

**MODELLING HYDROGEN PERMEATION IN A HYDROGEN EFFUSION
PROBE FOR MONITORING CORROSION OF CARBON STEELS**

Pongpat Santiwiparat

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole
2015


I28368526


Thesis Title: Modelling Hydrogen Permeation in a Hydrogen Effusion
Probe for Monitoring Corrosion of Carbon Steels
By: Pongpat Santiwiparat
Program: Petrochemical Technology
Thesis Advisors: Assoc. Prof. Thirasak Rirksomboon
Dr. Frank R. Steward
Dr. Derek H. Lister
Dr. William G. Cook


Accepted by The Petroleum and Petrochemical College, Chulalongkorn
University, in partial fulfillment of the requirements for the Degree of Master of
Science.



..... College Dean
(Asst. Prof. Pomthong Malakul)

Thesis Committee:

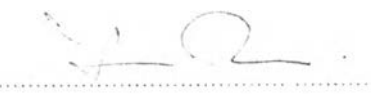

.....
(Assoc. Prof. Thirasak Rirksomboon)


.....
(Dr. Frank R. Steward)


.....
(Dr. Derek H. Lister)


.....
(Dr. William G. Cook)


.....
(Assoc. Prof. Pramoch Rangsunvigit)


.....
(Dr. Boonrod Sajjakulnukit)

ABSTRACT

5671028063: Petrochemical Technology Program

Pongpat Santiwiparat: Modelling Hydrogen Permeation in a Hydrogen Effusion Probe for Monitoring Corrosion of Carbon Steels.

Thesis Advisors: Assoc. Prof. Thirasak Rirksomboon, Dr. Frank R. Steward, Dr. Derek H. Lister, and Dr. William G. Cook 81 pp.

Keywords: Corrosion monitoring/ Hydrogen permeation/ Mathematical model/ Carbon steel/ Stainless steel

The Hydrogen Effusion Probe (HEP) is being developed for on-line corrosion monitoring of carbon steel by measuring the rate of hydrogen produced and transported through the metal which corresponds to the corrosion rate as the result of corrosion of the metal. Hydrogen accumulation inside carbon steel and stainless steel devices shaped like cylindrical cups attached to a pipe containing 5 psig hydrogen gas at 300 °C was modelled with MATLAB software. In this study, hydrogen transfer around the bottom of the cups (edge effect) and diffusion through the cup walls (material effect) were accounted in the development of the model of hydrogen accumulation inside the cup. The hydrogen pressure inside stainless steel and carbon steel cups were predicted to design cups for specific cases. The effect of size, wall thickness, and different materials on the hydrogen accumulation inside the cups was investigated to aid future designs of HEP. The results indicated that the trend of the variation of hydrogen pressure in the cups with time was similar for the two materials, although the magnitudes were substantially different. The time to steady state (the plateau pressure) depends on the material and geometry of the cup. The attainment of plateau pressure in carbon steel cups was faster than in stainless steel cups and the plateau pressure substantially lower. A thinner wall thickness yielded a lower hydrogen pressure at steady state. The achievement of the plateau pressure inside the carbon steel cup was faster as the thickness decreases which is in contrast to stainless steel cup, and the time to reach steady state in the larger cup was shorter and the plateau pressure was higher than the smaller cup.

บทคัดย่อ

พงษ์พัฒน์ สันติวิภากรณ์ : การจำลองการแพร่ผ่านของก๊าซไฮโดรเจนในเครื่องมือวัดการแพร่ผ่านของไฮโดรเจนสำหรับตรวจวัดการกัดกร่อนของเหล็กกล้า (Modelling Hydrogen Permeation in a Hydrogen Effusion Probe for Monitoring Corrosion of Carbon Steels) วิทยานิพนธ์ปริญญา: รัช.ดร. ชีรศักดิ์ ฤกษ์สมบุญ, ศ.ดร. แฟรงก์ อาร์ สจ๊วต, ศ.ดร. ดีเรก เอช ลิสเตอร์ และ ศ.ดร. วิลเลียม จี กุก 81 หน้า

