within the pipelines. If less the protective layer will be containing pores which could expose the steel to CO₂ corrosion. The main questions in this place are:

1. How to produce paraffin wax onto a steel surface in laboratory environment?
2. What is the effect of paraffin wax precipitation on the carbon steel corrosion?

1.3 Objective

There are 2 objectives that needed to be achieved in this final year project;

1. To design and develop method to produce wax precipitation onto a steel surface in laboratory environment.
2. To determine the effect of paraffin wax precipitation on the corrosion of steel

1.4 Scope of Study

In order to complete this project, literature review and research on the relevant works will be conducted throughout the 14 weeks to update on the knowledge of corrosion on the steel and paraffin wax precipitation. Experiments to find a method to precipitate paraffin wax on the steel will be conducted. Fabrication may required for the design This part of the study focuses on paraffin wax formation onto the steel pipelines. The later part of the study focuses on the effect of paraffin wax on the steel based on its corrosion rate. The study is required to know about the corrosion rate determination. The most common method is to use linear polarization resistance method to identify the corrosion rate against time.

CHAPTER 2: LITERATURE REVIEW

2.1 Paraffin wax

In Crude oil there are many substances, one of it is paraffin. Paraffin has define by many experts differently. Figure 2 shows the effect paraffin wax on structure such as the effect of wax deposition is shown on a well tubing string, a cross-section of a flowline, and the inside of a tubular.



Figure 2: The effect of wax deposition is shown on (a) a well tubing string, (b) a cross-section of a flowline, and (c) the inside of a tubular [4]

Based on Speight, saturated hydrocarbons are called paraffins. The paraffins are either straight (normal paraffin) or branched (isoparaffin) chains, however they do not contain ring structure. Crude oil can be named paraffinic or naphthenic crude based on the relative fraction of their compounds. Normally 20-50% of normal paraffin can be contained paraffinic in the oil and gas industry [5]. According to Gracia et al., Paraffin produced from the crude oil consist of mostly saturated long chain hydrocarbons. These carbon chains length from C8 to C75 +[6]. Paraffin wax's material is identified to be macrocrystalline wax.

Macrocrystalline waxes lead to paraffin problems in production and transport operations; microcrystalline waxes contribute the most to tank-bottom sludges. In understanding the paraffin's characteristic, it is crucial to learn about the wax appearance temperature (WAT), the temperature in wax-oil mixture can cause a natural precipitation of wax [7]. When a liquid solution or melt is lowered to the wax appearance temperature (WAT), the wax molecules form clusters of aligned chains. Once these nuclei reach a critical size, they become stable and further attachment of molecules leads to growth of

the crystal. Formation of these nuclei causes the fluid to take on a cloudy appearance, hence the name cloud point. This also is referred to as the wax crystallization temperature or wax appearance point. Determination of a WAT significantly higher than the temperatures expected to be encountered during production indicates the potential for wax deposition problems. This is why prior to the oil production and transportation, it is important to identify precisely the WAT [8].

Figure 3 shows the how the paraffin wax is deposited on to the pipelines. So, wax crystals trap oil molecules in a network. The network forms a hydro gel matrix. This hydro gel matrix ends up trapping other wax crystals in the surroundings, and the amount of wax in the pipes increases over time. Since the wall have the lowest temperature, this waxy, gel-like substance sticks to the walls of the pipe and hardens in which the hydrocarbons are being transported being affected.

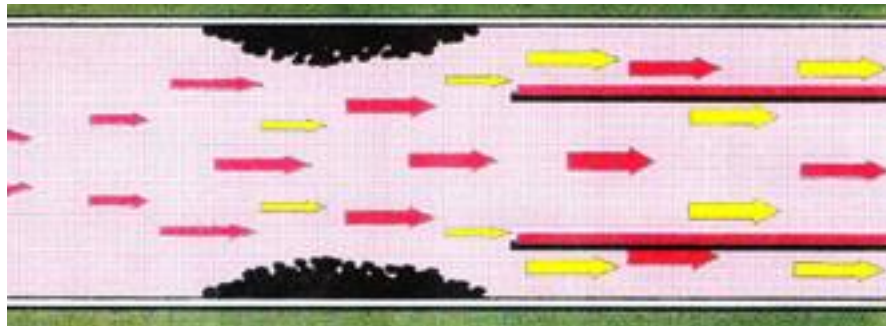


Figure 3 : The schematic diagram of paraffin wax deposition in pipeline

Factor that affect the paraffin wax deposition are determined in many case studies. The most common factor are temperature differential and cooling rate. In addition to the cooling rate, the temperature differential between the bulk of solution and cold surface is another factor for wax deposition [9]. Wax deposition increases with an increase in temperature difference. According to Cole and Jessen, the temperature differential between the solution cloud point and cold surface is more important than that between bulk and cold surface [10]. Wax deposition would occur only when the surface temperature is below both the solution temperature and the solution cloud point Y .

The thickness of the wax layer increases, and this layer acts as insulation and reduces the effective temperature differential. This lowers the availability of wax crystals for further deposition. The size and number of crystals formed are also important for wax deposition. At a higher rate of cooling, the wax precipitates out in smaller crystals and a large number of crystals are formed because of the large number of crystallization sites available.

If it is high, cooling is rapid and both lower and higher melting waxes crystallize simultaneously, forming a weak porous structure with cavities full of oil [9]. At a lower rate of cooling, the crystallization process is more uniform. Thus, more uniformly packed crystals are formed that possess a relatively small surface area and free energy. Temperature differential also affects the composition of deposited wax.

A study by Rashidi, M insulation systems has better performance and been found to in preventing heat loss and solid deposition during flow conditions [11]. However, the study utilized flow loop apparatus which will be difficult to use to take sample for corrosion rate testing.

2.1.1 Methods to precipitate Paraffin Wax

The wax precipitation on laboratory can be produced by using the following two methods;

- The Cold Spot Test

This method was proposed by Hunt, [12]. The cold spot test apparatus consists of a flat circular plate mounted on a curved tube and positioned in a vessel containing a wax-oil solution as shown in Figure 4. The apparatus is arranged so that the temperature of the central portion of the circular plate can be varied by means of a circulating liquid stream; the test equipment includes provisions for maintaining a constant wax-oil solution temperature and stirring speed. In the paraffin deposition studies, the modified cold spot tester was used as follows Jorda, [13]. The cold spot probe consisted of a flat circular plate 2 in. in diameter and 1/8-in. thick positioned in the wax-oil solution kept at constant temperature. A cold liquid was circulated through a tube connected to the circular plate so that the liquid impinged on one side of the plate cooling the plate from the center outward, causing paraffin to deposit on the side of the plate exposed to the wax-oil solution [13].

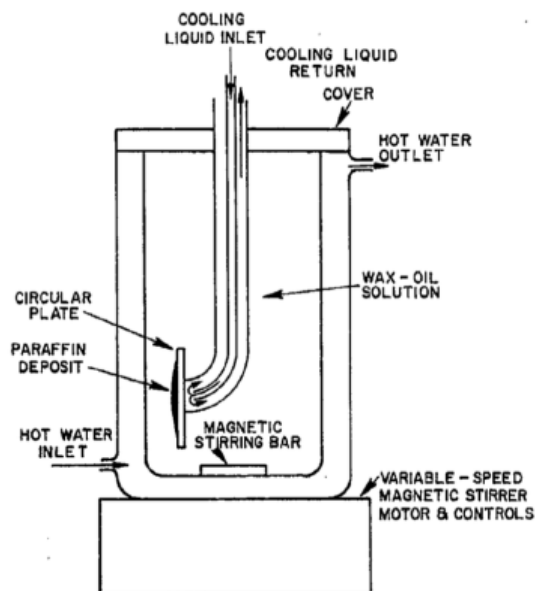


Figure 4: Apparatus set up for Hunts Cold Spot Test [13]

- Altered test conduct using Peltier cooler

This method was proposed by Yang, in which Yang used a Peltier cooler to cool the specimen. Peltier cooler is thermoelectric cooler which consume electrical energy for heat to travel from cold region of the device to hot region against the temperature gradient [14]. Efficiency of Peltier cooler is calculated based on electrical energy supplied and efficiency of heat released to hot region. It occurs when electric current passes through two conductors which is within the heat sink(solid-state heat pumps). Figure 5 contain the arrangement of cooling apparatus and experiment setup for the paraffin wax precipitation. Base of Peltier cooler is cooling region to cool specimen holder which implanted thermistor and the mild steel sample as shown in Figure 5. The hot region in the Peltier cooler is upper surface. In order to increase surface area for heat release on the hot region while to increase the proficiency of the Peltier cooler a heat sink is been used [14]. A temperature device is attached to the Peltier cooler which by adjusting the electrical energy input makes the temperature of specimen constant.

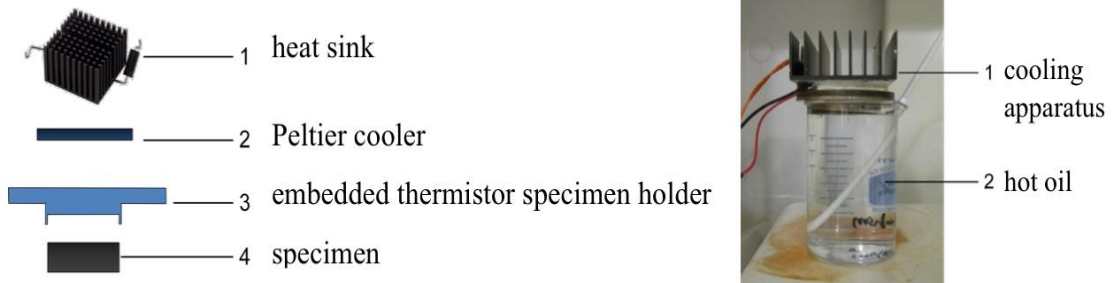


Figure 5: The configuration of cooling apparatus (on the left) and Setup for measurement of wax precipitation on the steel surface (on the right) [14].

Based on the comparison shown in Table 1, it is concluded that the experiment to be design requires wide range of temperature difference and high constant cooling rate. In order to get and accurate result, the cooling rate to configure near to the actual cooling rate in the oil and gas pipelines.

Table 1: Comparison Between Hunts Coldspot and Shan Yang Peltier Cooler

Cold spot Method	Peltier Cooler method
No power source require	Requires power source(60Watts)
Cooling rate is constant	Can Obtain High Cooling Rate
Temperature differences limited within small range	Temperature differences limited within wide range
Requires no Electrical Circuit	Require Electrical Circuit configuration
Requires small alteration	No alteration requires

The method to be the design for the paraffin wax precipitation experiment will be taken reference based on these 2 methods.

