Study on Heat Treatment Effect on Corrosion of API 5L X52 steel in CO_2 Environment

By

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

Assoc. Prof. Dr Othman Mamat

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
2012
SEPTEMBER 2011

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.

CHRISTINE ENGELBERT

ABSTRACT

The objective of the present work is to study the effect of microstructure on X52 steel corrosion in CO_2 environment. Based on API Specification 5L, pipe furnished to this specification may be as-rolled, normalized, normalized and tempered, subcritically stress relieved, subcritically age hardened or quenched and tempered. However, there is no specific type of heat treatment required by this specification standard. Thus, two types of heat treatment which are annealed and quenched and tempered will be use for this project. For this project, corrosion rates of both heat treated samples were examined using Linear Polarization method while microstructure and microhardness of these steels were examined by optical microscopy and hardness test, respectively. Experimental results have shown that quenched and tempered X52 steel has higher corrosion rate after 120 hour of immersion but it still has the highest strength compared to annealed X52 steel. Thus, it can be concluded that microstructure can influence the properties of materials and different heat treatment process can be used to obtain desired properties.

AKNOWLEDGEMENT

I would like to express my heartfelt gratitude to our creator for the opportunity and strength for me to complete the project within the time allocated.

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CHAPTER 1

INTRODUCTION

1.1 Project Background

Corrosion has a very important economy impact in the oil and gas industry. Oilfield production environments can range from practically zero corrosion to extremely high rates corrosion. The most predominant form of corrosion encountered in oil and gas production is the one caused by CO_2. Dissolved carbon dioxide in the produced brines is very corrosive to carbon and low alloy steel tubular and to process equipment used in this industry.

Corrosion control costs are significant and are mainly related to materials replacement and corrosion control programs. Approximately 60% of oilfield failures are related to CO_2 corrosion mainly due to inadequate knowledge/predictive capability and the poor resistance of carbon and low alloy steels to this type of corrosive attack. [1] CO_2 can cause not only general corrosion but also localized corrosion, which is a much more serious problem.

Carbon and low alloy steels performance in this type of environment depends on their microstructure and chemical composition. The importance of these two variables has been recognized and various researches have been done about this issue. However, there are still contradictions between the different available data. As a consequence it is not possible to make a general conclusions and a critical analysis from the existing information could help the end users when selecting the best materials.

The aim of the project is to conduct experimental research on the effect of microstructure to corrosion of API 5L X52 steels in CO_2 environment. Results from the experiment will be discuss on the later part in a hope that better understanding of microstructure effect in CO_2 corrosion environment will be gain at the end of the project.

1.2 Problem Statement

1.2.1 Problem Identification

Based on API Specification 5L, pipe furnished to this specification may be as-rolled, normalized, normalized and tempered, subcritically stress relieved, subcritically age hardened or quenched and tempered. However, there is no specific type of heat treatment required by this specification standard. Thus, two types of heat treatment which are annealed and quenched and tempered will be use for this project.

1.2.2 Significant of Project

API 5L X-52 line pipe steel (UNS G10220) will be used for this project, as it is used widely for product transportation in the oil and gas industry. Laboratory corrosion study in carbon dioxide environment will be done in this project to study the effect of microstructure of X-52 steel so that the best heat treatment process can be used in the future.

1.3 Objective

The objective of this project is to study the effect of heat treatment (annealing and quenching and tempering) on corrosion of API 5L X-52 steel in carbon dioxide environment.

1.4 Scope of study

In this project, two API 5L X-52 steel plates will be cut from the pipe line and will undergo different heat treatment; annealed and quenched and tempered. Laboratory corrosion test will be done for both samples in carbon dioxide environment. All parameters such as pH, temperature, carbon dioxide pressure, salt concentration and time will be the same for the corrosion test of both samples. Microstructure of the samples will be compare before corrosion test and after corrosion test. Besides, corrosion rate will also be recorded. At the end of the experiment, data will be analyzed to check the effect of the microstructure on the corrosion performance.

1.5 Relevancy of project

As recently as 1995, a major study concluded that the cost impact of corrosion to the U.S. economy totaled nearly $300 billion annually.[9] Jeffrey Guthrie, Brigitte Battat and Chris Grethlein explains that in many cases, corrosion is the life-limiting factor of a component. Corrosive failures can occur unexpectedly at the worst possible moment. Study of the microstructure effect on corrosion, will be able to help engineers to decide types of material to be use for a specific purpose to control the corrosion problem and reduce failures in the industry. By doing so, cost of maintenance can be minimize thus the profit will be maximize.

1.6 Feasibility

It is required for all the Final Year Students to complete their project within two semesters of study. Therefore, proper planning has been develop at the beginning of the project to make sure that the project can be completed and the objective of the project can be achieved within the time frame. Table 3.5 shows the overall planning using Gantt chart of this project.

CHAPTER 2

LITERATURE REVIEW

2.1 CO_2 corrosion basic reaction

Carbon dioxide dissolve in the presence of water phase and form carbonic acid, which is corrosive to carbon steel (Eq.(1)).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (1)$$

Several mechanisms have been proposed for the dissolution of iron in aqueous, deareated CO_2 solutions. The main corrosion process can be summarized by three cathodic (Eq. (2a), Eq. (2b) and Eq. (2c)) and one anodic (Eq. (3)) reactions.

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^- \qquad (2a)$$

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-} \qquad (2b)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2c)$$

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (3)$$

Due to these processes, corrosion layer is formed on the steel surface. The properties of this layer and its influence on the corrosion rate are important factors to be taken into account when studying the corrosion of steels in CO_2 aqueous solutions. Some evidence suggests that iron carbonate, $FeCO_3$ may be important in the protection of protective layers. Its formation can be explained using Eq. (4), Eq. (5a) and Eq. (5b). Because of its low solubility, $FeCO_3$ precipitates out of solution ($pK_{sp} = 10.54$ at 25°C).

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \qquad (4)$$

$$Fe^{2+} + 2HCO_3^- \rightarrow Fe(HCO_3)_2 \qquad (5a)$$

$$Fe(HCO_3)_2 \rightarrow FeCO_3 + CO_2 + H_2O \qquad (5b)$$

The morphology of the scale influences the level of protection observed. Below 40°C surface scales are formed mainly of cementite (Fe_3C) with some $FeCO_3$ and alloying elements of the steels. Fe_3C is part of the original steel in the non-oxidized state that accumulates in the surface after the preferential dissolution of ferrite. It is suggested that cementite provides an available area for cathodic reaction.

2.2 Heat Treatment

There was various heat treatment process commonly employed in engineering practice as follows:

2.2.1 Annealing:

Spherodizing

Spherodite forms when carbon steel is heated to approximately 700 °C for over 30 hours. The purpose is to soften higher carbon steel and allow more formability. This is the softest and most ductile form of steel. Here cementite is present.

Full Annealing

Carbon steel is heated to approximately above the upper critical temperature (550-650 °C) for 1 hour. Here all the ferrite transforms into austenite. The steel must then cooled in the realm of 38 per hour. This results in a coarse pearlite structure. Full annealed steel is soft and ductile with no internal stress.

Process Annealing

The steel is heated to a temperature below or close to the lower critical temperature (550-650 °C), held at this temperature for some time and then cooled slowly. The purpose is to relive stress in a cold worked carbon steel with less than 0.3%wt c.

Diffusion Annealing

The process consists of heating the steel to high temperature (1100-1200 °C). It is held at this temperature for 3 hours to 20 hours and then cooled to 800-850 °C inside the furnace for a period of about 6 to 8 hours. It is further cooled in the air to room temperature. This process is mainly used for ingots and large casting. It is also called isothermal annealing.

2.2.2 Normalising

The process of normalizing consist of heating the metal to a temperature of 30 to 50 °C above the upper critical temperature for hypo-eutectoid steels and by the same temperature above the lower critical temperature for hyper-eutectoid steel. It is held at this temperature for a considerable time and then quenched in suitable cooling medium. The purpose of normalizing is to refine grain structure, improve machinibility and improve tensile strength, to remove strain and to remove dislocation.

