



UNIVERSITI TEKNIKAL MALAYSIA MELAKA

**Microstructural Characterization of
Corrosion Product for Natural Gas
Pipelines in Malaysia**

Thesis submitted in accordance with the requirements of the Universiti Teknikal
Malaysia Melaka for the Bachelor of Manufacturing Engineering with Honours in
Engineering Materials

By

Mohd Khairu Azmi Bin Mohd Arshad

Faculty of Manufacturing Engineering

March 2008



KOLEJ UNIVERSITI TEKNIKAL KEBANGSAAN MALAYSIA

BORANG PENGESAHAN STATUS TESIS*

JUDUL: _____

SESI PENGAJIAN : _____

Saya _____
 (HURUF BESAR)

mengaku membenarkan tesis (PSM/Sarjana/Doktor Falsafah) ini disimpan di Perpustakaan Kolej Universiti Teknikal Kebangsaan Malaysia (KUTKM) dengan syarat-syarat kegunaan seperti berikut:

1. Tesis adalah hak milik Kolej Universiti Teknikal Kebangsaan Malaysia.
2. Perpustakaan Kolej Universiti Teknikal Kebangsaan Malaysia dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. **Sila tandakan (✓)

- | | |
|---------------------------------------|--|
| <input type="checkbox"/> SULIT | (Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia yang termaktub di dalam AKTA RAHSIA RASMI 1972) |
| <input type="checkbox"/> TERHAD | (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan) |
| <input type="checkbox"/> TIDAK TERHAD | |

Disahkan oleh:

 (TANDATANGAN PENULIS)

 (TANDATANGAN PENYELIA)

Alamat Tetap:

Cop Rasmi:

Tarikh: _____

Tarikh: _____

* Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan, atau disertasi bagi pengajian secara kerja kursus dan penyelidikan, atau Laporan Projek Sarjana Muda (PSM).

** Jika tesis ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai SULIT atau TERHAD.



APPENDIX E

KOLEJ UNIVERSITI TEKNIKAL KEBANGSAAN MALAYSIA

*Karung Berkunci 1200, Ayer Keroh, 75450 Melaka
Tel : 06-233 2421, Faks : 06 233 2414
Email : fkp@kutm.edu.my*

FAKULTI KEJURUTERAAN PEMBUATAN

Rujukan Kami (Our Ref) :
Rujukan Tuan (Your Ref):

17 Ogos 2005

Pustakawan
Perpustakawan Kolej Universiti Teknikal Kebangsaan Malaysia
KUTKM, Ayer Keroh
MELAKA.

Saudara,

PENGKELASAN TESIS SEBAGAI SULIT/TERHAD

- TESIS SARJANA MUDA KEJURUTERAAN PEMBUATAN (PROSES PEMBUATAN): ALI BIN KASIM
TAJUK: PRODUCT DEVELOPMENT USING QFD METHODOLOGY - CAR'S WIPER

Sukacita dimaklumkan bahawa tesis yang tersebut di atas bertajuk “*Product Development Using QFD Methodology - Car's Wiper*” mohon dikelaskan sebagai terhad untuk tempoh lima (5) tahun dari tarikh surat ini memandangkan ia mempunyai nilai dan potensi untuk dikomersialkan di masa hadapan.

Sekian dimaklumkan. Terima kasih.

“BERKHIDMAT UNTUK NEGARA KERANA ALLAH”

Yang benar,

WAN HASRULNIZZAM WAN MAHMOOD
*Pensyarah,
Fakulti Kejuruteraan Pembuatan
(Penyelia Bersama)*
06-2332122

s.k. - **Penyelia Utama:**
Abdul Rahim Samsudin

ABSTRACT

Malaysia is among the largest producer of gas industry which 12th largest gas reserves in the world. In 2004 Malaysia had 7,281 kilometers of pipelines and 5,047 kilometers for gas transporter. In this project, I study the characterization of corrosion product by using potentiostat and SEM as the core equipments. In this case, seawater at Terengganu (Kerteh, Marang) and Melaka (Klebang) can be uses as the solution and carbon steel pipelines API 5L X65 grade as the sample product. This product sample will be cut by using horizontal bandsaw machine follow dimension required. The next step is to perform continuous study on the sample subject by using EDX machine to confirm the composition of the sample subject.

