

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

THE EFFECT OF CRUDE OIL TO THE CORROSION PROPERTIES OF PETROLEUM PIPELINE

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

HAZWAN HASIF BIN HAMDAN B050910081 891108-01-5071

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Author's Name	: HAZWAN HASIF BIN HAMDAN
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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The members of the supervisory committee are as follow:

.....

(DR. MOHD. ASYADI 'AZAM BIN MOHD. ABID)



ABSTRACT

This project is about the pipeline corrosion caused by the composition of petroleum product in particular crude oil to the internal surface of carbon steel pipeline. Internal and external pipeline corrosion has been the main causes of pipeline failure in oil and gas industry not only in Malaysia but all over the world. However, the internal corrosion is preferred to be concerned in this project because it involved one of the corrosive media in crude oil such as sulfur content. The first objective in this project is to study the sulfur concentration in crude oil by using Fourier Transform Infrared (FTIR) spectroscopy and Atomic Absorption Spectroscopy (AAS). The corrosion rate, corrosion current (E_{corr}) and corrosion potential (I_{corr}) of API X65 grade carbon steel pipeline in different concentration of simulated H₂SO₄ solution were analyzed using Tafel extrapolation method. The corrosion properties on the sample were measured using Optical Microscope (OM), Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX).

The results showed that the corrosion rate of carbon steel increased significantly with the increase of H_2SO_4 concentration. The corrosion products formed on carbon steel surfaces were mainly composed of iron sulfate (FeSO₄), iron sulfide (FeS) and iron oxide (FeO). These findings is important to understand the crude oil corrosivity behavior and should be further investigated the other probability influence factor such as temperature.

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ABSTRAK

Projek ini adalah mengenai pengaratan saluran paip yang disebabkan oleh komposisi produk petroleum khususnya minyak mentah ke atas permukaan dalaman paip keluli karbon. Pengaratan luaran dan dalaman adalah punca utama kegagalan saluran paip dalam industri minyak dan gas bukan hanya di Malaysia sahaja tapi di seluruh dunia. Walau bagaimanapun, pengaratan dalaman adalah menjadi pilihan dalam projek ini kerana ia melibatkan salah satu media pengaratan dalam minyak mentah contohnya sulfur. Objektif pertama projek ini adalah untuk mempelajari kepekatan sulfur dalam minyak mentah dengan menggunakan Fourier Transform Infrared (FTIR) spektroskopi dan Spektroskopi Penyerapan Atom (AAS). Kadar pengaratan, potensi pengaratan (E_{corr}) dan arus pengaratan (I_{corr}) paip keluli karbon gred API X65 dalam simulasi larutan berasid H₂SO₄ dengan kepekatan berbeza telah dianalysis menggunakan kaedah ekstrapolasi Tafel. Ciri-ciri pengaratan pada sampel diuji dengan menggunakan Mikroskop Optik (OM), Mikroskop Imbasan Elektron (SEM) dan Sebaran Tenaga Sinar-X (EDX).

Hasil kajian menunjukkan bahawa kadar pengaratan keluli karbon meningkat dengan ketara dengan peningkatan kepekatan H₂SO₄. Produk-produk pengaratan terbentuk pada permukaan keluli karbon terutamanya terdiri daripada sulfat besi (FeSO₄), sulfida besi (FeS) dan oksida besi (FeO). Penemuan ini penting untuk memahami tingkah laku pengaratan oleh minyak mentah dan juga perlu disiasat faktor pengaruh lain contohnya suhu yang mungkin menyebabkan peningkatan mekanisma pengaratan.

DEDICATION

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

Α	-	Ampere
Ainitial	-	Exposed specimen area
Ag/AgCl	-	Silver/silver chloride
API	-	American Petroleum Institute
ASTM	-	America Society for testing and Materials
ATR	-	Attenuated Total Reflectance
AWD	-	Analytical Working Distance
BP	-	British Petroleum
СГ	-	Chloride
CPU	-	Control Processing Unit
CO ₂	-	Carbon Dioxide
CECER	-	Construction Engineering Research Laboratories
cm	-	Centimeter
Cu	-	Copper
С	-	Carbon
ССК	-	Corrosion Cell Kit
CE	-	Counter electrode
CR	-	Corrosion rate
daN	-	force display (Newton)
Et al	-	et alli (and others)
Ec	-	Current electrochemical parameter
Ecorr	-	Corrosion potential
EDS	-	Energy Dispersive X-ray Spectroscopy
EDX	-	Energy Dispersive X-ray Spectroscopy
EIA	-	Environmental Impact Assessment
Eq	-	Equation