2.2 CO₂ Corrosion on Carbon Steel

In the oil and gas pipeline, crude oil and water are normally in a mixture state and transported for a long distance. Due to the ability of water which can dissolve corrosive gases like carbon dioxide (CO₂), the presence of water in pipelines usually can trigger to serious internal corrosion. Carbonic acid is formed when carbon dioxide dissolves in the water which subsequently causing carbon steel to be corroded by carbonic acid formed. Even though, corrosion cause by CO₂ can be evaded using corrosion resistant alloys (CRAs), carbon steel is still being used widely as pipeline material due to the costing of CRAs is very high. Hence, understanding the concept of CO₂ corrosion is crucial to know more about carbon steel pipeline. Basic mechanism of CO₂ corrosion on carbon steel has been research thoroughly and broadly acknowledged. The idea about CO₂ corrosion on carbon steel being a combination of few chemical and electrochemical reaction were suggested Nordsveen et al. and Nestic [15]-[16].

When CO₂ dissolves in the water (Equation (1))while the solubility of CO₂ is to the ratio of 9:10 and the CO₂ proportion of aqueous to the portion of gaseous carbon dioxide in the room temperature is to the ration of 4:5 [17]. Following that, an equilibrium will be reached in between both aqueous carbon dioxide and carbonic acid at room temperature and atmospheric pressure where the constant of equilibrium for Equation (2) is 1.7×10^{-3} . This indicates only a minor portion of the aqueous CO₂ is truly convert to H₂CO₃ [17].

Thus, the corrosive carbonic acid is constantly being replenished as it is consumed by corrosion since there is a vast reservoir of gaseous and aqueous carbon dioxide.



Since the acid is weak acid, carbonic acid partially dissociates bicarbonate ion as shown in equation (2-3) then to form carbonate and hydrogen ion



Corrosion of Iron occurs when iron dissolves and produces ferrous (Fe^{2+}). When the concentration of Fe^{2+} and CO_3^{2-} is saturated, Both ion combine and forms solid iron carbonate (FeCO_3) which is formed on the surface of the steel. The solubility of FeCO_3 depends on a number of factors, primary pH and temperature[18].



Fe^{2+} has the tendency to oxidized further to form Fe^{3+} . However, Fe^{3+} does not form due to water mostly is deoxygenated because of the purging carbon dioxide[19].

At the surface of steel during CO_2 corrosion, there are electrochemical processes occurring as shown in Figure 6 are as follows:

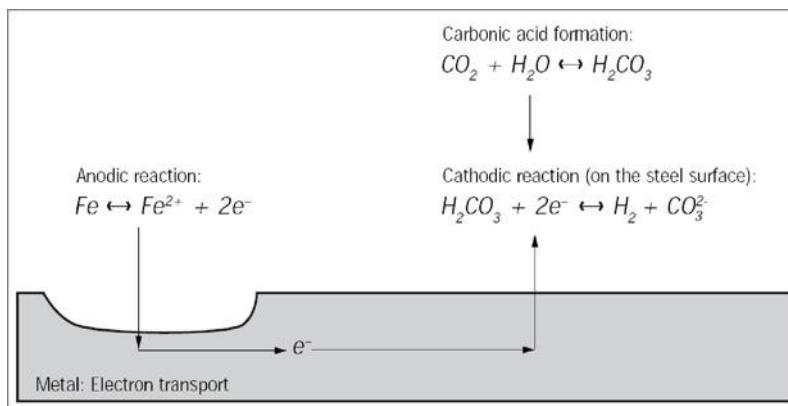
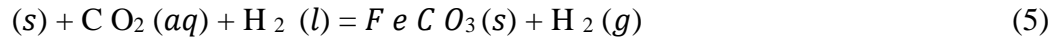


Figure 6: Anodic and cathodic reaction during corrosion of steel pipeline [20]

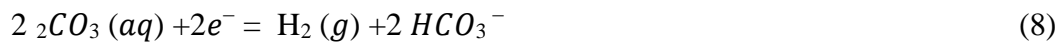
The overall reaction for the CO₂ corrosion is:



The anodic reaction which is major this corrosion is ferum to ferrous ions :



There are 2 main cathodic reactions which include both direct reduction of proton and direct reduction of carbonic acid as shown below:



The corrosion environment such as the pH determined the possibility of these two cathodic reactions to occur. Equation (7) is dominant when pH of the environment below 4 while Equation (8) is dominant at pH > 4 and the partial pressures of CO₂ is very high. Besides partial pressure, there are other environmental parameters that have been considered, to have effect the carbon dioxide corrosion. They are including temperature velocity of flow in the pipeline, water chemicals, pH, and also oil chemicals [15]-[19].

2.3 The Effect of paraffin wax precipitation on the corrosion of steel

A study was conducted by Yang on the Effect of Paraffins on Carbon Dioxide Corrosion where by the experiment has been conducted in precipitating wax in the laboratory environment using a Peltier cooler method [14]. The source of paraffin is the mixture of Eicosane powder and LVT200 oil solvent. The concentration of the eicosane was altered in order to check the result, rate of the wax precipitation in different concentration.

Hence, it can be concluded that the paraffin wax precipitated's weight in Yang's experiments was proportional to time however it is inversely proportional to oil temperature. This is totally opposing to the to Sanjay et. al theory where it is stated the higher temperature difference precipitate more paraffin wax [9].

The experiment on the effect of paraffin wax as corrosion inhibitor was also conducted by Yang [14]. This experiment contains 4 parts:

1. Corrosion inhibition above the WAT. The temperature of the NaCl solution is higher than WAT
2. Corrosion inhibition below the WAT. The temperature of the NaCl solution is lower than WAT
3. Effect of shear on corrosion inhibition
4. Corrosion inhibition at varying temperature

Only at temperatures below the WAT paraffin produce significant corrosion inhibition when a wax layer is formed on the surface of steel. The corrosion inhibition increases with time. However, the structure of the paraffin wax which has been precipitated on the steel was not discussed, it is difficult to assess whether they are completely packed or contain high amount of porous on the wax during the wax is precipitated.

Another study done by Morales, with a rotating cylinder electrode in gas sweetening conditions (temperature: 42 °C) and flow velocities up to 8 m/s showed a reduction of 50% on the corrosion rate of API- 5LB without inhibition and with a prefilmed wax treatment. For prefilmed asphaltene coupons at the same tests conditions, the reduction on corrosion rates were even higher with more than 70% of reduction in the range of 0 to 8 m/s [21]. Figure 7 shows the effect of asphaltene, paraffin and inhibitor films on the CO₂ /H₂S corrosion of carbon steels, at 42°C, where the paraffin wax shows the least corrosion rate lesser than 0.1 mm/year. Even though the thickness of the prefilmed is not mention as Yang, the results obtained is similar. The problem is that paraffin is applied on the strip rather than been precipitated.

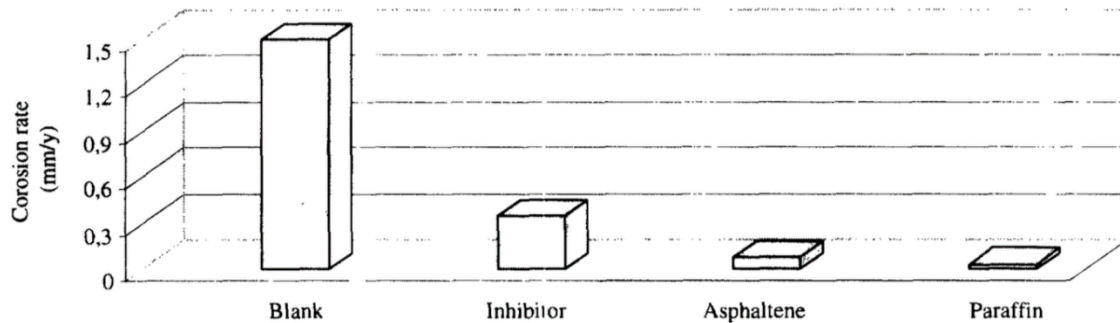


Figure 7: Effect of asphaltene, paraffin and inhibitor films on the CO₂ /H₂S corrosion of carbon steels, at 42°C,

2.4 Linear Polarization Resistance (LPR)

The linear polarization resistance (LPR) method enables determination of instantaneous reaction rates such as corrosion rates and exchange current densities [22]. LPR method is also conducted to determine the corrosion rate of the specimen by using electrolytic test cell.

The methods involved to determine instantaneous polarization resistance are the followings [22] ;

- potential step or sweep
- current step or sweep
- impedance spectroscopy
- statistical
- spectral noise methods

LPR also using direct current (DC) when conducts the test. According to Natarajan, there are two types of resistance which are Tafel extrapolation and polarization resistance which can determine the corrosion rate (CR). LPR work best in aqueous solution and had been proven to have rapid response technique [23].

In order to calculate a corrosion rate with the LPR technique, several fundamental assumptions must be made [22]. The assumptions included:

1. Uniform corrosion condition.
2. A single anodic and a single cathodic reaction.
3. Known values of the Tafel constants.
4. A stable free corrosion potential.

There are two common methods based on polarization measurements to determine the corrosion rates which are Tafel slopes extrapolation with corrosion potential and polarization resistance method or also known as Stern and Geary method [22].

The polarization resistant refer to Figure 8 which obtained the value of *Resistance* (R_p) from the Ohm's Law below:

$$V=IR$$

Where; $V = \text{Potential difference (volts)}$

$I = \text{Current (amperes)}$

$R = \text{Resistance (ohms)}$

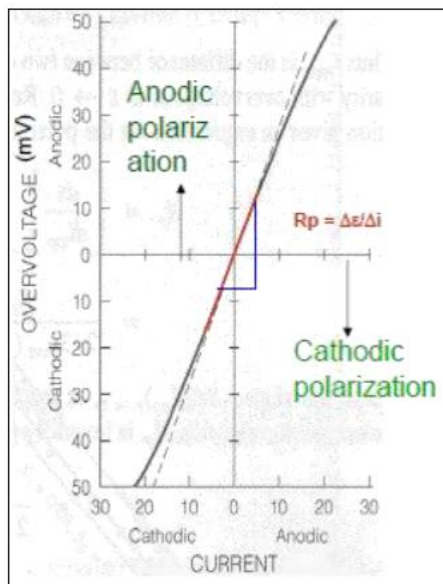


Figure 8 : The polarization resistant based on the gradient of overvoltage over current graph [22]

Tafel polarization can be determine in Figure 9 below, which always show linear behavior that consists of Potential (E) at y-axis and Log Current (Log i) at the x-axis. The intersection point can be determined by extrapolate the anodic and cathodic Tafel curve and the values of E_{corr} and i_{corr} are obtained [23]. After getting the R_p , the value will be inserted into the i_{corr} equation which also involves the Stern-Geary coefficient which is shown in Figure 9:

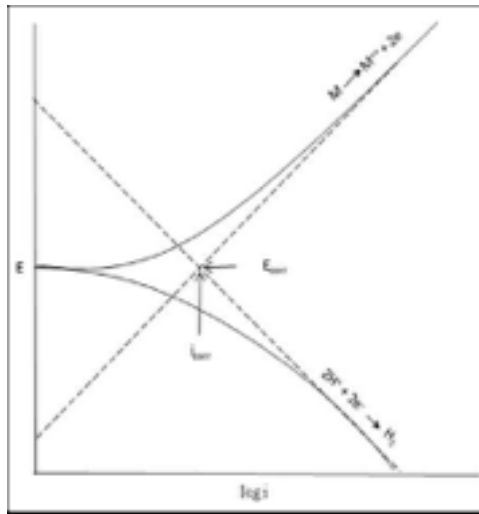


Figure 9 : Tafel polarization linear behavior that consists of Potential (E) at y-axis and Log Current (Log i) at the x-axis [23]

CHAPTER 3: METHODOLOGY

3.1 Project Work Flow

The work flow for this project is shown schematically in Figure 10.