Experiment between the sample product and seawater will proceed by immerse sample product into the seawater solution, than the observation of polarization curve and corrosion rate will be analyze. The last step for this project, the corrosion of the sample product would be analyzed with SEM and the microstructure, types of corrosion chemical can be identified.

ABSTRAK

Malaysia adalah diantara pengeluar terbesar industri gas dimana mempunyai simpanan gas ke-12 terbesar didunia. Pada tahun 2004, Malaysia telah mempunyai 7,281 kilometer saluran paip dan 5,047 kilometer adalah untuk penyaluran gas. Dalam projek kajian ini, saya mengkaji krateria pengaratan pada produk dengan menggunakan potentiostat dan SEM sebagai peralatan utama. Dalam kes ini, air laut di Negeri Terengganu (Kerteh, Marang) dan Melaka (Klebang) akan digunakan sebagai larutan dan besi karbon gred API 5L X65 sebagai produk kajian. Produk kajian akan dipotong dengan menggunakan mesin gergaji jenis melintang mengikut ukuran yang diperlukan. Langkah seterusnya adalah untuk menjalankan kajian berterusan keatas sampel subjek dengan menggunakan EDX bagi mengesahkan komposisi bahan subjek.

Kajian diantara sampel produk dan air laut akan diteruskan dengan merendam sampel produk ke dalam larutan air laut, kemudian pemerhatian pada lenguk pertambahan dan kadar pengaratan akan dianalisis. Langkah terakhir untuk kajian ini, pengaratan pada sampel produk akan dianalisis dengan menggunakan SEM dan struktur mikro, jenis bahan kimia pada karat akan diketahui.

DEDICATION

“Special to my parents, my family and all my friends that helps me in finishing this research”.

ACKNOWLEDGEMENTS

In the Name of Allah, the Most Gracious, the Most Merciful.

Alhamdullilah, be thanks to Allah S.W.T because of blessing I can finish this research. I wish to acknowledge the contribution of my parents for their continued support and understanding during the research of microstructural characterization of corrosion product for natural gas pipelines in Malaysia. Special thanks should also go to my supervisor Mohd Asyadi' Azam Bin Mohd Abid and my adviser Mr. Ahmad Zaki bin Abas and staffs at Petronas Research Sdn. Bhd. (PRSB) for their help me in finishing this research. Not to forget all lecturers, technicians, friends in UTeM for their help and full cooperation to finishing my research.

Lastly, I'm happy to present the following cumulative list of all those individuals who, in one way or another, made various contributions to this research.

APPROVAL

This thesis submitted to the senate of UTeM and has been accepted as partial
fulfillment of the requirements for the degree of Bachelor of Manufacturing
Engineering (Material Engineering)

The members of the supervisory committee are follow:

.....
Main Supervisor
(Mr. Mohd Asyadi' Azam Bin Mohd Abid)
28th March 2008

DECLARATION

I hereby, declared this thesis entitled “Microstructural Characterization of Corrosion Product for Natural Gas Pipeline in Malaysia” is the results of my own research except as cited in references.

Signature :
Author's Name : Mohd Khairu Azmi Bin Mohd Arshad
Date : 28th Mac 2008

TABLE OF CONTENTS

ABSTRACT	i
ABSTRAK	ii
DEDICATION.....	iii
ACKNOWLEDGEMENT.....	iv
APPROVAL.....	v
DECLARATION	vi
TABLE OF CONTENT	vii
LIST OF FIGURE.....	x
LIST OF TABLES.....	xiii
SIGN AND SYMBOLS.....	xiv
1. INTRODUCTION.....	1
1.1 Background.....	1
1.2 Problem Statements.....	3
1.2.1 Basic concepts of corrosion.....	4
1.2.2 Economic Consideration.....	4
1.3 Objectives.....	5
1.4 Scope.....	5
2. LITERATURES REVIEW.....	6
2.1 Natural Gas in Malaysia.....	6
2.2 Definition of Corrosion.....	8
2.3 Electrochemical Natural of Corrosion.....	8
2.3.1 Reaction with Gases.....	8
2.3.2 Reaction with Liquids.....	10
2.4 Types of Corrosion.....	14
2.4.1 Uniform or General Corrosion.....	14