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Ep	-	Editional photographers
Ew	-	Equivalent Weight
FKP	-	Fakulti Kejuruteraan Pembuatan
Fe	-	Iron
FeCO ₃	-	Iron carbonate
FTIR	-	Fourier Transform Infrared
GNP	-	Gross National Products
g/l	-	gram per liter
HNO ₃	-	Nitric acid
H ₂ S	-	Hydrogen Sulfide
H ₂ CO ₃	-	Carbonic acid
H ₂ SO ₄	-	Sulfuric acid
IR	-	Infrared
KM	-	Kilometer
К	-	Kelvin
Kw	-	Kilowatts
Kg	-	kilograms
KLCC	_	Kuala Lumpur City Centre
Ksi	-	Kilopound per square inch
L	-	Liter
LPC	-	Production Sharing Contracts
Μ	-	Metal
m/s	-	meter per second
max	-	Maximum
Мра	-	Mega Pascal
Mn	-	Manganese
mm	-	Millimeters
m/min		meter per minute
MHz	-	Megahertz
NaCl	-	Sodium Chloride
N	-	Nitrogen

NG	-	Not Good
0	-	Oxygen
OM	-	Optical Microscope
Р	-	Phosphorus
PETRONAS	-	Petroliam Nasional Berhad
PGU	-	Peninsular Gas utilization
pН	-	Potential of hydrogen
ppm	-	Parts per million
PS	-	Production Sharing
Psi	-	Pounds per Square Inch
PSL 1	-	Products Specification Level 1
PSM	-	Projek Sarjana Muda
Rp	-	Polarization resistance
S	-	Sulfur
SEM	-	Scanning Electron Microscope
Sdn. Bhd	-	Sendirian Berhad
SO4 ²⁻	-	Sulfate ion
U.S.	-	United States
UTeM	-	Universiti Teknikal Malaysia Melaka
v	-	volt
Wt %	-	Weight Percentages
XRD	-	X-ray diffraction
°C	-	Degree Celsius
%	-	Percentage
°F	-	Degrees Fahrenheit
е	-	Electron
Fe ²⁺	-	Iron (II) ion
Icorr	-	Corrosion current
μm	-	micron meter
ρ	-	Density

CHAPTER 1 INTRODUCTION

1.1 Background

Corrosion is the leading cause of failure of the pipelines in the world. Majority of the failures were due to internal corrosion which were more frequent than those due to external corrosion. Normally, large amount of crude oil usually needs effective transportation. So, pipeline is a great transportation to solve this problem. But any failure to ensure the safety and continuous operation on crude oil pipelines can be effected to economic, environment and life-safety implications.

The title of this project is the effect of crude oil to the corrosion properties of the petroleum pipeline. However, the focus of this project is to study compositions in the crude oil such as sulfur which have an effect on the corrosion properties of petroleum pipeline. This information is necessary in order to predict the corrosion mechanism where crude oil is flowing in the pipeline. This is because before this many studies of the corrosion in petroleum pipeline are mainly focused on the corrosion caused by gas rather than crude oil. So, this study is carried out to justify the corrosion caused by crude oil content itself. In addition, the analysis of crude oil composition that relates to the corrosion properties is very important in the corrosion behavior.

The understanding about crude oil composition and corrosion mechanism is a good method to predict the corrosion properties in the pipeline surface. So this study is



important to be carried out because the corrosion caused by crude oil is severally investigated rather than corrosion caused by gas in the pipeline.

1.2 Problem statement of the project

The effect of crude oil to pipelines may cause corrosion on the internal surface of pipeline. Corrosion issues in oil and gas industries have been costly, worldwide either directly or indirectly. According to Teevens et al. (2008), internal and external corrosion are leading causes of failures in petroleum pipeline operations. From these two major types of corrosion, internal corrosion which was costing the most than those due to external corrosion. The internal corrosion is preferred to be concerned in this project because the sulfur in the crude oil is one of the corrosive media that can attack the pipeline surface. Therefore, the corrosion on internal pipeline surface is usually caused by the gas and the most popular corrosion is carbon dioxide (CO_2) and hydrogen sulfide (H_2S) corrosion (Razmahwata, 2005). However, studies about crude oil composition especially sulfur content effect on pipeline corrosion behavior is less known. The sulfur concentration in the crude oil may affect the corrosion behavior of the pipeline. On the other hand, the corrosion rate is one of the important factor that must be take into consideration in order determine the how fast the mechanism of the corrosion.