2.2.3 Hardening

The process of hardening consist of heating the metal to a temperature of 30-50 °C above the upper critical point for hypo-eutectoid steels and by the same temperature above the lower critical temperature for hyper-eutectoid steels. It is held this temperature for some time and then quenched. The purposes of hardening are to increase the hardness of the metal and to make suitable cutting tools.

2.2.4 Austempering

It is a hardening process. It is also known as isothermal quenching. In this process, the steel is heated above the upper critical temperature at about 875 °C where the structure consists entirely of austenite. It is then suddenly cooled by quenching it in a salt bath maintained at a temperature of about 250 °C to 525 °C.

2.2.5 Martempering

This process is also known as steeped quenching or interrupted quenching. It consists of heating steel above the upper critical temperature and quenching it in a salt bath kept at a suitable temperature.

2.2.6 Tempering

This process consists of reheating the hardened steel to some temperature below the lower critical temperature, followed by any desired rate of cooling. The purpose is to relive internal stress, to reduce brittleness and to make steel tough to resist shock and fatigue.

2.3 Main environmental factors affecting CO_2 corrosion

There are few factors affecting CO_2 corrosion as stated below:

2.3.1 pH

Based on various researches done, it can be concluded that uniform corrosion rate in CO_2 saturated brines decreases as pH increases. This is related to the formation of bicarbonate and carbonate salts, and also because of decrease in the solubility of $FeCO_3$, which makes the formation of the protective film more feasible. [2-5]

2.3.2 Oxygen content

$FeCO_3$ is unstable in the presence of oxygen, thus the passive $FeCO_3$ films normally form under anaerobic conditions. In filed applications, oxygen may enter the production equipment due to water or inhibitors injection. Higher oxygen concentration causes increase in the rate of cathodic reaction.

2.3.3 Iron content

The content of ferrous cation in solution determines if it is possible to form $FeCO_3$ or not, as it is necessary to exceed the solubility limit in order to precipitate iron carbonate. Videm K and Dugstad A in their research show that $FeCO_3$ growth rate is depending on temperature and level of super saturation. [4, 5]

2.3.4 Flow

Usually corrosion rate increases with flow velocity as it can prevent the formation of passive $FeCO_3$ film by removing existing films or retarding the growth of such films by enhancing mass transfer of reactants near the surface. In CO_2 containing wells, erosion-corrosion due to high fluid velocities is reported as a serious problem.

2.3.5 CO_2 content

Uniform corrosion rate will increase with higher CO_2 partial pressure because the solution pH decreases and the rate of reduction of carbonic acid increase.

2.3.6 Temperature

At low temperature (less than 60°C), uniform corrosion rate increases with temperature. In order to calculate the corrosion rate, deWaard-Milliams equation is widely accepted. However, protective films are formed more easily at high temperature and the corrosion rate goes through a maximum.

2.4 Journals from previous research

The following Table 2.1 shows previous research journals that have been encountered throughout the background study research.

No	Authors/Title/Findings
10.	D.A. Lopez, T. Perez, S.N. Simison, The influence of microstructure and chemical composition of carbon and low alloy steels in CO_2 corrosion. A state-of-the-art appraisal. Materials and Design 24 (2003) 561-575. Findings: Objective(s): The objective of this work is to review and discuss the available information about the effect of microstructure and composition of carbon and low-alloyed steel on corrosion resistance in CO_2 environments. The influence of the parameters on the efficiency of corrosion inhibitors is also considered. Methodology: i) Annealed and quenched and tempered carbon steel samples with different compositions (X52 and X56) were prepared and corrosion test was done with corrosion inhibitors and without corrosion inhibitors. ii) Microstructure study was done for both samples under scanning electron microscope (SEM) and as well as study on the cross-sections of the corrosion layers. iii) There were various corrosion test done using different parameters from each other. iv) Images from scanning electron microscope and x-ray photoelectron spectroscopy were analyzed in the later part. v) Corrosion rates of all samples under various condition parameters were also analyzed to achieve a general conclusion. Efficiency of the corrosion inhibitor in CO_2 corrosion was also evaluated. Result: From analyzed data it can be seen that microstructure and chemical composition of carbon and low alloy steels are important factors and they have a significant influence on CO_2 corrosion performance. However, as remark throughout this

	work, it is not possible to come up with general behavior patterns, mainly because of the complexity of the issue and interrelation within the different factors involved. Relevancy to this project: The objective of this journal is almost similar to the objective of the research to be done. However, in this research experimental work will be done using the parameters such as temperature, pH, NaCl concentration and CO_2 pressure based on previous researches done before.

No	Authors/Title/Findings
11.	S. Al-Hassan, B.Mishra, D.L Olson, M.M Salama. Effect of Microstructure on Corrosion of Steels in Aqueous Solutions Containing Carbon Dioxide. NACE Journal No. 98060480 Findings: Objective: To measure the influence of microstructure on the corrosion rate of steels in a carbon dioxide –containing aqueous solution through experimental work as a function of pH, temperature, and partial pressure of CO_2. Methodology: i) API X-52 line pipe steel, type 1080 eutectoid steel, 2.25% Cr-1% Mo alloy steel, and pure iron used for corrosion tests under atmospheric pressure in CO_2 saturated synthetic brine solution as a function of temperature. ii) Each metal sample undergone different type of heat treatments such as annealed, normalized and quenched and tempered. iii) 3 wt% of NaCl solution was prepared and CO_2 gas was allowed to bubble in the solution at least 24 h to ensure total saturation prior to the test. iv) Measured pH of solution was 5.0 at the start of the experiments but gradually stabilized at 5.4 over the 800-h duration. v) Weight loss experiments were done after each corrosion test. Result: It shows that weight loss of X-52 steel in all the heat treated conditions increased with increasing temperature. At fixed temperature, weight losses of steels heat –treated differently showed a general trend in that the annealed specimen corroded the least, and the as-received material corroded the most, while the quenched and tempered group of steel coupons showed corrosion rates in between the two extremes.

	Relevancy to this project: The objective stated in this journal is the same as the objective of the research to be done. API X-52 line pipe steel as used in this journal will also be used for the current research. Similar heat treatment will be done to the material for this research. However the heat treatment temperature that will be used is slightly different than the temperature used in this journal.

No	Authors/Title/Findings
12.	L.J. Cosmes Lopez, E.Arce, J.Torres, J.Vazquez-Arenas, J.M. Hallen, and R.Cabrera-Sierra. Corrosion Process of API X52 Carbon Steel Immersed in an Aqueous Solution Simulating a Clay Soil. NACED Paper No. 116001. Findings: Objective: To characterize the corrosion process of API X52 steel in a solution simulation clay soil using linear sweep voltammetry, electrochemical impedance spectroscopy, scanning electron microscopy and x-ray diffraction techniques. Methodology: i) Working plate electrodes were made from a buried pipeline of API X52 carbon steel. The electrodes were mounted with epoxy resin and polished with silicon carbide papers from grade 220 to 600 until homogeneous finished surface was obtained. ii) Corrosion test was done for 15 days and minor variations from 0.1 to 0.2 units were evaluated after 24 hour of immersion. iii) Linear sweep voltammetry curves were recorded using scan rate of 0.1666mV. iv) Electrochemical Impedance Spectroscopy diagrams were recorded at the corrosion potential, scanning frequency from 10 kHz to 0.01 kHz using wave amplitude of 10 mV. v) X-Ray Diffraction was used to determine the iron phases formed on the API X52 steel. Result: In the corrosion process of API X52 carbon steel immersed in an aqueous solution simulating clay soil, LSV and EIS measurements allowed identification of transition in the oxidation of steel whose chemical composition is dependent of immersion time. Longer immersion time will cause pitting to the samples.

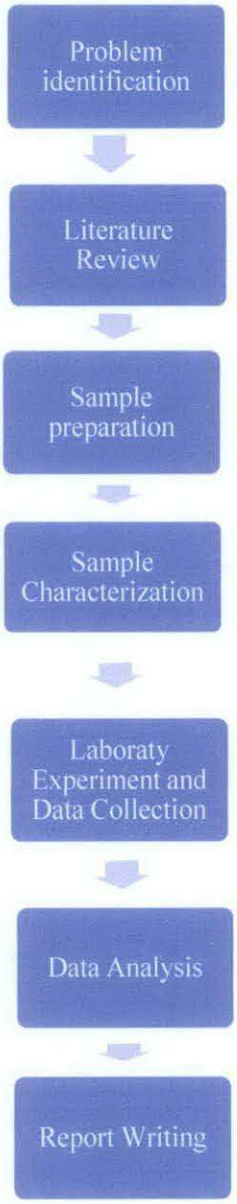
	Relevancy to this project: The material used in this work is the same as the material that is used in this research. The objective of this work is also similar to the objective if the research which is to study the corrosion of API X52 carbon steel with its microstructure

CHAPTER 3

METHODOLOGY

3.1) Research methodology

Figure 3.1 below shows the overall process flow of activity for this project.