เครื่องมือวัดการแพร่ผ่านของไฮโดรเจน (The Hydrogen Effusion Probe, HEP) ได้ถูกพัฒนาขึ้นเพื่อใช้ตรวจวัดการกัดกร่อนของโลหะโดยอาศัยการวัดปริมาณไฮโดรเจนที่เกิดขึ้นและเคลื่อนที่แพร่ผ่านโลหะซึ่งจะสัมพันธ์กับอัตราการกัดกร่อนของโลหะอันเป็นผลมาจากการกัดกร่อนของโลหะ การสะสมของก๊าซไฮโดรเจนในอุปกรณ์รูปร่างคล้ายถ้วยทรงกระบอกที่ทำจากเหล็กกล้าสแตนเลสและเหล็กกล้าคาร์บอนที่ถูกติดตั้งลงบนท่อซึ่งมีก๊าซไฮโดรเจนไหลอยู่ภายในที่ความดันคง 5 ปอนด์ต่อตารางนิ้วในอุณหภูมิ 300 องศาเซลเซียสถูกจำลองด้วยแมทแลบซอฟต์แวร์ (MATLAB) ในงานวิจัยนี้ผลของไฮโดรเจนแพร่ออกรอบก้นของถ้วย (edge effect) และผลของไฮโดรเจนแพร่ผ่านผนังของถ้วย (material effect) ถูกนำมารวมและพิจารณาเพื่อพัฒนาการจำลองการสะสมของก๊าซไฮโดรเจนในถ้วย โดยมีวัตถุประสงค์เพื่อจำลองความดันก๊าซไฮโดรเจนในถ้วยเหล็กกล้าสแตนเลสและเหล็กกล้าคาร์บอนสำหรับใช้เป็นข้อมูลในการออกแบบถ้วยสำหรับกรณีเฉพาะและศึกษาผลจากขนาด ความหนาของผนัง และ วัสดุที่ใช้ทำถ้วยต่อการสะสมของก๊าซไฮโดรเจนในถ้วยเพื่อการออกแบบของ HEP ในอนาคตเช่นกัน จากผลการทดลองพบว่าแนวโน้มการเปลี่ยนแปลงของก๊าซไฮโดรเจนในถ้วยต่อเวลาที่มีความคล้ายคลึงกันในวัสดุทั้ง 2 ชนิดแม้ว่าจะมีปริมาณต่างกันก็ตาม เวลาที่ใช้ในการเข้าสู่ภาวะคงตัวและความดันที่ภาวะคงตัว (plateau pressure) ขึ้นกับวัสดุและรูปร่างของถ้วย การเข้าสู่ความดันที่ภาวะคงตัวในถ้วยเหล็กกล้าคาร์บอนเร็วกว่าในเหล็กกล้าสแตนเลสแต่มีความดันที่ภาวะคงตัวต่ำกว่า ถ้วยที่มีผนังบางกว่าจะมีความดันไฮโดรเจนที่สภาวะคงตัวต่ำกว่าถ้วยที่หนา ถ้วยเหล็กกล้าคาร์บอนจะใช้เวลาเข้าสู่ความดันที่ภาวะคงตัวน้อยลงถ้าถ้วยมีความหนาลดลง ซึ่งตรงกันข้ามกับถ้วยเหล็กกล้าสแตนเลสและเวลาในการเข้าสู่ภาวะสมดุลในถ้วยที่ใหญ่กว่าจะสั้นกว่ารวมทั้งมีความดันที่สภาวะคงตัวที่สูงกว่าถ้วยที่มีขนาดเล็ก

ACKNOWLEDGEMENTS

I am grateful for the partial scholarship and partial funding of the thesis work provided by the Petroleum and Petrochemical College.

The completion of this research has been possible because of the assistance, advice, and support from many people in Thailand and Canada. The researcher would like to acknowledge the assistance and support of who have cooperated in this research.

First of all. I would like to express my deepest gratitude and thanks to my advisors, Dr. Frank R. Steward and Assoc. Prof. Thirasak Ricksomboon. for giving me an opportunity to work on my research at University of New Brunswick, Canada. I got a lot of invaluable experience here. I would like to thank them for their knowledge, teaching, suggestion, and other helps as well.

Next, I would like to extend my sincerely thanks to Dr. Frank R. Steward, Dr. Derek H. Lister, and Dr. William G. Cook. Without their intensive advice, priceless guidance, and persistent help, this research will not have been possible and completed.