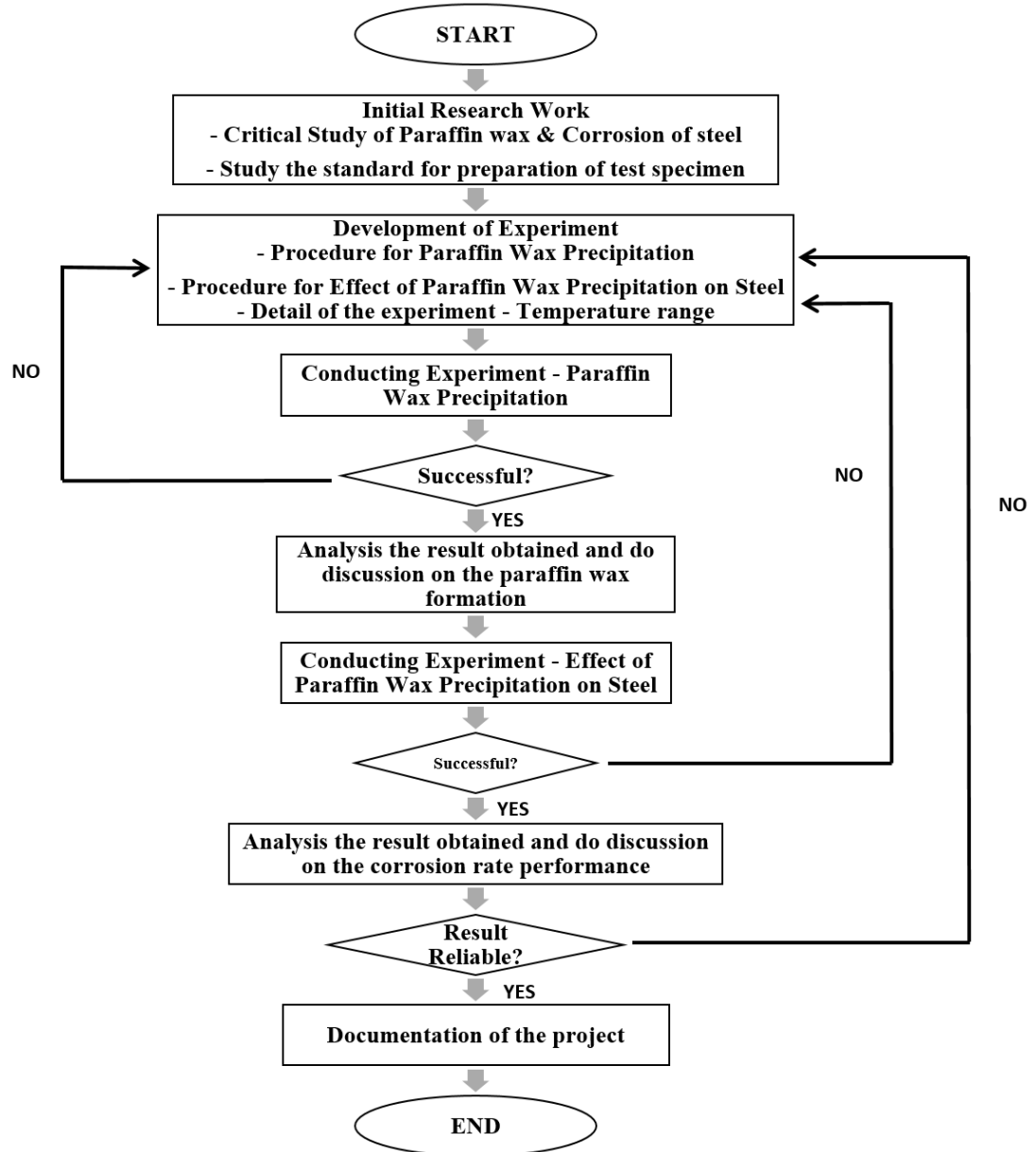


Figure 10: Project work flow

3.2 Gant Chart

Table 2: Gant Chart FYP1 & FYP 2

No.	Activities	Time in Weeks													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Literature Review														
	• What is wax precipitation?														
	• What is the procedure involved to deposit wax in lab scale?														
	• Corrosion within the wax formation														
	• Case Study done on steel behavior during corrosion														
	• Tabulate the findings and perform analysis														
	• Writing of literature review														
2	Project Planning														
3	Design Paraffin Wax Precipitation														
	- Design the Experiment														
	- Collecting Materials														
	- Fabrication of the Experiment														

No.	Activities	Time in Weeks														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1	Conducting Experiment			▶4				▶5			▶7					
	- Wax Appearance Temperature (WAT) <ul style="list-style-type: none"> • Material Gathering & Booking DSC • Conducting the DSC Test • Examine specimen 															
	- Modified Cold Spot Test <ul style="list-style-type: none"> • Material Gathering & Experiment Set up • Conducting the Experiment • Examine specimen 															
	- Corrosion Rate Determination <ul style="list-style-type: none"> • Material Gathering & Experiment Set up • Conducting the Experiment • Examine specimen 															
2	Results and Discussion							▶6			▶8		▶9			
	- Data gathering															
	- Results analysis															
3	Final Report and Presentation														▶10	

3.3 Key Milestone

Table 3: Project Key Milestones

Week	Marker	Date	Remark
FYP 1			
7	▶ 1	11/3/2015	Test Matrix & Parameters has been determined
13	▶ 2	17/12/2015	Completion of Fabrication for the Modified Cold Spot Test Paraffin Wax
14	▶ 3	31/12/2015	Completion of Interim Report
3	▶ 4	22/1/2016	Completion of WAT Experiment
7	▶ 5	4/3/2016	Completion of Modified Cold Spot Experiment
7	▶ 6	4/3/2016	Collection of Optical Microscope Data
10	▶ 7	21/3/2016	Completion of LPR Experiment
10	▶ 8	23/3/2016	Pre-SEDEX evaluation
12	▶ 9	9/4/2016	Submission of Technical Paper
14	▶ 10	22/4/2016	Final Oral Presentation / VIVA & Final Dissertation Submission

3.4 Experimental Details

3.4.1 Wax Appearance Temperature (WAT) Detection by Differential Scanning Calorimetry (DSC)

One of the method to determine WAT is by using (DSC). The sample being heated or being cool down DSC measures heat energy flowing from or to the paraffin wax. Due to the ability of crystallization which releases heat during cooling, DSC curve that produced by the machine will indicate as exothermic peak. The amount of kerosene- paraffin wax which is required for this DSC analysis is only minute. The paraffin wax sample can't be in even in dark apparent because the wax crystallization uses heat to determine the value [24]. The testing material is mixture of paraffin wax and kerosene with concentration of paraffin wax to be 10%, 30%, and 100%. The flash point for the mixture is to 52 °C while freezing point to be -12 °C.

In order to obtain WAT for chemicals in the industry, DSC is one of the efficient tool. DSC is also helpful in improving parameters for cost-effective wax control such as chemical treatment. This include choosing appropriate wax crystal modifier and formulation for the treatment [24].

1. A sample of oil - wax deposit is prepared for analysis.
2. The sample is shifted into a thermally safe container
3. In order to melt the additional wax, the sample is heated in an oven at 50 °C for 2 hours.
4. 30 micro-liter of the heated sample is placed into the DSC stainless steel hermetic pan to avoid evaporation of oil at high temperature [24].
5. A maximum and minimum temperature of sample (the flashpoint and freezing point of oil-paraffin wax) are set as temperature variables at a rate of 5 °C/minute in DSC machine
6. Once the DSC has completed the test, a graph will be produced. Figure 11 shows the oil-paraffin wax sample above WAT on the left and oil-paraffin wax sample below WAT on the right [24].



Figure 11: Crude oil sample above WAT (left) and crude oil sample below WAT (right) (The figure obtained from PerkinElmer to show the possible outcome after using DSC)[24].

A heat energy flow graph will be produced after DSC test has been completed the test. The data for exothermic reaction of paraffin wax crystallization produced from the graph is recorded. As shown in Figure 12, The temperature right after the heat flow curve and beginning stabilization is identify as the wax appearance temperature (WAT).

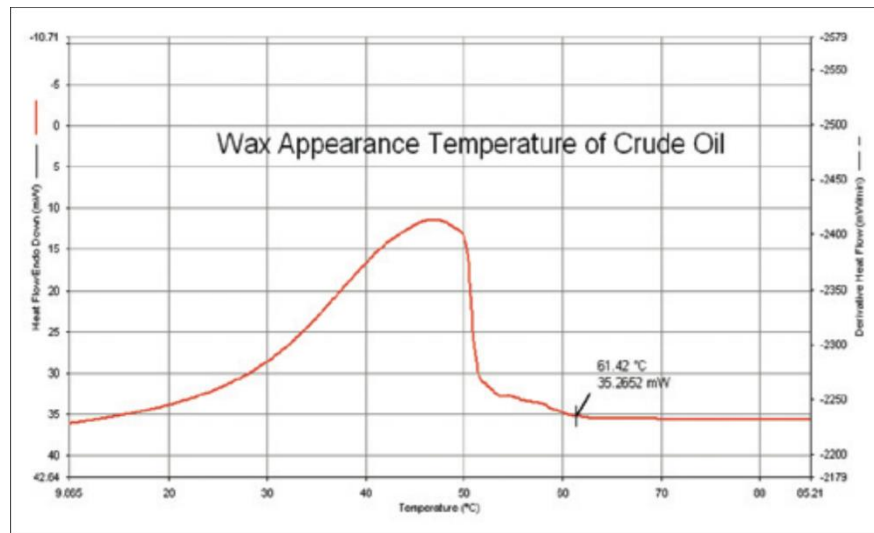


Figure 12: Notation of wax appearance temperature on Heat Flow Cool Down curve (The figure obtained from PerkinElmer to show the possible outcome after using DSC)[24].