Problem will be identified to initiates the project.

Previous researches will be studied to have better understanding of the problem as well as to get ideas on how to encounter the problem.

API 5L X52 Steel will be prepared for microstructure examination.

Samples will be examined under optical microscope or scanning electron microscope to study its metallography. Depending on the metallography result, sample will undergo heat treatment (annealing, quenched & tempered.)

Corrosion test will be conducted for every specified hour, and microstructure examination will be done after each specified hour.

Recorded data from the experiment and microstructure examination will be analyzed.

Results from the analysis will be used to write the report of the research.

Figure 3.1: Project Flow of activity

3.2) Project Activities

3.2.1) X52 carbon steel chemical composition

Based on API Spec 5L, Table 3.1 below are the chemical composition requirements by percentage weight for API 5L X52 steel.

Table 3.1: API 5L X52 chemical composition

Carbon	Manganese	Phosporus	Sulfur	Others
0.2	1.4	0.025	0.015	c,d

[c] Columbium [niobium], vanadium, titanium, or combinations thereof may be used at the discretion of the manufacturer.

[d] The sum of the columbium [niobium], vanadium, and titanium contents shall not exceed 0.15%.

3.2.2) Heat Treatment

The material used throughout this project is API 5L X52 steel and four square pieces of the material was provided in the beginning of project. Two steel undergo annealed process heat treatment, while another two samples undergo quenched and tempered heat treatment process. Heat treatment process was done using furnace oven in Block 17.

Figure 3.2: Furnace oven used for heat treatment

General Procedure:

Annealing Heat Treatment:

1. Two API 5L X52 sample were prepared for this heat treatment process.
2. Heat treatment process parameters was set (heating and cooling rate 14°C per minute, temperature is 820°C and dwell time 60 minutes).
3. Both samples were placed inside the furnace oven. Gas exhaust valve was opened fully to make sure hot air is induced out from furnace oven. Extra fan might be needed as we are operating in high temperature.
4. Samples were left inside the furnace oven to cool down after the heat treatment process end.

Quenching and Tempering Heat Treatment:

1. Another two API 5L X52 sample were prepared for this heat treatment process.
2. Process parameters of the heat treatment were set whereby the material is first heated to 870°C, held for 40 minutes then water quenched. It is then reheated to a lower temperature at 600°C, held for 2 hour.[6]
5. Both samples were placed inside the furnace oven. Gas exhaust valve was opened fully to make sure hot air is induced out from furnace oven. Extra fan might be needed as we are operating in high temperature.
3. Samples were taken out from furnace oven at the end of this heat treatment process to be air cooled.

3.2.3) Sample Preparation

As the sizes of the samples are quite big, all samples were cut into half using abrasive cutter. All samples were mounted with epoxy after cutting it and labeled according to their heat treatment process.

Figure 3.3: Abrasive cutter used to section the material

Figure 3.4: Hardener and resin used

Figure 3.5: API 5L X-52 samples during mounting

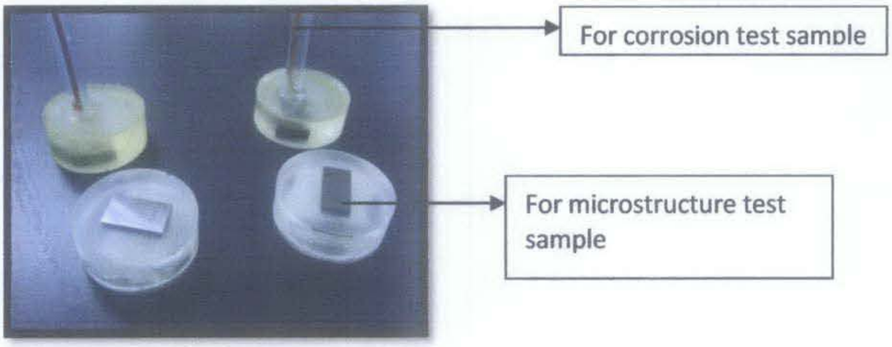


Figure 3.6: API 5L X-52 samples after mounting

General Procedure:

1. Samples were sectioned into half using abrasive cutter.
2. After that, measurement of samples' width and length were measured using digital vernier caliper in order to calculate the precise area of the samples for electrochemical testing use in the later part.
3. Samples from each heat treatment were soldered to connect the conductor (Copper wire) to the surface of the sample.
4. Mounting cups were greased with lubricant to ease the removal mounted part.
5. Soldered metals placed into the mounting cups along with the transparent tube covering the copper wire.
6. Mounting mixture consist of 5:1 ratio (5 parts of epoxy and 1 part of hardener) was weighted and this mixture was stirred until clear mixture color achieved.
7. Epoxy mixture then was poured into the mounting cups. Mixture must cover above the tube level.
8. Samples were left for 1 day for curing time of the mixture.
9. Samples were removed from the mounting cups when it is already hardened by pushing it outwards. All of the samples were labeled for ease of identification.

3.2.4) Electrochemical Testing – Linear Polarization Resistance

Electrochemical testing was done to study the corrosion rates for both annealed and quenched and tempered X52 steel samples. Below are the experimental setup and general test matrix for electrochemical testing which was done at Corrosion Research Centre Blok I.

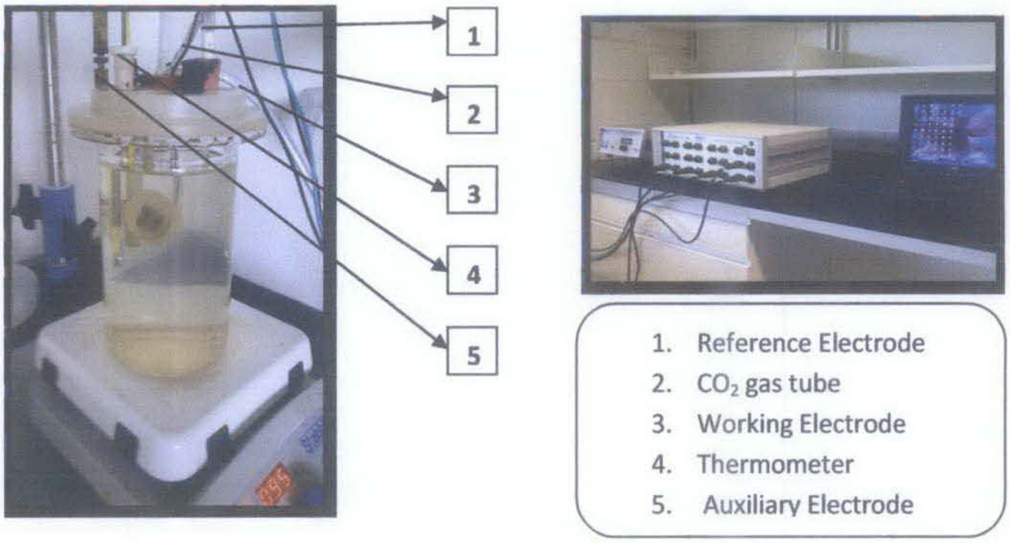


Figure 3.7: Experimental Setup

Table 3.2: General Test Parameters

Parameter	Value
Material	API 5L X52 steel
Solution	3% NaCl
Temperature	50°C
De-oxygenation gas	1 bar CO_2
pH	4
Measurement Technique	LPR

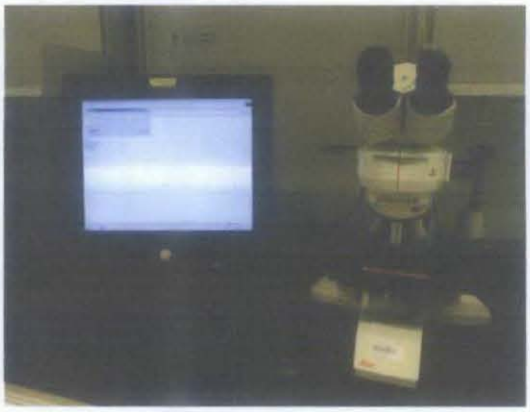
General Procedure:

1. 30 g NaCl weighted and mixed with 1L of de-ionized water to get 3% NaCl solution. This mixture was then stirred using StableTemp Cole-Palmer and left for approximately 2 minutes to make sure all the NaCl powder has already dissolved.
2. Solution is purged by providing CO_2 gas into the solution for 1 hour. Temperature was set to 120°C using hot plate to achieve solution temperature of 50°C at the end of purging process.
3. Sample is grinded with 240 grit, 320 grit, 400 grit, and 600 grit silicon carbide grinding paper.
4. After 1 hour purging, sample and other electrodes were placed in the glass cell and left for 24 hours. Temperature was lowered down to 95°C.
5. After both samples had been run for 24 hours, repeat procedures and run experiment for 5 days.
6. Samples were brought to Block 17 for metallographic and mechanical property study.