Subsequently, I am grateful to Centre for Nuclear Energy Research (CNER) for providing the laboratory facilities, support, and expertise.

Without this following person, I could not have performed my experiment, Naravit Leaukosol, who helped me set up my experiment, gave me a lot of useful information and suggestion about my experiment.

In addition, I would like to thank my friends in Thailand and Canada for always standing beside me, making me feel happy, reminding me many important things about schedule, helping me, and also cheering me up.

Last but not the least, the most important people is my family. I thank my beloved parents for their unending love, blessing, encouragement, and unwavering faith on me.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
Abbreviations	xiv
List of Symbols	xv
CHAPTER	
I INTRODUCTION	1
II LITERATURE REVIEW	3
2.1 Corrosion of Steel	3
2.1.1 Definition of Corrosion	3
2.1.2 Flow-accelerated Corrosion (FAC)	3
2.1.3 FAC in the Feeder Pipes in CANDU Reactors	4
2.2 Mechanism of Oxide Formation and Hydrogen Evolution	5
2.2.1 Magnetite Formation	5
2.2.2 Hydrogen Evolution	6
2.2.3 Hydrogen Emission During Steel Corrosion	8
2.3 Fundamental Law of Diffusion	9
2.3.1 Fick's Law of Diffusion	10
2.3.2 Arrhenius Equation	13
2.3.3 Sievert's Law	15
2.3.4 Graham's Law of Effusion	16

CHAPTER	PAGE
2.4 Transport of Hydrogen Through Steel	16
2.4.1 Mechanism of Hydrogen Transport Through Steel	17
2.4.2 Hydrogen Diffusion in Stainless Steel	18
2.4.3 Hydrogen Diffusion in Carbon Steel	20
2.5 Hydrogen Effusion Probe (HEP)	23
2.5.1 Hydrogen Probe Principle	24
2.5.2 Assumptions for Thinning Rate Measurement by the HEP	26
III EXPERIMENTAL	28
3.1 Materials	28
3.1.1 Equipment	28
3.1.2 Software	28
3.2 Experimental Procedures	28
3.2.1 Mathematical Models	28
3.2.2 Model Derivation and Model Parameters	30
IV RESULTS AND DISCUSSION	33
4.1 Modelling Hydrogen Pressure Build-Up in the Cups	33
4.1.1 Effect of Cup Materials	35
4.1.2 Effect of Wall Thickness of Cups	38
4.1.3 Effect of Size of Cups	40
4.2 Redesign the Cup	44
4.2.1 Effect of Cup Materials	48
4.2.2 Effect of Wall Thickness of Cups	50
4.2.3 Effect of Size of Cups	53
4.3 Response Time	55
4.4 Comparison Modelling Results with the Experimental Results	60

CHAPTER	PAGE
V CONCLUSIONS AND RECOMMENDATIONS	62
5.1 Conclusions	62
5.2 Recommendations	62
REFERENCES	64
APPENDICES	69
Appendix A Parameters of Hydrogen Accumulation Loop	69
Appendix B Calculations of Surface Area of Pipe under the Cup, Cup Volume, Cup Perimeter, Surface Area of Cup inside the Cup, and Mean Temperature	71
Appendix C Parameters of Hydrogen Accumulation Loop after Redesign of the Cups	78
CURRICULUM VITAE	80

LIST OF TABLES

TABLE		PAGE
2.1	Elemental content of carbon steel A106-B (mass fraction in %: balance Fe)	23
4.1	The materials and dimensions of each cup	33
4.2	Summarized modelling parameters	34
4.3	The new materials and dimensions of each redesigned cup	45
4.4	Summarized new modelling parameters of the cup that were redesigned	46
A1	Volume of accumulation loop	69
A2	Parameters of cups	70
C1	Volume of accumulation loop when the cups were redesigned	78
C2	Parameters of new cups	79