2.4.2	Galvanic or Two-Metal Corrosion.....	15
2.4.3	Crevice Corrosion.....	16
2.4.4	Pitting Corrosion.....	17
2.4.5	Intergranular Corrosion.....	19
2.4.6	Selective Leaching.....	21
2.4.7	Erosion Corrosion.....	22
2.4.8	Stress Corrosion.....	23
2.5	Polarization.....	25
2.6	Passivity.....	27
3.	METHODOLOGY.....	28
3.1	Selection of Material.....	30
3.2	Material Cutting	32
3.2.1	Operation Procedure.....	34
3.3	Sample Preparation.....	35
3.3.1	Grinding.....	35
3.3.2	Operation Procedure.....	37
3.3.3	Polishing.....	38
3.3.4	Operation Procedure.....	39
3.3.5	Aqueous Solution.....	40
3.3.6	Measuring pH with a pH Meter.....	41
3.4	Corrosion Testing.....	44
3.4.1	Potentiostat.....	44
3.4.2	Operation Procedure.....	47
3.5	Metallographic Analysis.....	48
3.5.1	Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy	48
3.5.2	Operation Procedure.....	52
3.5.3	Expected Result.....	53

4. RESULT AND DISCUSSION	54
4.1 The pH Result	54
4.2 Immersed Data	59
4.3 Scanning Electron microscope (SEM)	62
4.4 Energy Dispersive X-ray Spectroscopy	68
4.5 Tafel Graph	74
4.6 Anodic Polarization Curve	78
5. CONCLUSION AND RECOMMENDATION	82
REFERENCES.....	84
APPENDIX	
A	CLASSIFICATION OR CARBON AND LOW CARBON STEEL
B	STANDARD EMF SERIES OF METAL
C	MALAYSIA MAP
D	PENINSULAR GAS UTILISATION PROJECT IN MALAYSIA
E	NATURAL GAS DISTRIBUTION SYSTEM
F	GAS MALAYSIA INVESTING RM220MIL ON PIPELINE
G	GAS MALAYSIA EXPANDS CAPACITY
H	GALVANIC SERIES OF SOME COMERCIAL METAL AND ALLOY IN SEAWATER
I	PERODIC TABLE OF THE ELEMENTS
J	EFFECT OF ALLOYING ON PITTING RESISTANCE OF STEEL ALLOY
K	THE GALVANIC SERIES IN SEAWATER

LIST OF FIGURES

2.1	Natural gas supply schematic	7
2.2	Electrochemical reaction occurring during corrosion of Iron metal in air condition	9
2.3	The electrochemical reaction associated with the corrosion of zinc in an acid solution	12
2.4	The stainless steel screws show below corroded in the moist atmosphere of a pleasure boat hull.	16
2.5	Diagrammatically pits shapes of pitting corrosion	18
2.6	Weld decay in a stainless steel. The regions along which the grooves have formed were sensitized as the weld cooled	19
2.7	Plug-type dezincification	21
2.8	Impingement failure of an elbow that was part of a steam condensate line	22
2.9	(a) Intergranular high-pH stress-corrosion crack in line pipe steel. (b) Transgranular near-neutral-pH stress-corrosion crack	24
2.10	Polarization curve of X 60 low carbon micro allied steel in NS ₄ test solution of soil environment at 30 °C.	26
3.1	Methodology flowchart	29
3.2	Dimension of samples under potentiostat and SEM machine	32
3.3	Dimension of samples under EDX	32
3.4	Horizontal bandsaw machine model HB 320	33
3.5	Grinding and polishing machine	36
3.6	A standard pH meter uses a probe to test the acidity of sample	42
3.7	The pH meter	43