3.2.5) Metallographic Study

Metallographic study was done to study the microstructure of each sample and analyze the difference of microstructure. Metallographic study also will be related to the corrosion rate from electrochemical testing result and microhardness result.

Table 3.3: Equipments used for metallographic study

General Procedure:

1. Samples were grinded using grinder machine in Block 17 and grinding process starts with 120 grit, 240 grit, 320 grit, 400 grit, 600 grit, 800 grit and 1200 grit. Water is used as lubricant during grinding process. The speed used for grinding process is 300n/min.
2. After grinding, samples were then polished to remove the deformation zone produced by fine grinding. The diamond paste 1 micron was rubbed on the samples and on a rotating polishing cloth. Small pressure is applied to the sample to get a mirror finish surface.
3. Samples were rinsed with distilled water followed by methanol after polishing to avoid contaminants which will give false indication on microstructure. Samples were dried using drying machine.
4. 2% of Nital was prepared using 9.8ml Methanol mixed with 0.2ml Nitric Acid. Samples were etched using swabbing methods and left for 15 seconds. Samples then rinsed with distilled water and methanol and dried using drying machine.
5. Microstructure of every sample studied under optical microscope. Magnification of the optical microscope was calibrated to get the microstructure picture that is needed.
6. Microstructure of every sample were captured and stored in the computer.

3.2.6) Mechanical Property Test (Microhardness Test)

Microhardness test was done using Vicker's Hardness Technique. The purpose of this testing is to evaluate the strength of the samples and relate it with the microstructure from optical microscope.

Figure 3.8: Hardness Testing Machine

General Procedure:

1. Set the load to 300 gram for all samples.
2. Placed sample under the microscope and calibrate the handle to make sure we can see the microstructure of the sample.
3. Values in machine were reset and the testing is started by pressing start button.
4. Dwell time for the indentation was 20s.
5. After indentation is done, D_1, D_2 and HV values were recorded from the value in the machine.

3.3) Equipments and Tools Required

There are few types of equipment that will be used throughout the experiment such as below:

i. Beaker
ii. Stirrer
iii. Electronic Balance
iv. Spatula
v. Connecting wires

In conducting the laboratory experiment, few tools are required for analysis purposes. Table 3.4 shows the type of tools required as well as brief description on their function(s). (American Society for Metals, Definition of Metallurgical Terms, 1977)

Table 3.4: Tools required and their function(s)

Tool	Function(s)
1) Vicker's Hardness Tester	The Vickers hardness test was developed in 1921 by Robert L. Smith and George E. Sandland at Vickers Ltd as an alternative to the Brinell method to measure the hardness of materials. The Vickers test is often easier to use than other hardness tests since the required calculations are independent of the size of the indenter, and the indenter can be used for all materials irrespective of hardness. The basic principle, as with all common measures of hardness, is to observe the questioned material's ability to resist plastic deformation from a standard source. The Vickers test can be used for all metals and has one of the widest scales among hardness tests. The unit of hardness given by the test is known as the Vickers Pyramid Number (HV).

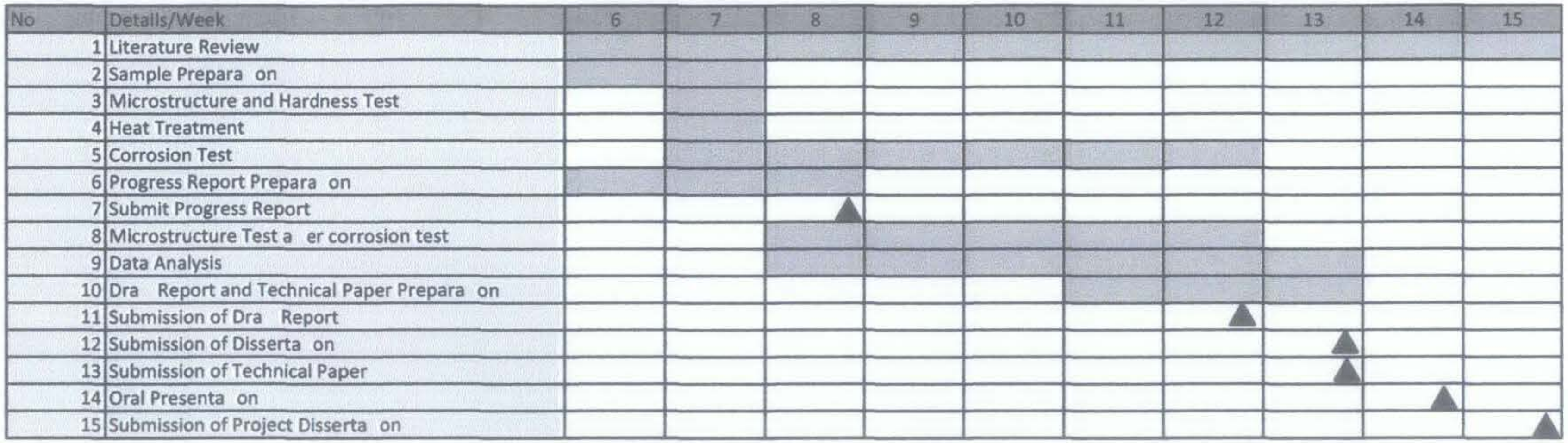
2) Optical Microscope	The optical microscope remains the fundamental tool for phase identification. The optical microscope magnifies an image by sending a beam of light through the object as seen in the schematic diagram of Figure 1. The condenser lens focuses the light on the sample and the objective lenses (10X, 40X,etc) magnifies the beam, which contains the image, to the projector lens so the image can be viewed by the observer.[7]
3) Potentiostat	The Gill AC is a high specification automated Potentiostat; Galvanostat; Zero Resistance Ammeter and Frequency Response Analyser in one neat enclosure. It can be used on its own or as part of an array of Gill ACs controlled from the same PC. It has an extensive range of off the peg options to suit most requirements. The Gill AC is typically controlled via our Sequencer and Core Running programs. Program nodules within the Sequencer dictate what tests the Gill AC can perform. In this specific case the instrument is supplied with the following nodules:- Cyclic Sweeps; Long Term; Current & Voltage Noise; and ACImpedance. These nodules will enable the instrument to perform the following types of test :- Single or Multiple Cycle Sweeps including Customised Sweep types;tests with respect to time including Linear Polarisation Resistance [15]

4) Abrasive Cutter	The machine is being manually operated. The cutting process can be controlled using manually controlled cutting lever. The sample will be clamped using cam-lock vises. Start with pushing the start push-button. After the sectioning process is done, push the stop button as the hood lock safety switch prevents the hood from being opened unless the stop button has been depressed. When the hood is in an open position, there is a safety switch that prevents power supplied to the motor and cutting wheel. It will prevent any accidents from happened. The grinding process will create a deformation zone on the samples. The mechanical properties also will change due to stress put on the part during grinding.

3.6) Gantt Chart

Table 3.5 below shows the Gantt Chart of the overall project.