3.4.2 Paraffin Wax Precipitation Experiment

Based on the 2 methods (cold spot test and peltier cooler method), a list of equipment required for the design. Table 4 show the lists of equipment required. The sample of carbon steel used is Carbon Steel API 5L X65. This is because carbon steel particularly X65 is used as the material for the pipeline in the oil and gas industry. Table 5 shows the chemical composition API 5L X65. The paraffin wax used to precipitate is lab grade Sigma Aldrich PARAFFIN WAX, M.P. 53-57 DEG. C (ASTM D 87).

Table 4: The lists of equipment required

Material/Equipment	Quantity	Purpose
Immersed Pump	1	To pump the cold water
Tube	4	To circulate the cold water and warm water
Hotplate	1	To heat up the paraffin wax mixture to determine temperature
Glass cell	1	To contain the paraffin wax mixture to be precipitated
Thermometer	1	To ensure the temperature is maintained throughout the experiment
Chiller	1	To reduce and maintain the temperature of cold water
Paraffin wax-oil	10%, 30%	To precipitate the paraffin wax on to the steel sample
Carbon Steel (X65)	2	The sample for testing
Epoxy resin	100 g	To produce mould to hold the steel and paraffin wax oil
Condenser	1	To transfer the heat from the steel to cold water

Table 5: Composition of Carbon Steel API 5L X65 sample

Al	Cr	Mo	S	V	B	Cu	Nb	Si
0.0032	0.011	0.103	0.004	0.055	0.002	0.010	0.030	0.240
C	Fe	Ni	Sn	Ca	Mn	P	Ti	
0.150	Balance	0.020	0.005	0.0032	1.340	0.001	<0.001	

Fabrication of Modified Cold Spot Test

Figure 13 shows the schematic diagram of the Wax Precipitation Experiment which is the modified version of cold spot test. The cold water is regulated using chiller to 24°C and pump to the condenser. The top surface of sample is expose to the coolant and below surface is expose to heated paraffin wax for the precipitation to form. The paraffin is evenly heated in a hot water bath. The condenser shown in the diagram need to be fabricated as it is design specifically for this experiment. The condenser was designed in AUTOCAD 2014. The selected design for the condenser is fabricated. Perspex with thickness of 5mm is used as the base material and silicate adhesive were used to stick the Perspex part together parts together. After the cleaning process, the fabricated condenser is test for leakage using hydro test.

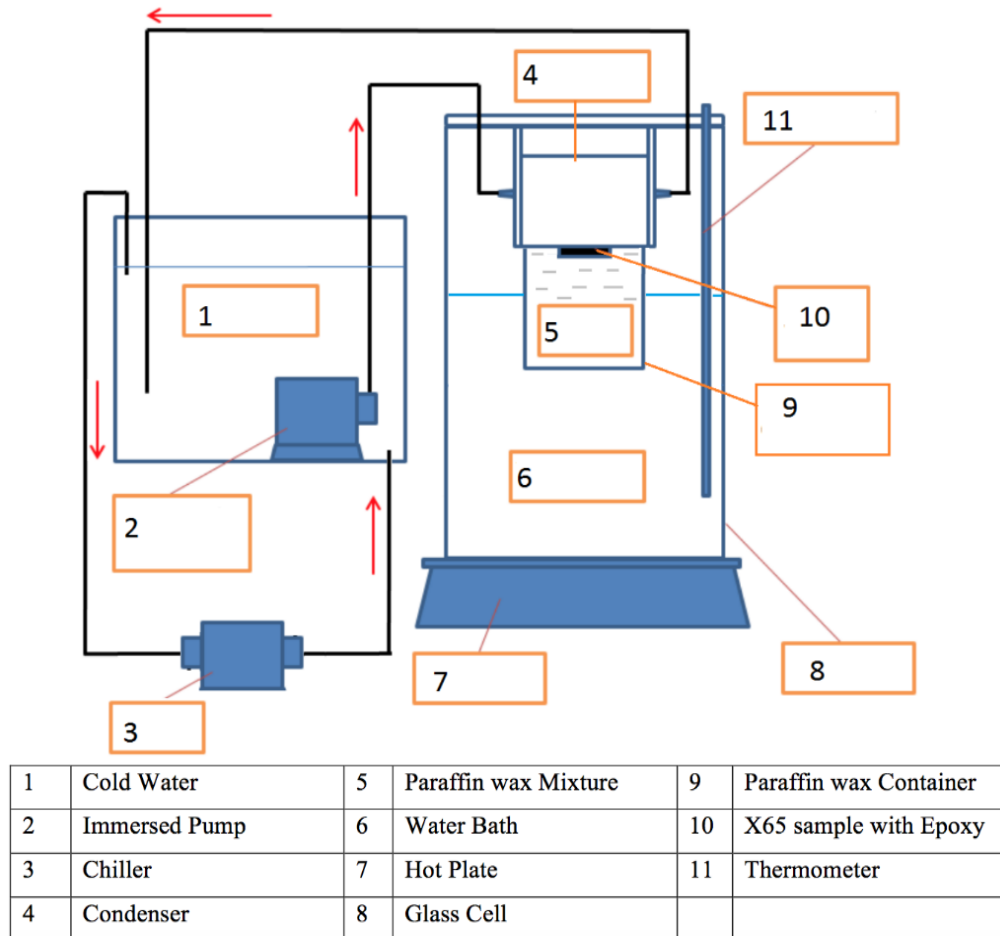


Figure 13: Design for Modified Cold Spot Test

Sample Preparation

The specimens were cut into rectangular shape with dimension 1.7 cm by 1.2 cm and undergo grinding process using emery papers that have different size (Refer ASTM G31). The orientation of specimens must be synchronized and frequently when conducting the grind and polishing process. The scratches from the previous need to remove before advancing to finer grit. Sample were rinsed with distilled water and acetone. After that specimen kept in proper medium to prevent moisture from the surrounding. Before the mounting process, the front of the sample is stick with 1.5mm thickness clay to create a hollow region to control the thickness of paraffin wax precipitated. The pre-preparation of specimen by mounted using epoxy resin with low viscosity while exposed area was carefully tended. After cold mounting, the clay is removed from the sample.

Solution preparation (Paraffin wax – kerosene mixture)

The mixture was prepared by adding paraffin wax to the kerosene oil. The mixture is later mix heated above WAT and mix using magnetic stirrer. The percentage of paraffin wax was determined by the following formula;

$$\text{Percentage of paraffin wax} = \frac{\text{Mass of paraffin wax}}{\text{Mass of paraffin wax} + \text{Mass of kerosene}}$$

Table 6: The mass of paraffin wax required to produce 10% and 30% mixture

Percentage of Paraffin Wax	Total Mass (g)	Mass of Paraffin Wax (g)
10%	150	15
30%	150	45

Modified Cold Spot Test

The sample is pasted to the condenser using silicate adhesive and left for 12 hours for curing. After curing, inspection for any leakage within the sample and condenser took place. A hot water bath is prepared for the paraffin wax and kerosene mixture at above WAT. This is to ensure an even heating on the 100 ml paraffin wax and kerosene mixture. The sample together with the condenser is place on 100 ml paraffin wax and kerosene mixture. The sample is ensured to be fully immersed in the solution and closed tightly to

avoid any spillage. Water cooled to 24.0 °C is pumped to the condenser. Figure 14 shows the setup of the experiment



Figure 14: Setup for Modified Cold Spot Experiment(Left) and close up on the experiment(Right)

3.4.3 Test Matrix for Precipitation of Paraffin Wax Experiment

In this research as shown in Table 4, the carbon steel used is API X65 as the base sample for the corrosion, as this material is widely used in oil and gas pipelines. The mixture of paraffin wax and kerosene as the replacement for crude oil. Crude oil is expensive and limited in access, hence paraffin wax which is the main component to be tested. Kerosene is one of the organic compound found in the crude oil which can dissolve the paraffin wax same as the crude oil. The temperature of wax appearance is the point where the paraffin starts to precipitate. Table 7 shows the test matrix for the paraffin wax precipitation experiment. After the DSC test has been conducted, the paraffin wax precipitate on the steel surface will be experimented (as design shown in Figure 13).

Table 7: the test matrix for the precipitation of paraffin wax experiment

Test	Mixture 1	Mixture 2
Precipitation time(hours)	24	
Composition of paraffin wax	10%	30%
Composition of kerosene	90%	70%
Temperature of the coolant (°C)	24.5	
Temperature of the mixture (°C)	40	45
Thickness	1.5mm	1.5mm

3.4.4 Linear Polarization Resistance (LPR) test

LPR experiment is to be conducted to test the corrosion rate of API X65 carbon steel in the 3% of NaCl solution without any precipitation of paraffin wax onto the steel.

Solution preparation/electrolytes

The brine was prepared by adding Sodium Chloride (NaCl) only. 2 liters 3% of NaCl was used in LPR test and the calculation can be shown below:

3% NaCl Brine:

3.0% → 30g/L

$$\begin{aligned}\text{Mass of NaCl} &= \frac{30\text{ g}}{1\text{ L}} \times 2\text{ liters} \\ &= 60\text{ grams of NaCl required for 2 liters of diluted distilled water} \\ &\text{in order to produced 3\% NaCl solution}\end{aligned}$$

Electrode preparation (Sample electrode)

The pre-preparation of specimen by mounted using epoxy resin with low viscosity while exposed area was carefully tended. Before mounting, the electric contact was made to the back surface of specimen by attaching a thin copper wire using solder.

LPR Test

The setup of apparatuses according to ASTM G59 and ASTM G31. 3% NaCl solution was measured 2000ml and pour into the 2 liters' glass cell. Purging process was conducted by inserting CO₂ gas into the brine until reaching the desired pH value. There were three probe using throughout the test which were ribbon electrode, auxiliary probe and references probe. The sample electrode was immersed into the brine solution and the temperature was fixed accordingly. The sample electrode position lowered near to reference electrode. The LPR test uses direct current and connected to the ACM software. Table 8 shows the test matrix for the LPR Experiment. The test was running continuously based on the test matrix while it was observed and recorded every hour.

Cleaning procedure

The specimen was examined visually and note if there any change in appearance such as discoloration, corrosion product, pitting and etc. Using distilled water and acetone, the specimen was cleaned. After drying using hot air The specimen was observed, and if there is any corrosion occurs, the photo of specimen was taken as the permanent record. Corrosion damage was assessing according to ASTM G1. The samples were kept inside the desiccators to avoid moisture from surrounding.