3.8	Equipment of potential Reference 600	44
3.9	The equipment setup for potentiostat experiment	46
3.10	Nomenclature of SEM	49
3.11	Scanning Electron Microscope (SEM) model Evo 50 series	50
3.12	Equipment setup for SEM and EDX	50
4.1	The pH seawater at Kerteh, Terengganu	55
4.2	The pH seawater at Marang, Terengganu	56
4.3	The pH seawater at Klebang, Melaka	56
4.4	The pH seawater at Kerteh, Terengganu after experiment	57
4.5	The pH seawater at Marang, Terengganu after experiment	58
4.6	The pH seawater at Klebang, Melaka after experiment	58
4.7	The first day immersing carbon steel in seawater	59
4.8	Corrosion product on carbon steel later than 7 days immersed in seawater	59
4.9	Magnification 5 X 0.25 of carbon steel by using Laser Microscope	60
4.10	The pitting corrosion (in circle) and general corrosion on carbon steel after potentiostat experimental	60
4.11	The 1000X magnification at Kerteh, Terengganu	62
4.12	The 2000X magnification at Kerteh, Terengganu	63
4.13	The 3000X magnification at Kerteh, Terengganu	63
4.14	The 1000X magnification at Marang, Terengganu	64
4.15	The 2000X magnification at Marang, Terengganu	65
4.16	The 3000X magnification at Marang, Terengganu	65
4.17	The 1000X magnification at Klebang, Melaka	66
4.18	The 2000X magnification at Klebang, Melaka	66
4.19	The 3000X magnification at Klebang, Melaka	67
4.20	The spectroscopy data of carbon steel specimen	68
4.21	The spectroscopy data of corrosion product at Kerteh, Terengganu	70
4.22	The spectroscopy data of corrosion product at Marang, Terengganu	71

4.23	The spectroscopy data of corrosion product at Klebang, Melaka	73
4.24	Tafel graph at Kerteh, Terengganu	74
4.25	Tafel graph at Marang, Terengganu	75
4.26	Tafel graph at Klebang, Melaka	77
4.27	Anodic Polarization Curve at Kerteh, Terengganu	79
4.28	Anodic Polarization Curve at Marang, Terengganu	79
4.29	Anodic Polarization Curve at Klebang, Melaka	80

LIST OF TABLES

2.1	Natural gas composition	6
3.1	Products specification level 1	30
3.2	Products specification level 2	31
3.3	Yield to tensile ratio and elongation API 5L X65	31
3.4	The standard of chemicals analysis API 5L X65	31
3.5	Specification of horizontal bandsaw machine	33
3.6	Specification of grinding machine	36
3.7	Standardization of seawater	40
3.8	Many food and household solution are strongly acidic or basic	41
3.9	Specification of pH meter Accumet AB 15	43
3.10	Specification of potentiostat reference 600	45
3.11	Specification of scanning electron microscopic	51
4.1	The elements analyzed of carbon steel specimen	69
4.2	The elements analyzed of corrosion product at Kerteh, Terengganu	70
4.3	The elements analyzed of corrosion product at Marang, Terengganu	71
4.4	The elements analyzed of corrosion product at Klebang, Melaka	73
4.5	The corrosion rate measurement at Kerteh, Terengganu	74
4.6	The corrosion rate measurement at Marang, Terengganu	76
4.7	The corrosion rate measurement at Klebang, Melaka	77

SIGN AND SYMBOLS

API	-	American Petroleum Institute
ASTM	-	America Society for testing and Materials
A	-	Ampere
Ag/AgCl	-	Silver/silver chloride
AWD	-	Analytical Working Distance
BSD	-	Berkeley Software Distribution
Cl ⁻	-	Chloride
C ₃ H ₈	-	Propane
C ₄ H ₁₀	-	Butane
CH ₄	-	Methane
C ₂ H ₆	-	Ethane
CO ₂	-	Carbon Dioxide
CECER	-	Construction Engineering Research Laboratories
cm	-	Centimeter
Cu	-	Copper
C	-	Carbon
CE	-	Counter electrode
daN	-	force display (Newton)
E	-	Electron
Et al	-	et alli (and others)
Ec	-	Current electrochemical parameter
EDX	-	Energy Dispersive X-ray Spectroscopy
Eq	-	Equation
Ep	-	Editorial photographers
EW	-	Equivalent Weight
FKM	-	Fakulti Kejuruteraan Mekanikal