Table 3.5: Gantt Chart for FYP 2



No	Details/Week	6	7	8	9	10	11	12	13	14	15
1	Literature Review	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
2	Sample Preparation	▨	▨								
3	Microstructure and Hardness Test		▨								
4	Heat Treatment		▨								
5	Corrosion Test		▨	▨	▨	▨	▨	▨			
6	Progress Report Preparation	▨	▨	▨							
7	Submit Progress Report			▲							
8	Microstructure Test after corrosion test			▨	▨	▨	▨	▨			
9	Data Analysis			▨	▨	▨	▨	▨	▨		
10	Draft Report and Technical Paper Preparation						▨	▨	▨		
11	Submission of Draft Report							▲			
12	Submission of Dissertation								▲		
13	Submission of Technical Paper								▲		
14	Oral Presentation									▲	
15	Submission of Project Dissertation										▲

▲ Milestone
▨ Progress

CHAPTER 4

RESULT AND DISCUSSION

4.1 Corrosion Test (Electrochemical Techniques)

The corrosion rates of annealed and quenched and tempered samples were measured using Linear Polarization Resistance (LPR) at 50 °C for 24 hours and 5 days are shown at Figure 4.1 and Figure 4.2.

4.1.1 Corrosion rates over time

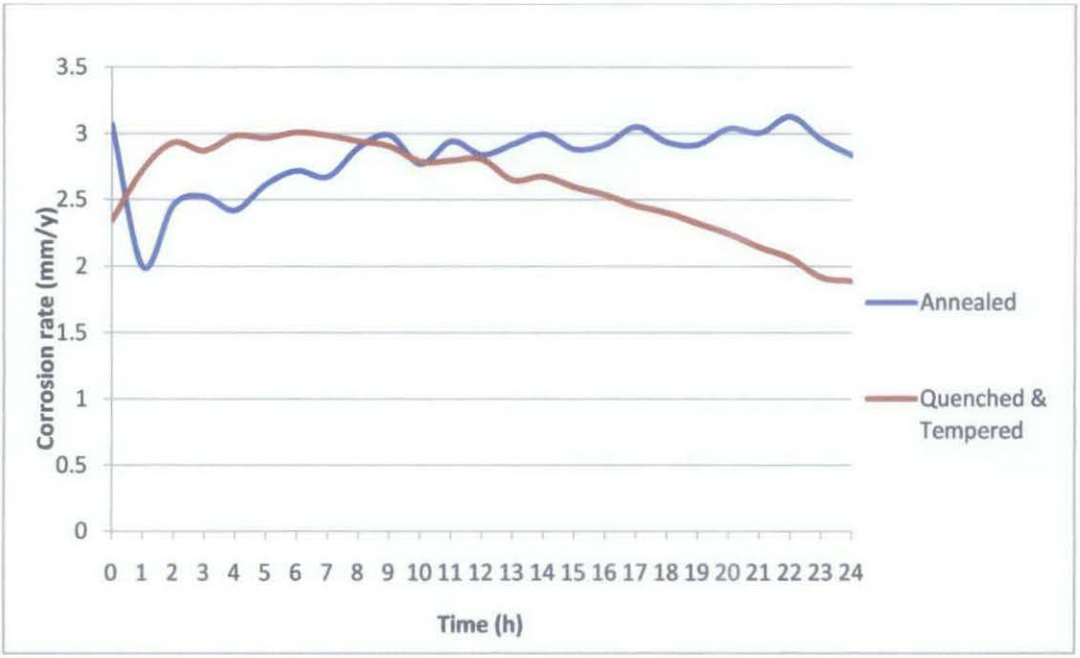


Figure 4.1: Corrosion rates recorded for annealed and quenched and tempered API X52 steel after 24 hours immersion at 50°C, 3% NaCl solution, 1 bar CO_2.

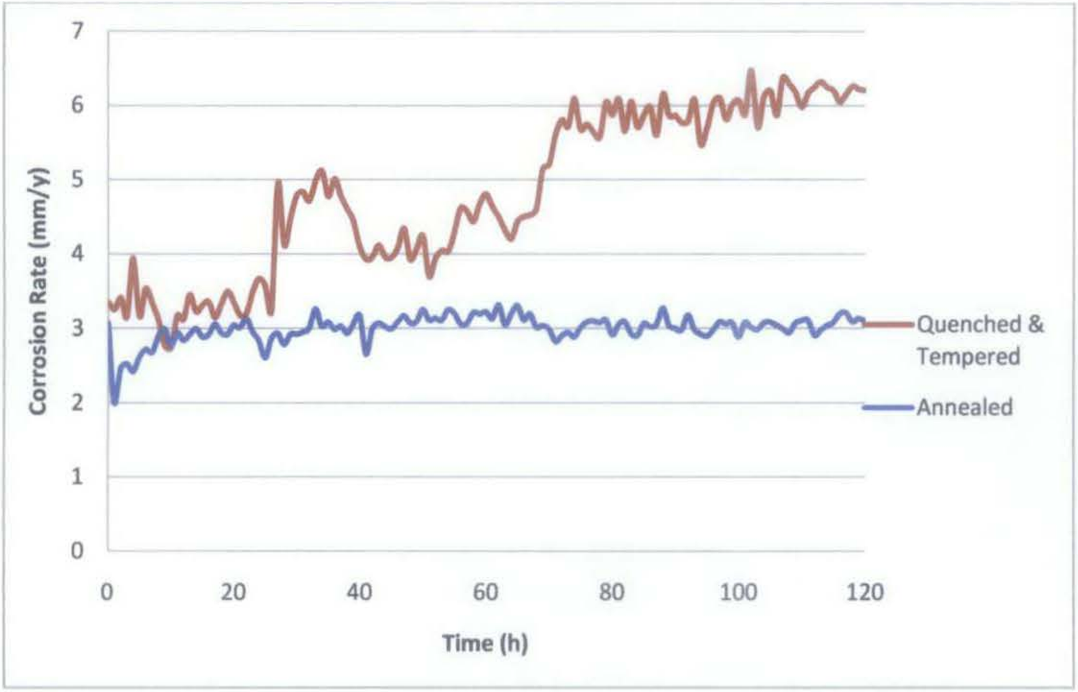


Figure 4.2: Corrosion rates recorded for annealed and quenched and tempered API X52 steel after 5 days immersion at 50°C, 3% NaCl solution, 1 bar CO_2.

From Figure 4.1 it is shown that the corrosion rate for quenched and tempered API 5L X52 steel is reducing when time increases with the lowest corrosion rate 1.89 mm/year at the end of 24 hours immersion. However, for annealed API 5L X52 steel it shows an increment of corrosion rate with time and the highest corrosion rate occurs at 22nd hour with 3.13 mm/year. After 24 hours immersion, quenched and tempered sample shows lower corrosion rate compared to annealed sample. In Figure 4.2 there is an increasing trend of corrosion rates for both sample annealed and quenched and tempered after 5 days immersion in the NaCl solution but quenched and tempered sample shows the highest corrosion rates increment with 6.37mm/year The reduction of corrosion rate shown by quenched and tempered sample after 24 hours of immersion indicates that $FeCO_3$ film formed on the surface of the sample and this prevent further corrosion to occur on the sample. However, both samples for 5 days immersion show unstable result with increasing corrosion rates. This situation might happen due to unstable condition of the electrolyte solution or error from the connection. This might also happen from unwanted changes of the solution environment during the experiment. During the experiment for 5 days immersion, there was reduction of water volume which might cause changes in pH of the water as well as salt concentration of the solution. Slight changes in the temperature might also be one of the possibility of getting such a result because if the temperature increase, then the corrosion rate will also increase.

4.1.2 Resistance Polarization over time

The resistance polarization of the samples after 24 hours and 5 days immersion in a CO_2 environment can be presented in Figure 4.3 and Figure 4.4 below.