Table 8: Test Matrix for the LPR experiment

Test	1	2	3
NaCl (%)	3%		
Carbon Dioxide	Purged through out the Experiment		
pH	4		
Temperature of NaCl Solution (°C)	27		
Composition of paraffin wax in sample	Baseline	10%	30%

The procedure as follows;

1. The sample was dried and kept in the desiccator
2. 3% NaCl solution was prepared and filled in to the glass cell
3. The solution was purged with CO₂ until the pH of the NaCl solution dropped to 4 for 45 minutes.
4. A reference electrode, an electrode and steel sample is immersed into 3% NaCl solution in the glass cell. Figure 15 shows the setup of the experiment

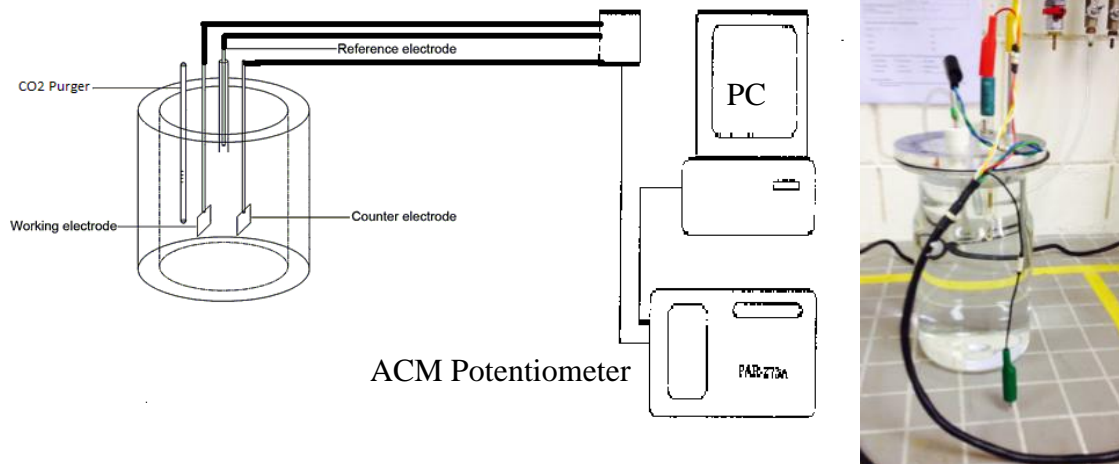


Figure 15: Setup for the LPR experiment

5. The purging of CO₂ is continued in order to maintain the pH value at 4 throughout the experiment.
6. The readings were recorded hourly for the next 24 hours.

CHAPTER 4: RESULTS & DISCUSSION

4.1 Paraffin wax Precipitation

4.1.1 WAT determination based on DSC

Wax Appearance Temperature (WAT) has been determined using DSC. The results are important criteria in the wax precipitation. Temperature of the paraffin wax- kerosene mixture should be higher than WAT while the temperature of the surface of the steel which influence by the temperature of the coolant should be lower than WAT.

As mentioned in the experimental procedure the reaction is exothermic reaction where heat is released from the sample hence the values heat flow obtained are in negative. Figure 16 & Figure 17 shows the DSC graph obtained for 10% and 30% respectively.

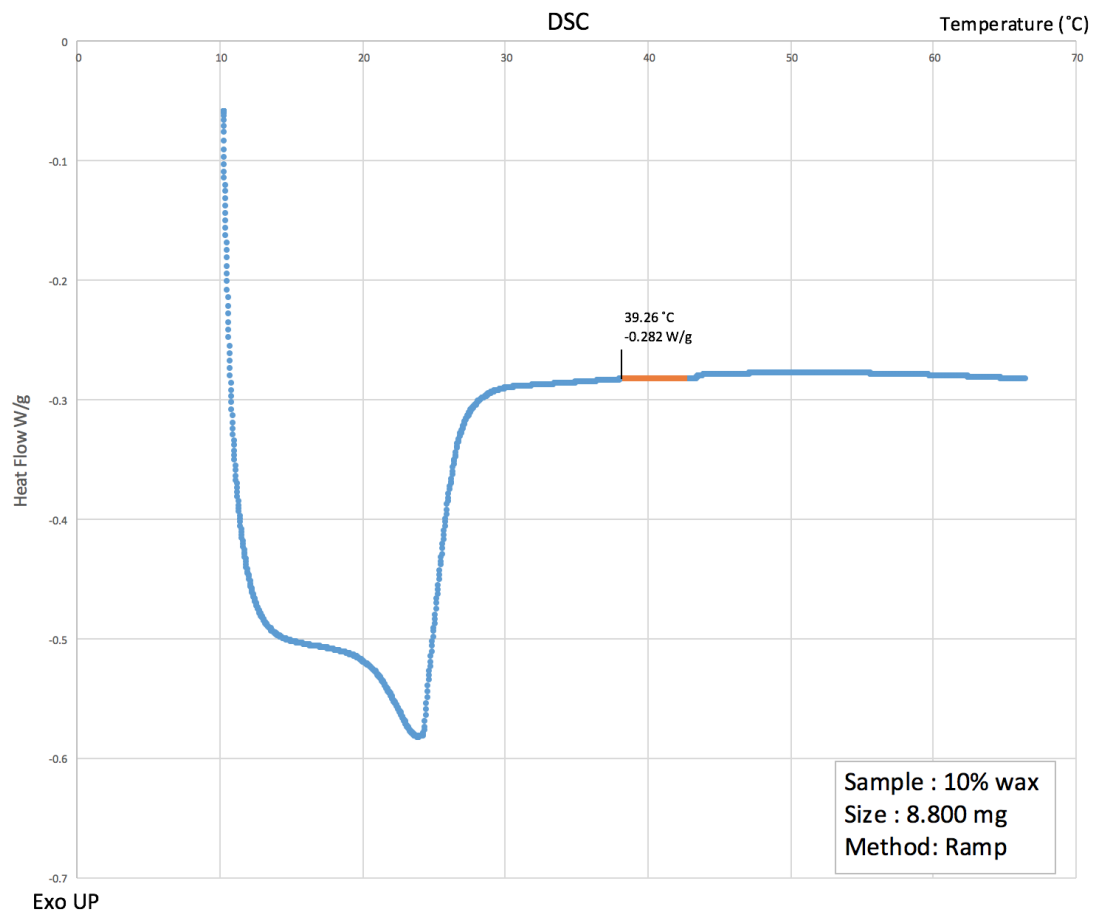


Figure 16: WAT determination for 10% paraffin wax-kerosene using DSC

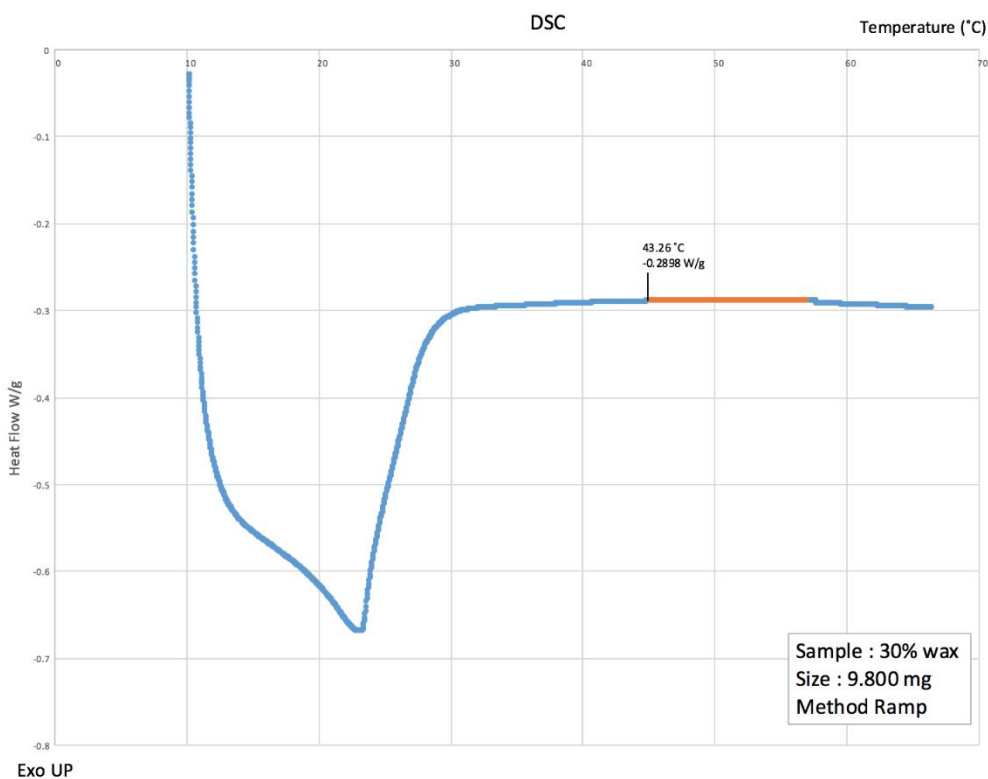


Figure 17: WAT determination for 30% paraffin wax-kerosene using DSC

Based on the Figure 16 & Figure 17, it can be deduced that the WAT is the point of stabilization after the exothermic reaction occurs. Hence the point chosen based on the initial straight line of the graph. It is also can be seen that the high the concentration paraffin wax the higher the WAT and its heat flow value. The exothermic reaction reaction releases higher amount of heat energy in 30% compared to 10% paraffin wax-kerosene. This is cause by the amount of paraffin wax in mixture require more energy to convert from solid to liquid than kerosene in the mixture. Table 6 shows the wax appearance temperature for the sample.

Table 6: Wax Appearance Temperature (WAT) from DSC

Composition of Paraffin Wax (%)	Weight of the sample (mg)	Temperature (°C)	Heat Flow (W/g)
10	8.8	39.3	- 0.282
30	9.8	43.3	-0.290

4.1.2 Modified Cold Spot test

The sample is placed as shown in Figure 14. However, the sample was not be able to be formed with the paraffin deposit. The case is being the same to both 10% and 30% mixture. The 10% mixture has the no deposits at all while the 30% paraffin wax sample had deposited with paraffin wax but fell off (showing that the wax did not stick on to the steel sample surface. This situation however changes when the surface has been scratched with sandpaper to give a rough surface on the X65 steel samples. The reason for this action is because the surface area also affects the precipitation of wax on to the surface according to P.Singh [7]. In this manner, it is inferred that wax does not hold fast to steel but rather that deposits which frame on steel surfaces are held set up by surface roughness. All the samples were immersed and exposed to the paraffin wax mixture in the beaker for 1 day. After they were removed from the glass cell digital picture were taken immediately. The OM analysis is presented sample by sample from Figure 18 to Figure 22.