FKP	-	Fakulti Kejuruteraan Pembuatan
Fe	-	Iron
GPP	-	Gas Processing Plants
g/l	-	gram per liter
H ₂ S	-	Hydrogen Sulphide
He	-	Helium
Hz	-	Hertz
HT	-	High tension generator
IAPSO	-	International Association for the Physical Sciences of the Ocean
KM	-	Kilometer
K	-	Kelvin
Kw	-	Kilowatts
Kg	-	kilograms
L	-	Liter
M	-	Metal
m/s	-	meter per second
max	-	Maximum
Mpa	-	Mega Pascal
Mn	-	Manganese
mm	-	Millimeters
m/min	-	meter per minute
MHz	-	Megahertz
NaCl	-	Sodium Chloride
N ₂	-	Nitrogen
NS ₄	-	Synthetic electrolytic solution
NG	-	Not Good
N	-	Newton
PRSB	-	Petronas Research Sdn. Bhd
PGU	-	Peninsular Gas utilization
pH	-	Potential of hydrogen

PSL 1	-	Products Specification Level 1
Psi	-	Pounds Per Square Inch
P	-	Phosphorus
Rpm	-	Rotation per minute
Rp	-	Polarization resistance
RE	-	Reference electrode
SEM	-	Scanning Electron Microscope
Sdn. Bhd	-	Sendirian Berhad
SCC	-	Stress corrosion cracking
S	-	Sulfur
SAXS	-	Small Angle X-ray Scattering
Tcf	-	Trillion cubic feet
UTeM	-	Universiti Teknikal Malaysia Melaka
V	-	volt
Wt %	-	Weight Percentages
WE	-	Working Electrode
XRD	-	X-ray diffraction
XVGA	-	Extended Video Graphes Array
XVP	-	X-View Package
Zn	-	Zinc
°C	-	Degree Celsius
%	-	Percentage
°F	-	Degrees Fahrenheit
µm	-	micron meter
pA	-	picoAmpere (10^{-12})
aA	-	attoAmpere (10^{-18})
ρ	-	Density
nm	-	nanometer

CHAPTER 1

INTODUCTION

1.1 Background

Malaysia is placed in Southeast Asia with alienated by about 530 kilometers of the South China Sea. Malaysian have two regions are Peninsular Malaysia and East Malaysia or also known as island of Borneo which collected of two states Sabah and Sarawak (*library of congress, 2006*). Based on library of congress information, the coastline in Peninsular Malaysia is 2,068 kilometers and for East Malaysia is 2,608 kilometers. Malaysian annual average temperatures between 23 °C to 34 °C and the economics generally from natural resources such as tin, bauxite, copper, gold, iron ore, timber, petroleum and natural gas. In 2004, Malaysia had 7,281 kilometers of pipelines: 5,047 kilometers for gas, 1,841 kilometers for oil, 279 kilometers for condensate, and 114 kilometers for refined products (*library of congress, 2006*).

Natural gas is one type of gas fuel and it's very important to global and Malaysian economy. Normally, large amount of natural gas from the main source usually need effective transportation. So, pipeline is great method to solve this problem. But, any failure to ensure the safe and continuous operation on natural gas pipelines can be effects to economic, environmental and life-safety implications. The observations and

consideration of natural gas pipeline at initial stages during fabrication, installation, selection of material and operation are good criteria to avoid bigger defects on pipelines in further. However, the observations and consideration on natural gas pipeline it is not practical to prevent all defects from occurring because not all defects are destructive to pipeline integrity; it is essential to be able to differentiate defects that can be tolerated from those that cannot. The understandings about characterization and corrosion behavior in natural gas pipeline that good method can be avoid problems in natural gas pipeline.

So, this project is very importance to known the phenomena of initial stage of corrosion behavior for natural gas pipeline in artificial groundwater condition with specify to observe the microstructural of natural gas pipeline. Normally, natural gas pipeline used carbon steel to transports natural gas at main source. This pipeline not just received damaged by earth rust fluctuation and corrosion, but also suffered from the corrosion caused by anions that were dissolved in sea and groundwater. Based on this situation, the applications of an anodic polarization curve measurement with potentiostat and observation analysis through Scanning Electron Microscope (SEM), the microstructure and corrosion rate can be look at in a laboratory experiments. By using this system, formation and dissolution process of corrosion product in artificial groundwater could be examined.