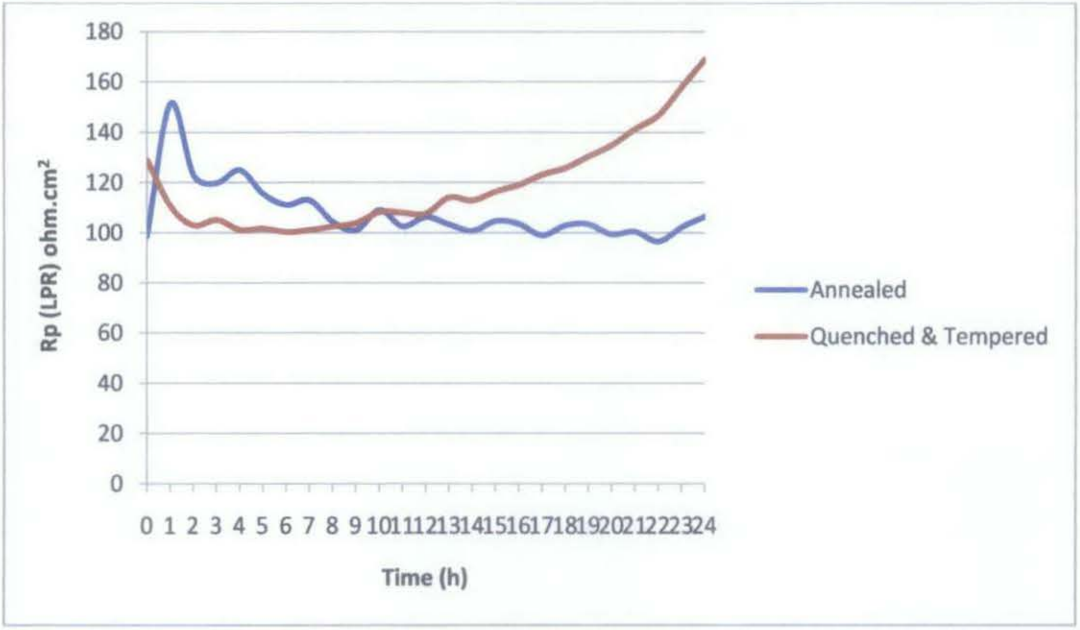


Figure 4.3: Resistance polarization (*Rp*) recorded for annealed and quenched and tempered API X52 steel after 24 hours immersion at 50°C, 3% NaCl solution, 1 bar CO_2.

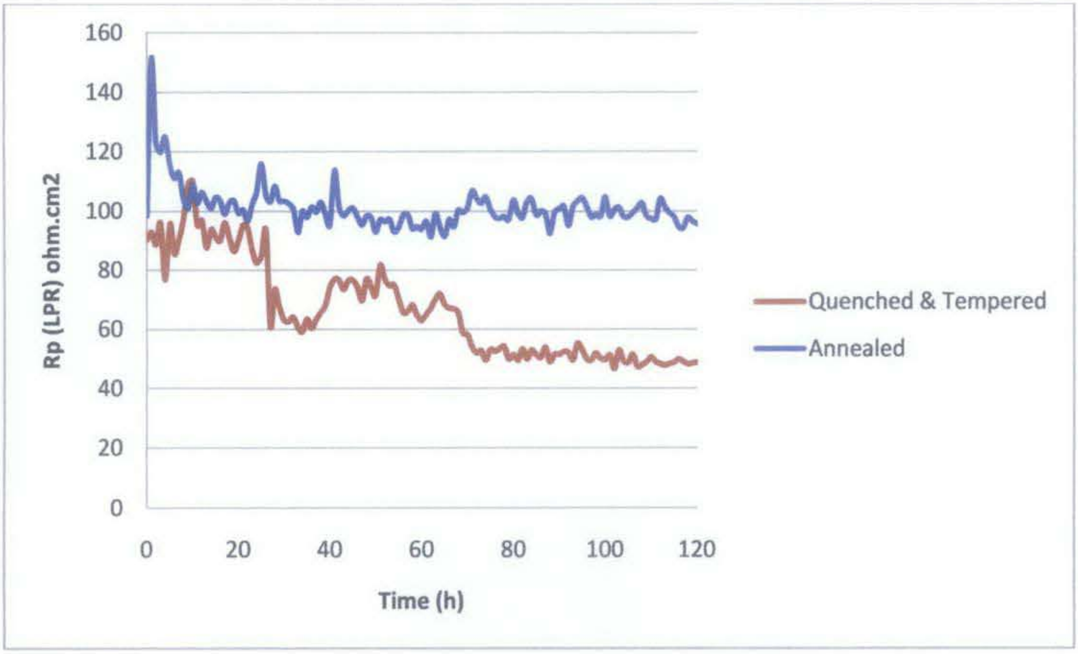


Figure 4.4: Resistance polarization (*Rp*) recorded for annealed and quenched and tempered API X52 steel after 5 days immersion at 50°C, 3% NaCl solution, 1 bar CO_2.

Resistance polarization (*Rp*) is inversely proportional to the corrosion rate, which can be calculated using Equation (6) below. [8]

$$r\,(\text{mm/y}) = 1.16 \times (B/Rp) \qquad (6)$$

where B is a proportionality constant (considered as 0.022V) and *Rp* is in ohm.cm^2. Figure 4.3 show that for long term study, quenched and tempered API 5L X52 sample present higher resistance polarization (*Rp*) values and therefore have a better corrosion resistance than the annealed one. However, for Figure 4.4 annealed API 5L X52 has higher resistance polarization (*Rp*) values compares to quenched and tempered sample. This shows that after 5 days of immersion, annealed sample has better corrosion resistance. Similarly, the corrosion rate can be calculated using Equation 6 above.

4.1.3 Potential over time

Measurement of the potential as a function of immersion time for both sample are shown in Figure 4.5 and Figure 4.6 below.

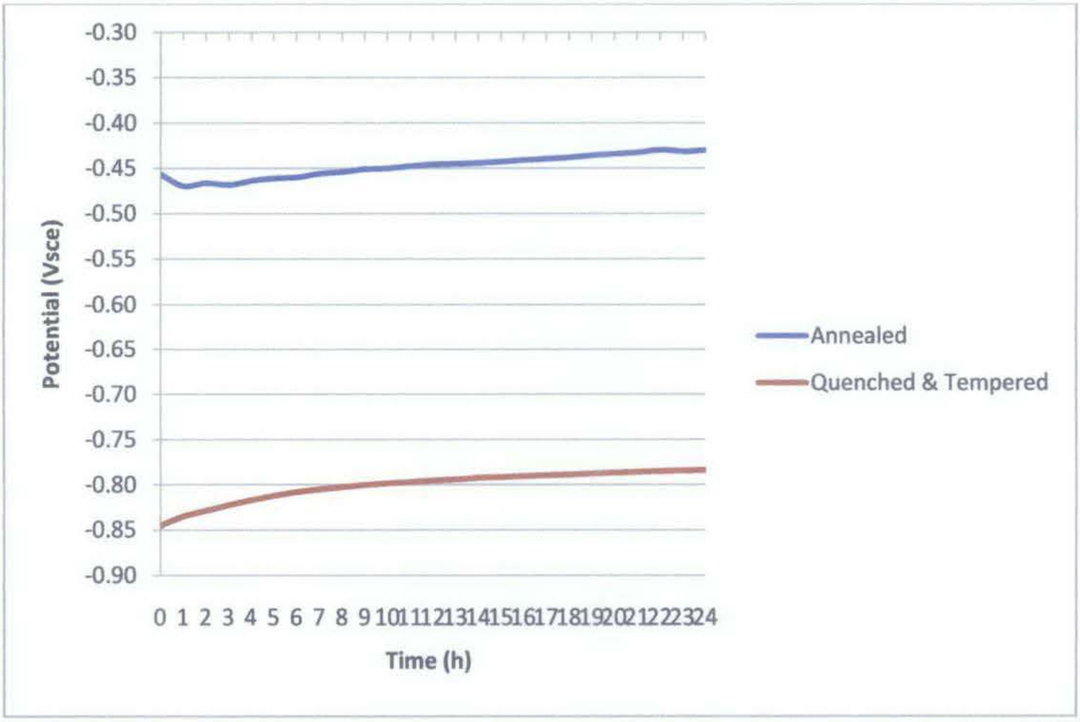


Figure 4.5: Measurement of Potential recorded for annealed and quenched and tempered API X52 steel after 24 hours immersion at 50°C, 3% NaCl solution, 1 bar CO_2.