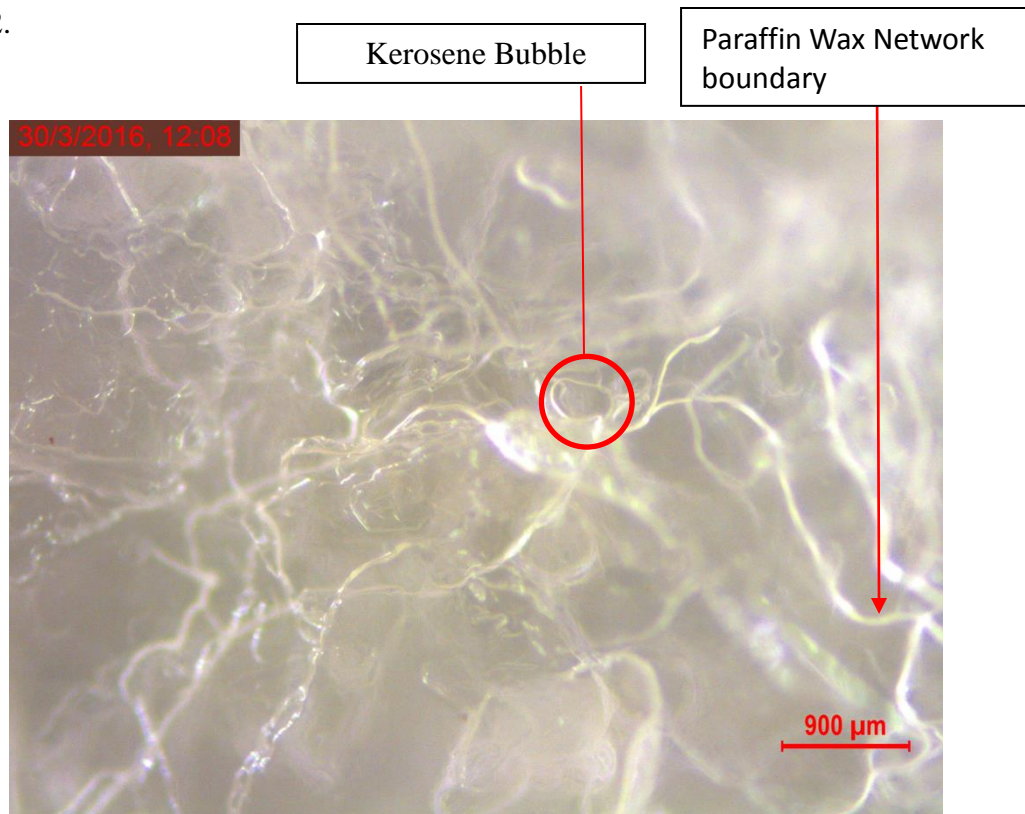


Figure 18: OM image for steel X65 Precipitated with 30% paraffin wax (x5 magnification) Red circle indicate kerosene drops.

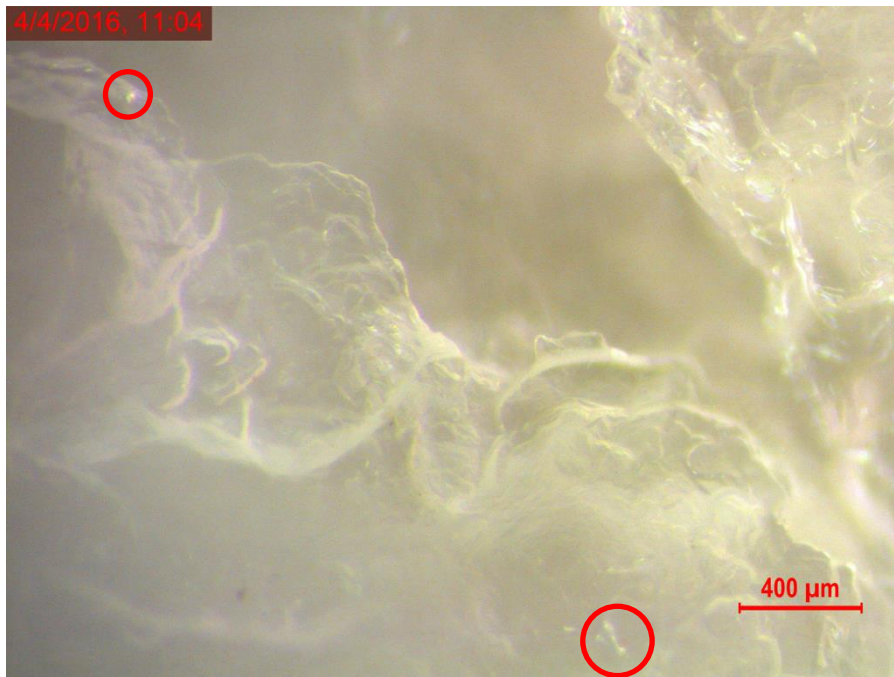


Figure 19: OM image for steel X65 Precipitated with 30% paraffin wax (x10 magnification). Red circle indicate kerosene drops.

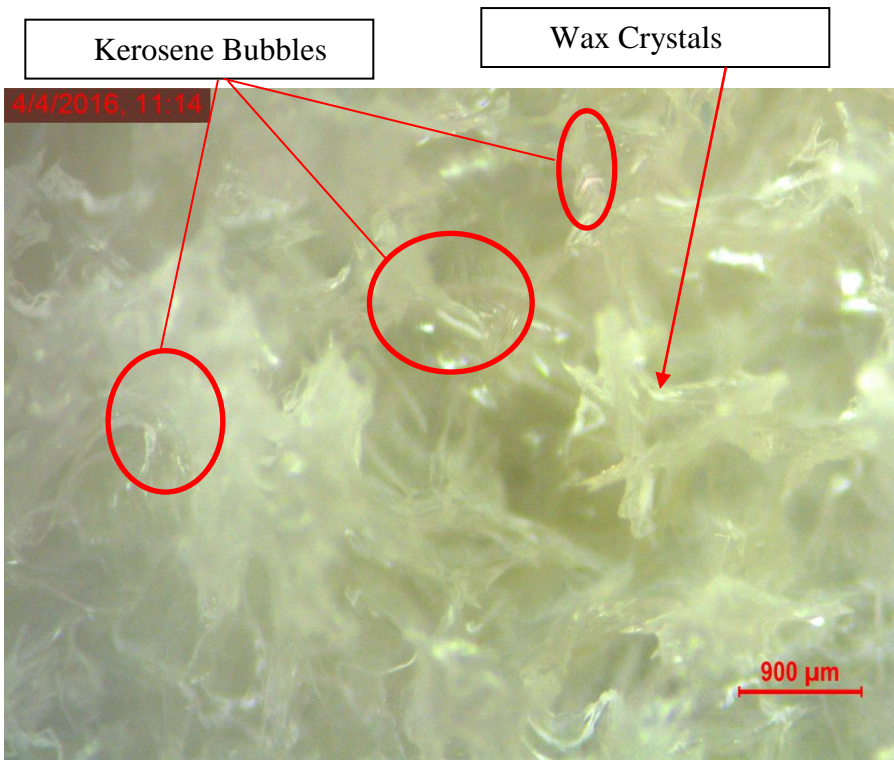


Figure 20: OM image for steel X65 Precipitated with 10% paraffin wax (x5 magnification). Red circle indicate kerosene drops.



Figure 21: OM image for steel X65 Precipitated with 10% paraffin wax (x10 magnification) Red circle indicate kerosene drops.



Figure 22: OM image for steel X65 Precipitated with 10% paraffin wax (x10 magnification) Red circle indicate kerosene drops.

10% sample seem to have precipitated lesser paraffin wax compared to the 30% this may due to the composition of the solution used to precipitate paraffin wax on sample in 30% contain higher composition of paraffin wax compared to 10%. This can be seen in where 30% paraffin wax sample (Figure 18 & Figure 19) contain less kerosene bubbles and pores compared to 10% paraffin wax sample (Figure 20-Figure 22).

The 10% paraffin wax can also been seen in its crystallization state as the WAT is nearer to room temperature compared WAT of 30% paraffin wax. The 30% paraffin wax sample has much smoother surface compared to 10% paraffin wax sample as they arranged compactly and can be seen through naked eye. shows the 30% paraffin wax sample and 10% paraffin wax sample after the wax precipitation

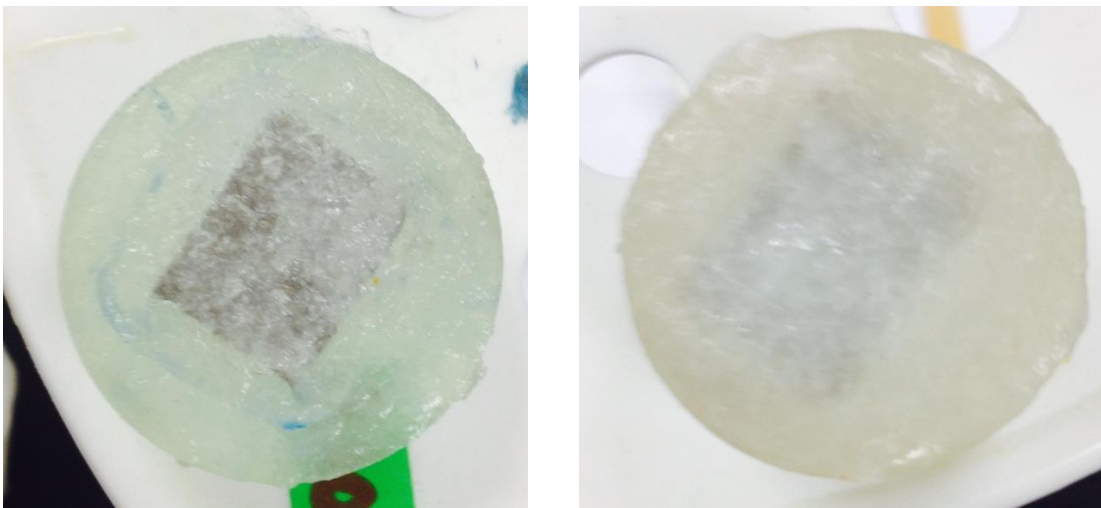


Figure 23: Sample after the wax precipitation for 10% paraffin wax (left) and 30% paraffin wax (right)

This explains the phenomena that happening in oil and gas industry where by the inner surface of steel pipeline has uneven surface due to the long service and aid wax precipitation. Another factor is that if the surface has higher composition of paraffin wax, the precipitate to be more compact and difficult to remove. Since the crude oil can contains up to 50% of paraffin wax, the severity will increase. The temperature can contribute majorly in controlling the paraffin wax precipitation.