To complete my study in microstructural characterization of corrosion product for natural gas pipeline in Malaysia, the exact samples of API 5L X65 pipe grade was taken from PETRONAS RESEARCH SDN.BHD (PRSB) as main sample laboratory test to realize objective in this study.

1.2 Problem statement

Natural gas transport reliability depends on environment factors and exact choice of pipeline material. The life of a potentially corrosive pipeline structure depends on the choice of material or a method of surface treatment which will avoid damage by corrosion. Carbon steel pipeline usually used in gas transmission is manufactured according to the specified chemical composition and mechanical parameters. It's commonly manufactured to the API 5L specification grade X65 and others grades. All of API 5L pipeline grades is already set of mechanical parameters such as tensile strength, yield strength, elongation and toughness. So, carbon steel pipe is very suitable use in natural gas transportation applications because of its low cost, high strength and the ease of field makeup by welding.

However, the presence of chemical elements in seawater similar to sodium ion (Na^+), chloride ion (Cl^-), sulfate (SO_4^{2-}), magnesium ion (Mg^{2+}), calcium (Ca^{2+}) and potassium (K^+) on carbon steel can cause several corrosion problems in oil and gas pipeline transmissions. So, this project is importance in order to get knowledge of how seawater can be effect specified to microstructure and corrosion behavior on carbon steel pipeline API 5L X65 grade toward to seawater.

1.2.1 Basic Concept of Corrosion

Corrosion is a common problems around us where it involves many factors how do the corrosion behavior happens in engineering field. In order to perform corrosion behavior in the general practices and principle of corrosion, *Mars G. Fontana, (1986)* mentions that, the chemical, metallurgical, physical, and mechanical properties of materials; corrosion testing; the nature of corrosion environments; the availability and fabrication of materials; computer; and design (*p. 3*) must be considered before an engineer produce their product, design the materials, build the building and others to prevent causes producing corrosion layer in engineering applications.

1.2.2 Economic Consideration

Cost is an important aspect in engineering study and corrosion is a main problem in gas field especially in transporting gas by using pipeline. In this case, *Thompson (2001)* has written down in his journal that, a “find it and fix it” strategy utilizing in-line inspection at the expense of corrosion prevention may save money in the short term, but will greatly increase capital expenditures for pipeline replacement and major rehabilitation in the long-term. So, the best strategy in the practices corrosion prevention is to give more concerned for before and after constructions of pipelines transmission in every aspect can cause corrosion on the product using. Hence, the costing to repairing and replacement of the damaged product caused by corrosion is capable of avoided.

1.3 Objectives

The objectives of this study were:

- 1.2.1 To develop a test technology for the in-situ analyses of corrosion under wet condition, including the characterization of the electrolyte chemistry and the redox reactions occurring in the corrosion product.
- 1.2.2 To observe the microstructural characterization of corrosion product by using SEM and EDX equipments.
- 1.2.3 To study polarization curve measurement for API 5L X65 pipeline grade by using potentiostat.
- 1.2.4 To study the effect of Malaysia countries seawater specified at Terengganu (Kerteh, Marang) and Melaka (Klebang) on API 5L X65 pipelines grade.

1.4 Scope

This project focus on the corrosion behavior for pipeline steel API 5L X65 grade in artificial groundwater especially under wet condition and electrolyte chemistry specified for seawater at Terengganu and Melaka under 25 °C average temperature in Malaysia. In this study, the utilizing of equipment like SEM (Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray Spectroscopy) machine as main software to see the external corrosion microstructural characterization and checking types of corrosion product elements on carbon steel samples is important. Otherwise, the potentiostat machine is used to search out the corrosion rate, anodic polarization curve and Tafel graph between carbon steel API 5L X65 pipeline grade and seawater. Meanwhile, this study not covers the coating selection, mechanical testing and seawaters as the matter during experimentation.