LIST OF FIGURES

FIGURE	PAGE
2.1 Mechanism of FAC.	4
2.2 The change in hydrogen pressure inside the carbon steel tube with time after the removal of the oxide film formed on the outside surface (Initial hydrogen pressure: 100 psig at 25 °C. Set point temperature: 310 °C. Tube temperature: 306 °C).	5
2.3 Schematic of double oxide layer formed on carbon steel.	6
2.4 Schematic view of the formation mechanism of the magnetite film on the steel surface in high temperature water.	8
2.5 Schematic representation of (a) vacancy diffusion and (b) interstitial diffusion.	10
2.6 Plot of the logarithm of the diffusion coefficient versus the reciprocal of absolute temperature for several materials.	14
2.7 Seven steps of hydrogen permeation.	17
2.8 Hydrogen permeability constants in various metals as a function of temperature.	20
2.9 Hydrogen permeability in 1045 steel as a function of temperature.	22
2.10 Schematic of the hydrogen effusion probe components.	24
3.1 Schematic diagram of gas permeation loop.	29
4.1 Model of hydrogen pressure accumulation inside all cups.	35
4.2 Model of hydrogen pressure accumulation inside carbon steel cups.	35
4.3 Model of hydrogen pressure accumulation inside stainless steel cups.	36
4.4 Model of hydrogen pressure accumulation inside carbon steel cups in 50 hours.	36

FIGURE	PAGE
4.5 Model of hydrogen pressure accumulation inside carbon steel cup 1 and 2.	38
4.6 Model of hydrogen pressure accumulation inside carbon steel cup 3 and 4.	39
4.7 Model of hydrogen pressure accumulation inside stainless steel cup 5 and 6.	39
4.8 Model of hydrogen pressure accumulation inside stainless steel cup 7 and 8.	40
4.9 Model of hydrogen pressure accumulation inside carbon steel cup 1 and 3.	41
4.10 Model of hydrogen pressure accumulation inside carbon steel cup 2 and 4.	41
4.11 Model of hydrogen pressure accumulation inside stainless steel cup 5 and 7.	42
4.12 Model of hydrogen pressure accumulation inside stainless steel cup 6 and 8.	42
4.13 Model of hydrogen pressure accumulation inside all redesigned cups.	47
4.14 Model of hydrogen pressure accumulation inside redesigned carbon steel cups in 1500 hours.	47
4.15 Model of hydrogen pressure accumulation inside redesigned stainless steel cups.	48
4.16 Model of hydrogen pressure accumulation inside carbon steel cup 1 and stainless steel cup 6.	49
4.17 Model of hydrogen pressure accumulation inside carbon steel cup 3 and stainless steel cup 8.	49
4.18 Model of hydrogen pressure accumulation inside carbon steel cup 1 and 2.	51

FIGURE	PAGE
4.19 Model of hydrogen pressure accumulation inside carbon steel cup 3 and 4.	51
4.20 Model of hydrogen pressure accumulation inside stainless steel cup 5 and 6.	52
4.21 Model of hydrogen pressure accumulation inside stainless steel cup 7 and 8.	52
4.22 Model of hydrogen pressure accumulation inside carbon steel cup 1 and 3.	53
4.23 Model of hydrogen pressure accumulation inside carbon steel cup 2 and 4.	54
4.24 Model of hydrogen pressure accumulation inside stainless steel cup 5 and 7.	54
4.25 Model of hydrogen pressure accumulation inside stainless steel cup 6 and 8.	55
4.26 Model of hydrogen pressure accumulation inside carbon steel cup 1 when initial hydrogen pressure is changed after steady state was achieved.	56
4.27 Model of hydrogen pressure accumulation inside carbon steel cup 2 when initial hydrogen pressure is changed after steady state was achieved.	56
4.28 Model of hydrogen pressure accumulation inside carbon steel cup 3 when initial hydrogen pressure is changed after steady state was achieved.	57
4.29 Model of hydrogen pressure accumulation inside carbon steel cup 3 when initial hydrogen pressure is changed after steady state was achieved.	57
4.30 Model of hydrogen pressure accumulation inside stainless steel cup 5 when initial hydrogen pressure is changed after steady state was achieved.	58