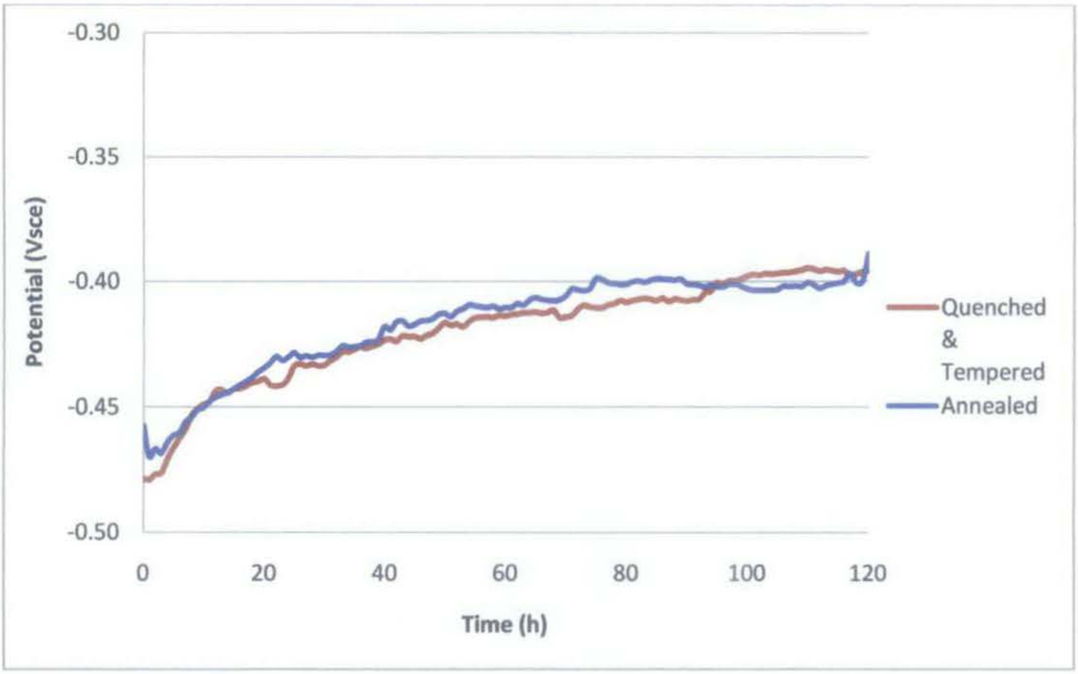
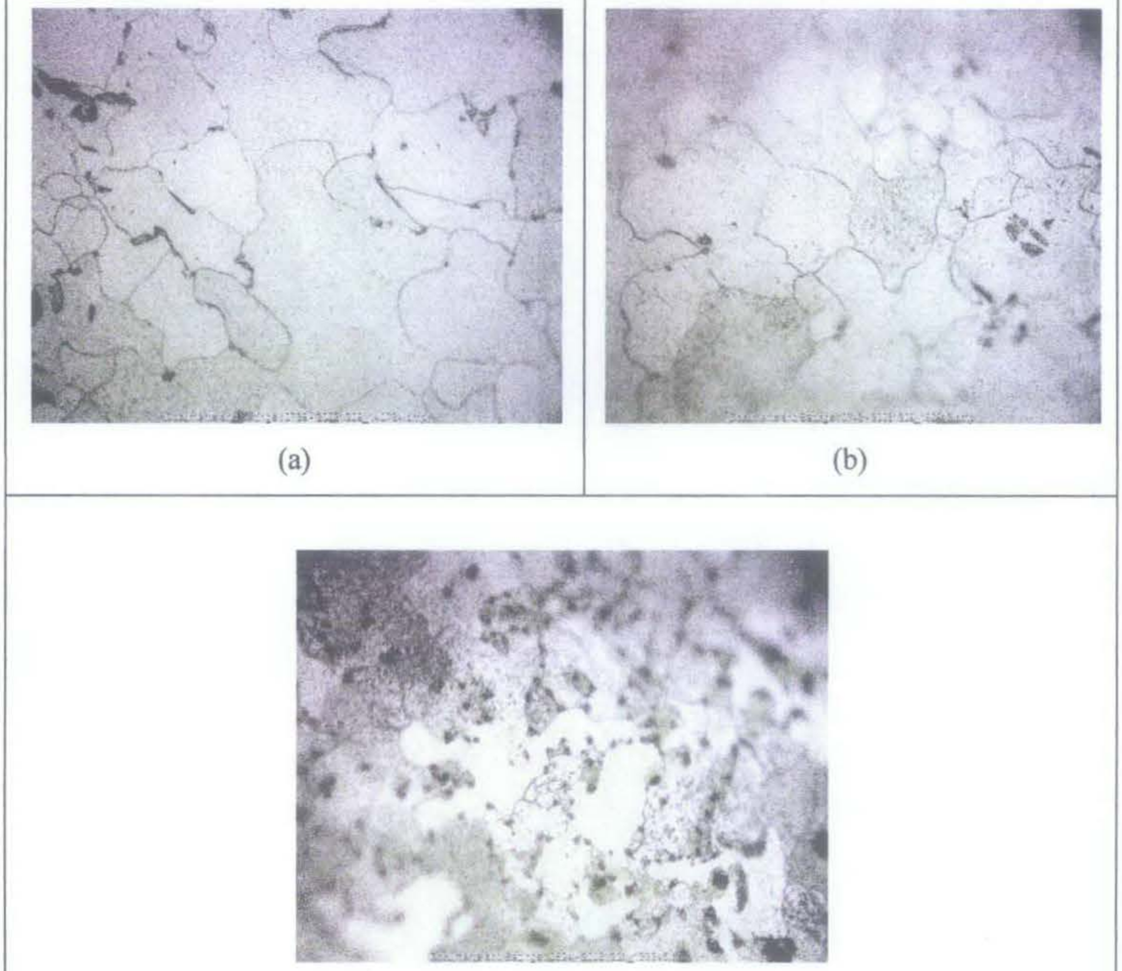


Figure 4.6: Measurement of Potential recorded for annealed and quenched and tempered API X52 steel after 5 days immersion at 50°C, 3% NaCl solution, 1 bar CO_2.

Figure 4.5 and Figure 4.6 shows the variation of corrosion potential as a function of time for annealed and quenched and tempered API X52 steel immersed in CO_2 solution for 24 hours as well as after 5 days. In overall, both of the samples shows a potential shifting towards the noble direction which could be related with modifications in the chemical composition of the corrosion films, an increase in the thickness or both. However, for Figure 4.5 we can conclude that quenched and tempered API 5L X52 sample have greater changes towards the noble direction as compared with the annealed sample and this can be related with the decrease in corrosion rate of quenched and tempered sample towards the end of 24 hours immersion. In Figure 4.6 both the samples have almost similar changes of potential throughout the experiment. Variation in this potential through time is important in buried pipelines applying cathodic protection criteria, because more negative potentials (overpotential) often are imposed, affecting the protection by coatings.

4.2 Microstructure Study

The microstructure of API 5L X52 after light etching with 2% Nital is shown in Figure 4.7 and Figure 4.8.



(a) (b)

(c)

Figure 4.7: Annealed API 5L X52 microstructure after etching (50X)(a) before corrosion testing, (b) 24 hours immersion, (c) 5 days immersion.