1.3 Objectives

This project is therefore to study the corrosion on the internal surface of petroleum pipelines. The main aim of this project is to study the effect of the crude oil to the corrosion behavior of petroleum pipelines. Also, this project related to the corrosion properties in the internal surface of pipelines. Therefore to achieve the aim, the following objectives are in focus:

- a) To determine the sulfur concentration in crude oil by using FTIR spectroscopy and AAS.
- b) To conduct an electrochemical measurement to determine corrosion rate and morphological analysis using OM, SEM and EDX spectroscopy.
- c) To study the corrosion mechanism caused by sulfur in crude oil to the internal surface in petroleum pipeline.

1.4 Scope

This project focuses on the composition of the crude oil which affects the corrosion properties of petroleum pipeline. In this project, FTIR spectroscopy, electrochemical measurement, microscopy and phase analysis are main equipment to obtain the chemical composition and microstructural characterization of corrosion product. Besides that, Tafel extrapolation method will be used to determine how fast the corrosion rate mechanism between carbon steel specimen and simulated acidic of sulfate ion (SO₄²⁻). The sulfur content is selected in this project to determine its effect to the pipeline corrosivity by varying concentrations. After the results has shown, it will compare together to analyze the effect from lowest to highest sulfur concentrations. Though, the prediction and assumptions will be discussed between the supervisor, Dr. Mohd. Asyadi Azam Bin Mohd. Abid in order to ensure the hypothesis about the problems raised and come up with better solutions. However, this project not covers the corrosion protection method at the carbon steel pipeline.



CHAPTER 2 LITERATURE REVIEW

2.1 Oil and gas industry in Malaysia

2.1.1 History

Oil was first discovered in Malaysia in 1910 in Miri, Sarawak. Since then, two other ground breaking events has helped shape Malaysia's Oil & Gas Industry. First, Malaysia's Parliament passed the Petroleum Development Act and second, Petroliam Nasional Berhad or PETRONAS was established to manage the country's petroleum resources. It also provides support in terms of resource planning, distribution and marketing. PETRONAS was incorporated on 17 August 1974 under the Companies Act, 1965. It is wholly-owned by the Malaysian Government and is vested with the entire ownership and control of the petroleum resources in Malaysia through the Petroleum Development Act, 1974. Over the years, PETRONAS has grown to become a fully integrated oil and gas corporation and is ranked among the FORTUNE Global 500 largest corporations in the world (Halliburton, 2012).

Malaysia has approximately 615,100 square kilometers of acreages available for oil and gas exploration. Of these, 218,678 square kilometers or 36 % of the total acreages is currently covered by Production Sharing Contracts (LPC). Exploration drilling in Malaysia by the Production Sharing Contractors has resulted in the discovery of 163 oil fields and 216 gas fields. Many significant discoveries were made in shelfal shallow waters as well as in deep water environments. Increasingly, new discoveries have been

made through new play types such as fractured basements, pinnacle reefs, low CO_2 gas and turbidities. Application of new technologies has also greatly contributed to exploration successes, especially in deep water areas (Halliburton, 2012).

Malaysia's national oil company, Petroliam Nasional Berhad (PETRONAS), dominate upstream and downstream activities in the country's oil sector. PETRONAS is the only remaining wholly state-owned enterprise in Malaysia, and is the single-largest contributor of Government revenues. It holds exclusive ownership rights to all exploration and production projects in Malaysia, and all foreign and private companies must operate through Production Sharing Contracts (PSCs) with the national oil company. ExxonMobil (through its local subsidiary Esso Production Malaysia Inc.) is the largest oil company by production volume, and there are numerous other foreign companies operating in Malaysia via PSCs. PETRONAS is a major player in the retail and marketing sector, but faces competition from Shell, Chevron and BP (Razmahwata, 2005). Figure 2.1 shows the Malaysia's oil production and consumption from year 1991 until 2010.



Figure 2.1: Malaysia's oil production and consumption, 1991 - 2010 (Razmahwata, 2005).