FIGURE	PAGE
4.31 Model of hydrogen pressure accumulation inside stainless steel cup 6 when initial hydrogen pressure is changed after steady state was achieved.	58
4.32 Model of hydrogen pressure accumulation inside stainless steel cup 7 when initial hydrogen pressure is changed after steady state was achieved.	59
4.33 Model of hydrogen pressure accumulation inside stainless steel cup 8 when initial hydrogen pressure is changed after steady state was achieved.	59
4.34 Comparison of the results from experiment in thesis of Kongvarhodom (2014) with the result from modelling in this work.	60
B1 Schematic of cup mounted on a carbon steel pipe for the calculation of surface area under the cup.	71
B2 Schematic of cup mounted on a carbon steel pipe showing The breakdown of the cup volume.	72
B3 Schematic of cup mounted on a carbon steel pipe for the calculation of the perimeter of the cup.	74
B4 Schematic of cup mounted on a carbon steel pipe for the calculation of surface area of cup inside the cup.	75

ABBREVIATIONS

CANDU	Canada Deuterium Uranium
CNER	Centre for Nuclear Energy Research
CS	Carbon Steel
FAC	Flow-Accelerated Corrosion
FM	Flow Meter
HEP	Hydrogen Effusion Probe
IHPF	Initial Hydrogen Pressure on the Feeder side
PT	Pressure Transducer
SS	Stainless Steel
TC	Thermocouple
V	Valve
VP	Vacuum Pump

LIST OF SYMBOLS

ϕ	Hydrogen permeability
ϕ_c	Permeability of cup's material
ϕ_D	Deuterium permeability
ϕ_H	Hydrogen permeability
ρ_{Fe}	Density of iron
a	Height of element
a_c	Conversion of days to year
A	Diffusing area which is the outer surface area of pipe under the cup
A_c	Surface area of cup inside the cup
A_i	Internal area of pipe
C	Concentration of the diffusing substance
$\frac{dC}{dx}$	Driving force
C_r	Corrosion rate
D	Diffusion coefficient or diffusivity
D_0	Maximum diffusion coefficient (at infinite temperature)
D_D	Diffusivities of deuterium
D_H	Diffusivities of hydrogen
D_o	Outer diameter of pipe
E	Hydrogen permeation activation energy
ΔH	Activation energy for diffusion
h	Height of cup
h_m	Inner height of cup
J	Diffusion flux
K	Dissociative adsorption equilibrium constant
l	Thickness of the diffusion path

l_c	Width of diffusing element which is the thickness of cup wall and silver solder around the cup
l_H	Width of hydrogen diffusion path leaving the cup
L	Length of pipe
L_c	Length around the edge of the cup as a function of α
M_1	Molar mass of gas 1
M_2	Molar mass of gas 2
M_{Fe}	Molar mass of iron
$\frac{\partial n_d}{\partial t_d}$	Daily accumulation of hydrogen gas
n	Moles of hydrogen gas inside the cup
n_m	Number of moles of hydrogen gas accumulated in the components which are inside the furnace
n_{out}	Number of moles of hydrogen gas accumulated in the components which are outside the furnace
n_T	Total moles hydrogen gas
$\frac{\partial P_{H_2}}{\partial t_d}$	Rate of pressure increase per day
p_c	Perimeter of cup
P	Pressure rise inside the cup over the test of time t
P_{H_2}	Hydrogen partial pressure
P_{H_2}	Feed side partial pressures of hydrogen
P_H	Permeate side partial pressures of hydrogen
Q	Permeability of hydrogen through membrane
Q_0	Hydrogen permeability coefficient
r	Radius direction
$r_{c,i}$	Inner radius of cup
$r_{c,o}$	Outer radius of cup
$r_{p,i}$	Inner radius of pipe
$r_{p,o}$	Outer radius of pipe
R	Gas constant

s	Distance between the center of cup and edge of cup
S	Solubility
S_D	Deuterium Solubility
S_H	Hydrogen Solubility
t	Time
T	Absolute temperature
T_{eff}	Effective temperature in the system
T_{mean}	Mean absolute temperature
V	Total hydrogen gas volume of the HEP
V_{cup}	Cup volume
$V_{cup,min}$	Cylindrical cup volume based on the minimum height of the cup
$V_{element}$	Remaining element volume of the cup
V_m	Hydrogen gas volume accumulated in the components which are inside the furnace
V_{out}	Hydrogen gas volume accumulated in the components which are outside the furnace
x	Coordinate chosen perpendicular to the reference surface