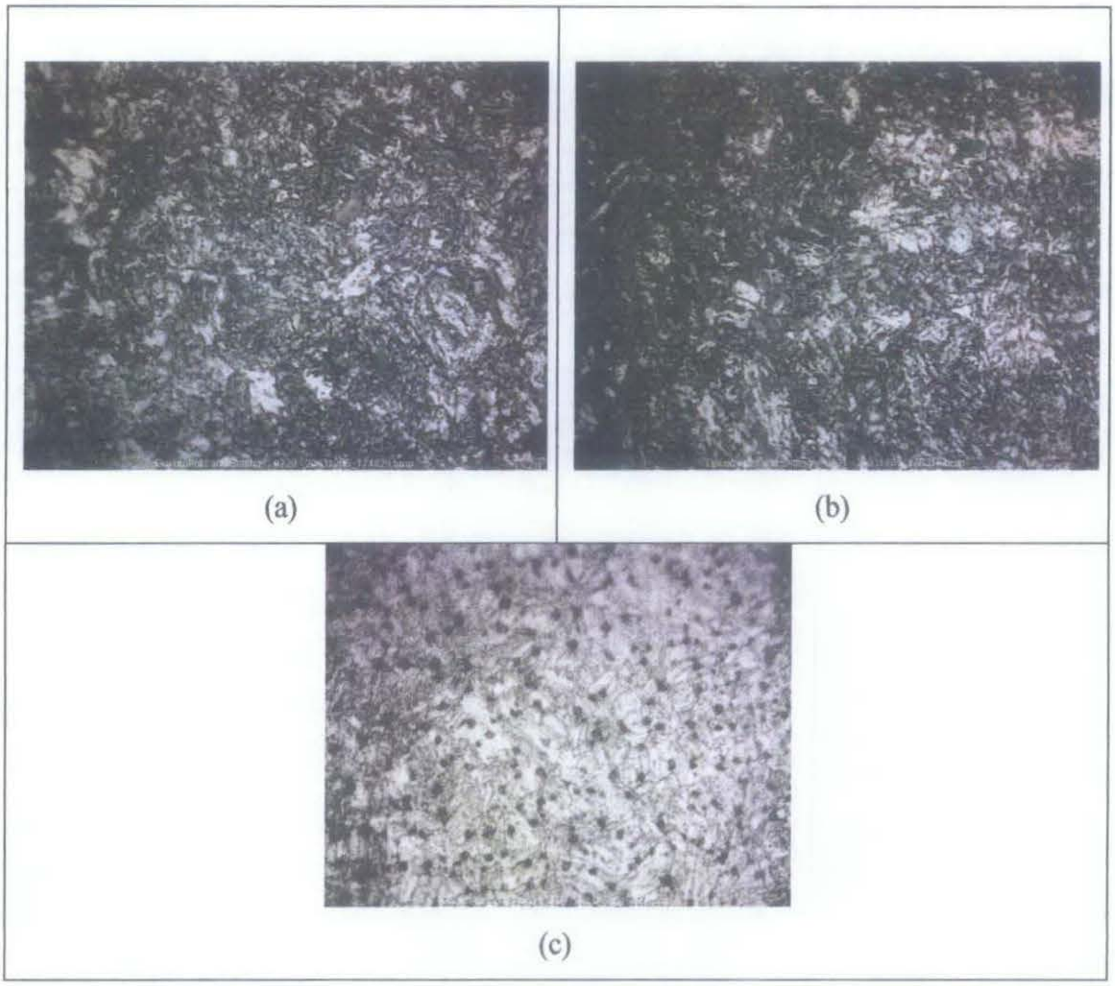

(a)
(b)
(c)

Figure 4.8: Quenched and Tempered API 5L X52 microstructure (10X)(a) before corrosion testing, (b) 24 hours immersion, (c) 5 days immersion.

After heat treatment on both samples, annealed sample shows pearlite/ferrite microstructure while quenched and tempered sample shows martensite microstructure. From Figure 4.7 and Figure 4.8, both sample microstructures does not show significant difference after 24 hours and 5 days immersion in CO_2 environment. Based on the LPR result after 24 hours immersion, annealed API 5L X52 has lower corrosion resistance in CO_2 environment. This phenomenon in pearlite/ferrite microstructure was attributed to the fact that the more the sample (ferrite) corroded, the higher was the exposure of Fe_3C to the solution, leading to larger cathodic sites in the microcells. However, based on LPR measurement in Figure 4.2, contradicting result was achieved after 5 days of samples immersion in CO_2 environment whereby annealed API 5L X52 sample shows higher corrosion resistance in CO_2 environment. This behavior suggested that surface area of contact between pearlite and ferrite was more important in determining the alloy corrosion rate than the contact area between pearlite and the solution.

4.3 Mechanical Properties

Hardness test Parameters:

Load: 300 gram, Dwell Time: 20s

Table 4.1: Mechanical Properties of Annealed API 5L X52

Data/Specimen	Before corrosion test	1 day	5 days
Diameter, D_1 (μm)			
1	62.26	60.36	59.02
2	68.30	69.18	64.05
3	61.97	66.92	64.99
average	64.18	65.49	62.69
Diameter, D_2 (μm)			
1	61.80	55.60	55.27
2	66.28	69.51	58.90
3	61.91	67.93	60.15
average	63.33	64.35	58.11
Hardness (HV)			
1	143.50	180.00	182.10
2	126.60	115.10	160.40
3	145.10	120.60	153.80
average	138.40	138.57	165.43

Table 4.2: Mechanical Properties of Quenched and Tempered API 5L X52

Data/Specimen	Before corrosion test	1 day	5 days
Diameter, D_1 (μm)			
1	42.23	54.50	55.85
2	43.17	53.50	51.41
3	46.29	53.51	49.95
average	43.90	53.84	52.40
Diameter, D_2 (μm)			
1	41.72	52.45	51.84
2	44.20	53.65	52.41
3	50.08	53.82	51.96
average	45.33	53.31	52.07
Hardness (HV)			
1	319.60	202.20	207.00
2	284.80	193.30	202.50
3	221.80	192.10	206.10
average	275.40	195.87	205.20

It can be seen from Table 4.1 that microhardness annealed API 5L X52 sample increases with increasing time of immersion with the highest hardness 165.43 HV after 5 days of immersion. Annealed sample have a microstructure of ferrite and pearlite (FP) two-phase and from microstructure captured using optical microscope in Figure 4.7(c) it is shown that pearlite phase (dark region) increases after 5 days of immersion. Increment of pearlite phase contains in annealed sample influence the hardness of the sample. Because of dual phase strengthening, annealed sample have a good balance on strength and ductility.[11] However, quenched and tempered API 5L X52 steel have better strength based on Table 4.2 compared to annealed API 5L X52 sample. Based on microstructure study on Figure 4.8, quenched and tempered API 5L X52 steel has martensitic microstructure. The microhardness values obtained by quenched and tempered sample increased by a factor close 3 of the microhardness obtained from annealed sample. This is because martensite is one of the most common strengthening phases in steels. Microhardness value of quenched and tempered sample decreases after 5 days of immersion test, and this is caused by the reduction of martensite phases referring to the microstructure picture in Figure 4.8. From this test analysis, we can claim that microstructure of material has an influence to the strength of API 5L X52 steels. API 5L X52 steels will have better strength with higher pearlite contain as well as martensitic composition.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

There are few parameters involved in determining the corrosion rate in CO_2 environment such as pH, oxygen content, temperature and flow rate. Besides that, it is also seen that microstructure plays a role in determining level of corrosion resistant for a particular material. In this research, API 5L X52 carbon steel has undergo two different heat treatment which is annealing and quenched and tempered. These heat treatment provides different microstructure to the materials where by pearlite/ferrite microstructures were seen in annealed API 5L X52 sample while martensite microstructures were seen in quenched and tempered API 5L X52 sample.

Based on the electrochemical testing result, it is shown that after longer time of immersion (5 days) quenched and tempered API 5L X52 steel has lower corrosion resistance in CO_2 environment (pH: 4, temperature: 50°C). This observation implied that $FeCO_3$ precipitated under this condition was not protective to the sample. However, it is also observed that quenched and tempered API 5L X52 steel has higher strength compared to annealed API 5L X52 steel even after 5 days of immersion. It is because quenched and tempered sample has the martensitic microstructure which is the most common strengthening phase in steel.

5.2 Recommendation

Based on previous journals, it is said that temperature plays an important role in determining corrosion rates of materials. Corrosion rate starts to decrease at 58°C and 65°C and the comparative decrease in corrosion rate was significant at 65°C, where a parabolic rate of corrosion was evident as opposed to the linear rate at lower temperatures. Thus, wider range of temperature can be used to study the effect of microstructure in CO_2 environment in the future work.

Besides, this study can also be continued using longer immersion duration. At higher periods of immersion, we can clearly see the influence of microstructure towards the material. We could also examine level of protection $FeCO_3$ can provide after longer expose time. By this study we probably will know what should be done in order to increase the corrosion resistance of material.

Other test such as energy dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD) should be included to analyze the elemental composition and chemical composition of the samples. The corrosion scales on the material can also be examined using x-ray diffraction technique which can help to determine the end product of the corrosion.

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