4.2 LPR Test

Based on the data value obtained from the LPR test (Appendices) a graph is plotted corrosion rate against time to analyze as shown in Figure 24.

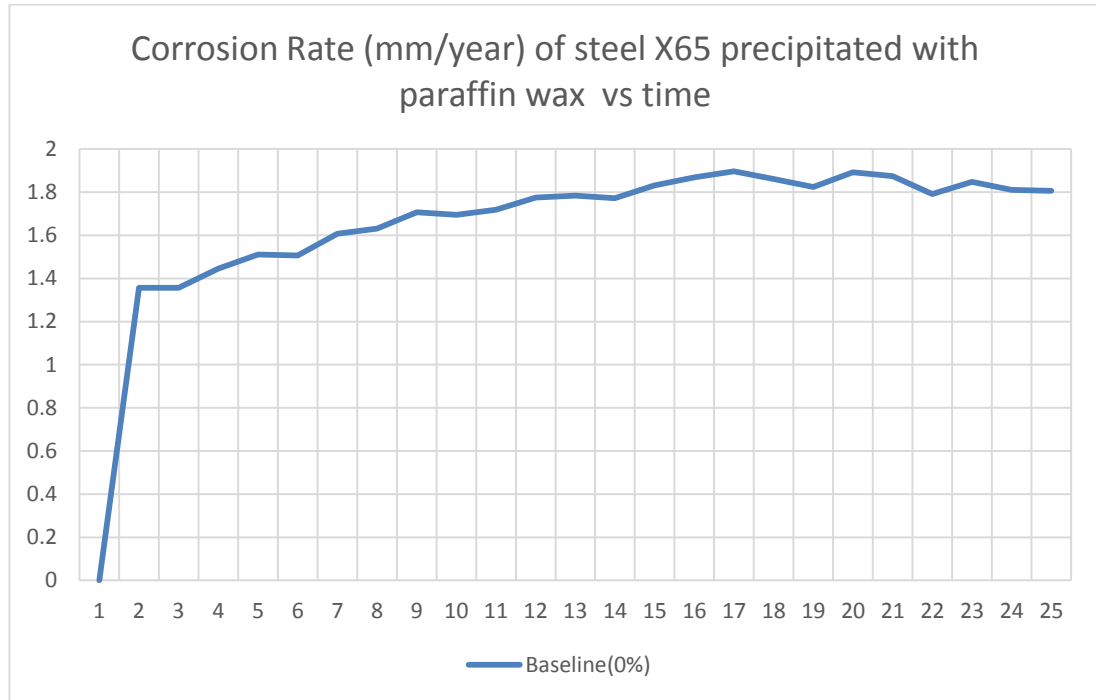


Figure 24: Corrosion Rate (mm/year) of steel X65 precipitated with paraffin wax vs time

Based on Figure 24, the baseline with no precipitation of paraffin wax show the normal corrosion occurring in the steel surface. As can be seen the corrosion rate at the 24th hour is precipitation of wax in 1.805 mm/year under atmospheric pressure at room temperature. For all the temperatures, the trend clearly shows that the corrosion rate is slightly fluctuated and increased at the beginning until the end of test (24 hours). The results is nearly identical to Shan yang and Morales J.L et al baseline as without precipitation of paraffin wax [14],[21]. The fluctuation of corrosion rate of steel X65 precipitated with 10% paraffin wax can be seen in Figure 25 while corrosion rate of steel X65 precipitated with 30% paraffin wax in Figure 26.

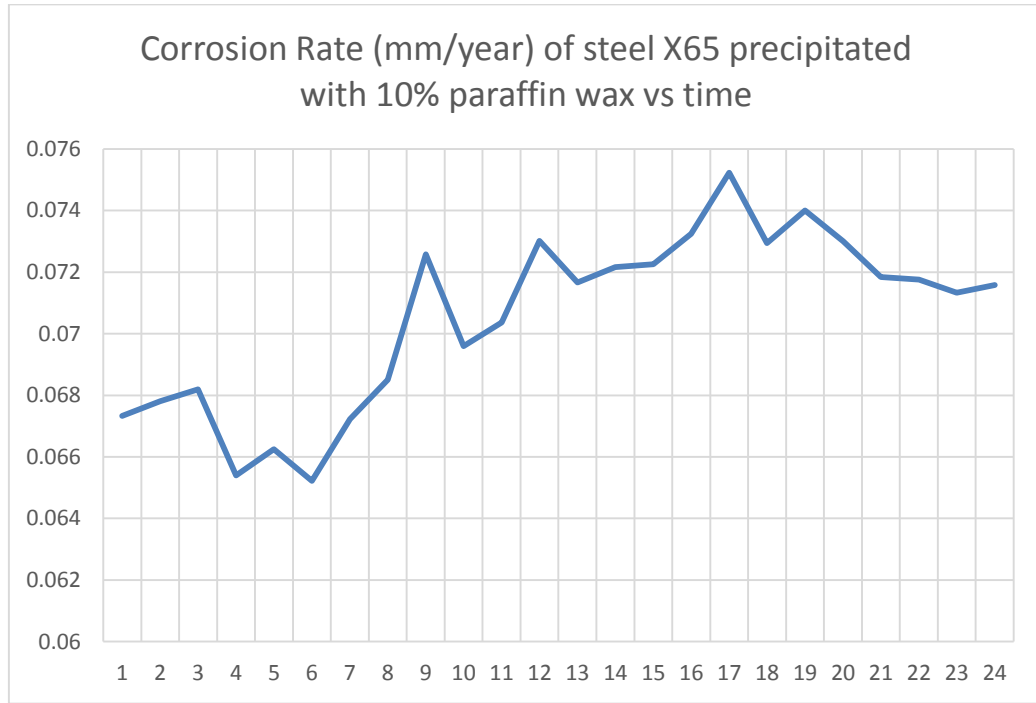


Figure 25: Corrosion Rate (mm/year) of steel X65 precipitated with 10% paraffin wax versus time

From the graph of corrosion rate against time, when the time is at 24th hours, the corrosion rate is 0.072 mm/year. The corrosion rate is first decreases with time. At the 2nd hour, the corrosion rate is fluctuated, which is in the range of 0.065 mm/year and 0.076 mm/year. The corrosion rate shows that paraffin wax has the ability to curb corrosion since the normal corrosion rate of X65 is more than 1mm/year. This is cause by the nature of the paraffin which precipitate on the X65 carbon steel to act as a protective layer which act as barrier between carbon steel and CO₂.

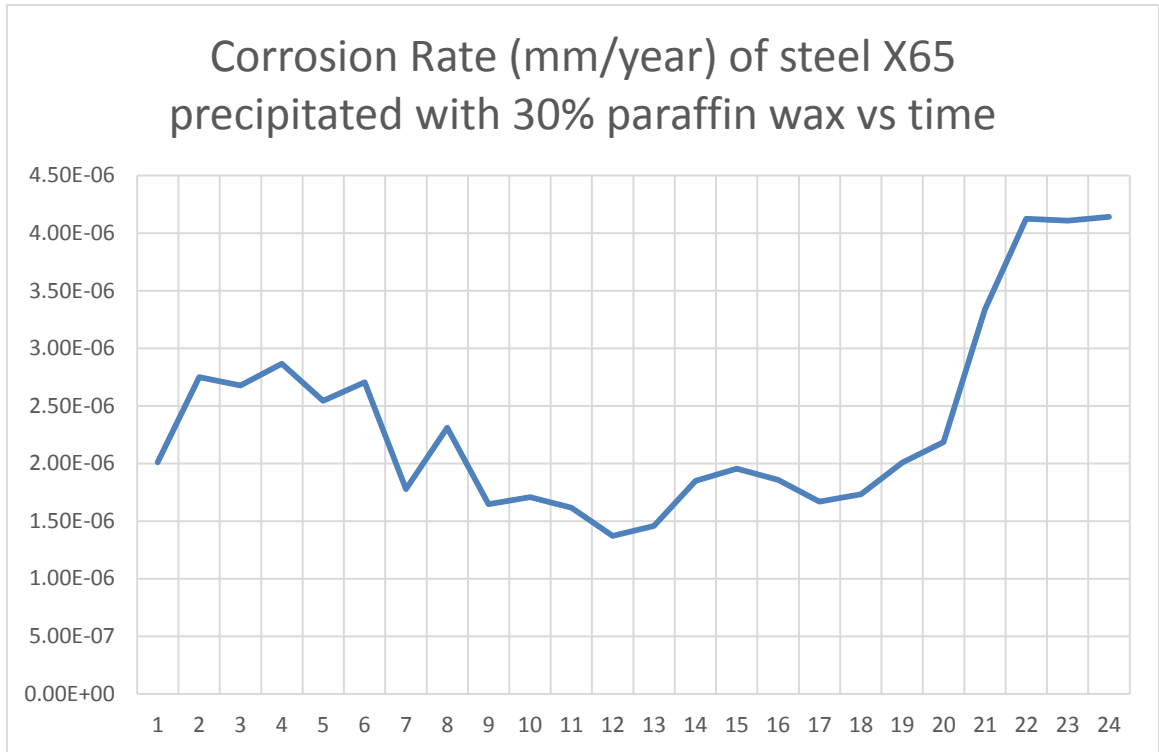


Figure 26: Corrosion Rate (mm/year) of steel X65 precipitated with 30% paraffin wax versus time

Figure 26 shows corrosion rate of steel X65 precipitated with 30% paraffin wax versus time. The corrosion rate is near to 0 mm/year due to the fact that the 30% paraffin wax has more compactly precipitate compare to 10% paraffin wax mixture. From the graph, when the time is at 24th hours, the corrosion rate is 4.14×10^{-6} mm/year. The results is nearly identical to Morales J.L et al 30% paraffin wax precipitation of paraffin wax [21]. The corrosion rate is first increases with time. From the 2nd hour until 19th hour, the corrosion rate is fluctuates, which is in the range of 1.37×10^{-6} mm/year and 2.87×10^{-6} mm/year. At 20th hour, the corrosion rate increase constantly from 2.19×10^{-6} mm/year to 4.13×10^{-6} mm/year in 2hour and remain constant till the end of the experiment. Figure 27 shows the comparison final corrosion rate between baseline 10% paraffin wax precipitation and 30% paraffin wax precipitation.

Comparison of Final LPR Result

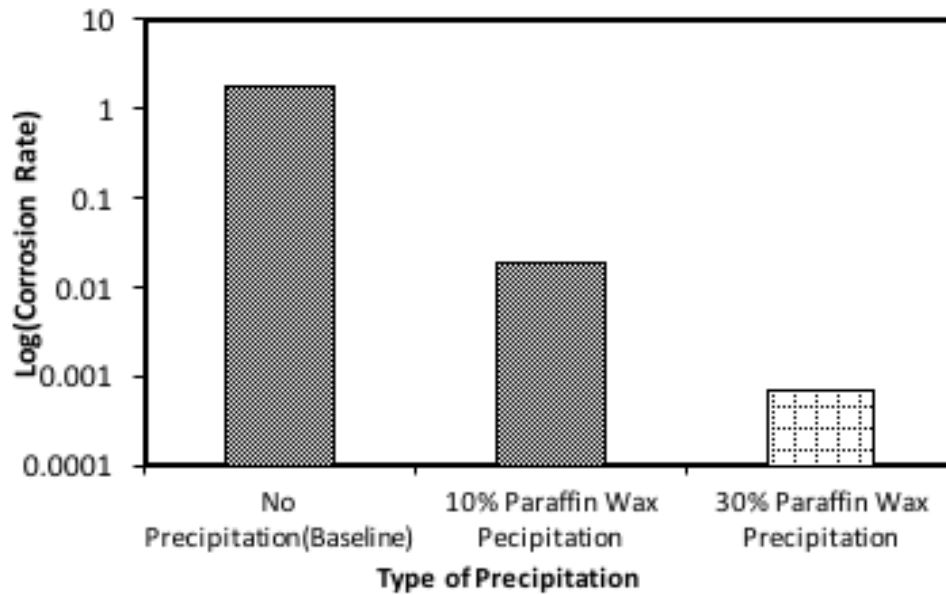


Figure 27: Comparison final corrosion rate between baseline, 10% paraffin wax precipitation and 30% paraffin wax precipitation.

Comparing the log corrosion, more than 90% of reduction in corrosion compared to baseline can be seen in both 10% paraffin wax precipitation and 30% paraffin wax precipitation. The reduction was calculated:

$$\text{Reduction in corrosion rate for 10\% Paraffin wax} = \frac{1.8059 - 0.072}{1.8059} \times 100\% = 96\%$$

$$\text{Reduction in corrosion rate for 30\% Paraffin wax} = \frac{1.8059 - 4.14 \times 10^{-6}}{1.8059} \times 100\% = 99\%$$

Even though the thickness is same for the both paraffin wax precipitation is same the 30 % paraffin wax paraffin wax has managed to block most of substance that can cause corrosion to the steel steel surface. Natural paraffin wax precipitated in pipeline will be remove through pigging only when the thickness is more than 2mm.

CHAPTER 5: CONCLUSION & RECOMMENDATION

5.1 Conclusion

Paraffin wax precipitation and CO₂ corrosion are long standing problem in the oil industry. In the case of the paraffin, Heavy paraffin deposits are undesirable because they reduce the effective size of the flow conduits and restrict the production rate from the well. Factors that are causing the wax formation are the flow rate and temperature difference. CO₂ corrosion on the steel occurs due to the water presence in transportation pipelines. This have the tendency to produce a bad internal corrosion, as it has ability to dissolve corrosive gases in this case carbon dioxide (CO₂). The formation of carbonic acid occurs when carbon dioxide gas dissolve in the water, which result in acid corrosion of carbon steel. The effect of paraffin wax on the corrosion of steel would allow a higher knowledge on the prevention CO₂ corrosion in the steel pipelines. Based on the experiment conducted and results analyze, The paraffin wax act as a protective layer on to the steel and can provide minimal protection on the steel pipelines.

Based on the Hunt's cold spot test and the Shan Yang Peltier cooler method, a modified Cold spot test was fabricated in order to to produce wax onto a steel surface in laboratory environment. Using WAT determine from DSC the paraffin wax with the composition of 10% and 30% of paraffin wax was successfully precipitated. This completes the first objective. The study show that at room temperature, the effect of paraffin wax precipitation on the corrosion of steel (2nd Objective) is that paraffin wax act as layer that protects the steel from corrosion.

5.2 Recommendation

Some recommendation which may provide a better results in the future experiments

1. Temperature difference factor: Conducting the precipitation in a hot environment to see the effect of sea environment on the precipitation.
2. Flow factor: Including flow rate as one of the variables or conducting the experiment in a flow loop which can give a better scenario and accurate result.
3. Sample Orientation: Inversing the sample position in paraffin wax precipitation experiment can allow the paraffin wax to precipitate faster and more stable.
4. Time factor: Precipitating the paraffin wax longer than a week to identify how aging of paraffin wax effects the corrosion rate.

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APPENDICES

Table 9: LPR Data for Corrosion rate of Baseline experiment (No Precipitation)

Time (Sec)	LPR (ohm.cm ²)	I _{corr} (mA/cm ²)	Corrosion Rate (mm/year)	Total metal loss (mm)	Potential (mV)
0	222.84	0.1170654	1.3567	0	-692.7
4541.5	222.93	0.1170173	1.3562	0.0002002	-688.67
7067.9	209.12	0.1247439	1.4457	0.000319	-688.63
11087	200.01	0.130428	1.5116	0.0005165	-688.62
21370	200.78	0.1299239	1.5058	0.00102	-688.96
21797	188.13	0.1386577	1.607	0.0010423	-688.93
25103	185.39	0.1407068	1.6307	0.0012176	-688.93
28703	177.08	0.1473121	1.7073	0.0014174	-688.82
32304	178.34	0.1462717	1.6952	0.0016158	-689.03
35904	175.94	0.1482644	1.7183	0.001817	-688.67
39504	170.28	0.1531954	1.7755	0.0020248	-688.21
43104	169.51	0.1538907	1.7835	0.0022336	-687.9
46704	170.63	0.1528774	1.7718	0.002441	-687.94
50305	165.06	0.1580428	1.8317	0.0026554	-687.42
53905	161.76	0.1612665	1.869	0.0028741	-687.08
57505	159.43	0.1636257	1.8964	0.0030961	-686.73
61106	162.5	0.1605341	1.8605	0.0033139	-686.52
64706	165.7	0.1574277	1.8245	0.0035275	-686.28
68306	159.76	0.1632837	1.8924	0.003749	-685.91
71906	161.3	0.1617266	1.8744	0.0039684	-686.05
78234	168.78	0.1545553	1.7912	0.0043369	-684.9
79479	163.66	0.1593903	1.8473	0.0044116	-684.62
83400	166.95	0.156256	1.811	0.0046425	-684.08
86822	167.42	0.1558173	1.8059	0.0048435	-684.07

Table 10: LPR Data for Corrosion rate of of steel X65 precipitated with 10% paraffin wax

Time (Sec)	LPR (ohm.cm ²)	I _{corr} (mA/cm ²)	Corrosion Rate (mm/year)	Total metal loss (mm)	Potential (mV)
0	4458.5	0.005851	0.0678133	0	-657.12
3291.7	4490.2	0.0058097	0.067334	7.21E-06	-654.09
6891.9	3244.1	0.0080412	0.0931975	1.81E-05	-654.33
10856	4623.3	0.0056425	0.0653964	2.65E-05	-654.92
15185	4563.8	0.005716	0.0662487	3.59E-05	-655.51
17692	4635.9	0.0056272	0.0652187	4.12E-05	-655.59
21292	4497.4	0.0058004	0.0672264	4.91E-05	-655.83
24892	4413.8	0.0059103	0.0684999	5.71E-05	-656.04
28492	4165.5	0.0062626	0.0725836	6.56E-05	-656.43
32093	4344.5	0.0060045	0.0695926	7.37E-05	-656.64
35693	4296.9	0.006071	0.0703628	8.20E-05	-656.98
39293	4140.6	0.0063002	0.0730189	0.0000905	-656.97
42894	4219	0.0061832	0.0716631	0.0000989	-657.21
46494	4189.5	0.0062266	0.0721668	0.0001073	-657.44
50094	4184.3	0.0062344	0.0722568	0.0001158	-657.38
53695	4127.7	0.00632	0.0732484	0.0001244	-657.54
57295	4019.1	0.0064907	0.0752274	0.0001332	-657.75
60895	4144.6	0.0062941	0.0729481	0.0001417	-657.7
64495	4085.6	0.006385	0.0740024	0.0001504	-657.85
68095	4141.1	0.0062994	0.0730103	0.0001589	-657.89
71696	4208.7	0.0061983	0.0718383	0.0001673	-658.01
75382	4213.5	0.0061912	0.0717563	0.0001759	-658.09
78896	4238.5	0.0061547	0.0713327	0.0001841	-658.02
82496	4223.6	0.0061764	0.0715843	0.0001924	-657.96

Table 11: LPR Data for Corrosion rate of of steel X65 precipitated with 30% paraffin wax

Time (Sec)	LPR (ohm.cm ²)	I _{corr} (mA/cm ²)	Corrosion Rate (mm/year)	Total metal loss (mm)	Potential (mV)
0	3.77E+07	6.91E-07	8.01E-06	0	15.08
2603.2	4.48E+07	5.82E-07	6.75E-06	5.71E-10	596.84
6203.3	6.46E+07	4.04E-07	4.68E-06	1.12E-09	336.28
9803.6	6.22E+07	4.20E-07	4.87E-06	1.69E-09	119.18
13403	5.45E+07	4.78E-07	5.54E-06	2.34E-09	42.859
17004	1.12E+08	2.33E-07	2.71E-06	2.65E-09	15.483
20604	1.70E+08	1.53E-07	1.78E-06	2.86E-09	11.607
24204	1.31E+08	1.99E-07	2.31E-06	3.13E-09	7.0094
27804	1.84E+08	1.42E-07	1.65E-06	3.33E-09	3.0249
31404	1.77E+08	1.47E-07	1.71E-06	3.53E-09	3.2999
35005	1.87E+08	1.39E-07	1.62E-06	3.71E-09	4.6358
38605	2.21E+08	1.18E-07	1.37E-06	3.87E-09	6.1665
42205	2.08E+08	1.26E-07	1.46E-06	4.05E-09	6.277
45805	1.63E+08	1.60E-07	1.85E-06	4.26E-09	7.5348
49406	1.55E+08	1.69E-07	1.96E-06	4.49E-09	8.8579
53006	1.63E+08	1.60E-07	1.86E-06	4.71E-09	9.7878
56606	1.81E+08	1.44E-07	1.67E-06	4.90E-09	9.1335
60328	1.75E+08	1.50E-07	1.73E-06	5.11E-09	4.4415
63867	1.51E+08	1.73E-07	2.01E-06	5.34E-09	-727.48
68166	1.38E+08	1.89E-07	2.19E-06	5.65E-09	-708.39
71007	9.06E+07	2.88E-07	3.34E-06	5.96E-09	-690.1
74607	7.33E+07	3.56E-07	4.13E-06	6.44E-09	-677.76
78208	5.92E+07	4.41E-07	5.11E-06	7.04E-09	-675.1
81808	3.31E+07	7.89E-07	9.14E-06	8.11E-09	-645.74