

**ELECTROCHEMICAL CHARACTERIZATION OF OXIDE FILM ON  
FEEDER PIPE STEELS IN HIGH TEMPERATURE WATER**

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A Thesis Submitted in Partial Fulfilment 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  
2005  
ISBN 974-9937-32-5

I 22242697

**Thesis Title:** Electrochemical Characterization of Oxide Film on Feeder  
Pipe Steels in High Temperature Water  
**By:** Teerapong Taenumtrakul  
**Program:** Petrochemical Technology  
**Thesis Advisors:** Assoc. Prof. Thirasak Rirksomboon  
Prof. Frank R. Steward

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Accepted by the Petroleum and Petrochemical College, Chulalongkorn  
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## ABSTRACT

4671020063: Petrochemical Technology Program  
Teerapong Taenumtrakul: Electrochemical Characterization of  
Oxide Film on Feeder Pipe Steels in High Temperature Water.  
Thesis Advisors: Assoc. Prof. Thirasak Rirksomboon and Prof.  
Frank R. Steward, 118 pp. ISBN 974-9937-32-5  
Keywords: CANDU/Corrosion/Chromium/ EIS/ Outlet Feeder Pipes/ Oxide  
Film

Surface characterization including Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) and Electrochemical characterization including Electrochemical Impedance Spectroscopy (EIS) and Polarization Curve Analysis were performed on four steels with different chromium (Cr) contents, i.e., A106B Carbon Steel (0.03%Cr), Qinshan Steel (0.33%Cr), 2.5%Cr / 1.0%Mo Steel and 304SS (19.1%Cr). All oxide films were developed under the simulated outlet feeder pipes condition of the primary heat transfer system of a CANDU reactor. Based on the distribution of the oxidized alloying constituents and the electron diffraction pattern with respect to depth, it was found that the oxide film consists of two spinel oxide layers, i.e., an iron rich outer layer covering a chromium rich inner layer. Steel with a higher Cr content has a smaller particle size and a higher packing density. Polarization curves and EIS were obtained at room temperature. The anodic current density from the polarization curve decreases with increasing Cr content. The impedance spectra of oxide film coated steel exhibit two capacitance loops. The film resistance ( $R_f$ ) and charge transfer resistance ( $R_{ct}$ ) increase with increasing Cr content in the steel.

## บทคัดย่อ

ธีรพงษ์ แต่นำตระกูล : การศึกษาลักษณะทางเคมีไฟฟ้าของฟิล์มออกไซด์บนผิวท่อในน้ำที่มีอุณหภูมิสูง (Electrochemical Characterization of Oxide Film on Feeder Pipe Steels in High Temperature Water) อ. ที่ปรึกษา : รศ. ดร. ธีรศักดิ์ ฤกษ์สมบูรณ์ และ ศ. ดร.แฟรงค์ อาร์ สจิวัด (Prof. Frank R. Steward) 118 หน้า ISBN 974-9937-32-5

การศึกษาลักษณะของฟิล์มออกไซด์ในงานนี้ประกอบด้วย 2 วิธี 1) การศึกษาพื้นผิวของฟิล์มออกไซด์โดยใช้กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) และ กล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน (TEM) 2) การศึกษาคุณลักษณะทางเคมีไฟฟ้าโดยใช้ เทคนิคอิเล็กโตรเคมีคอลอิมพีแดนซ์สเปคโตรสโคปีและการวิเคราะห์เส้นโค้งโพลาริเซชัน โดยทำการศึกษาบนฟิล์มออกไซด์ซึ่งก่อตัวภายใต้สภาวะจำลองในท่อทางออกของเตาปฏิกรณ์ CANDU เหล็กกล้าที่ใช้เป็นวัสดุของท่อในการศึกษามีปริมาณของธาตุโครเมียมต่างกัน 4 ชนิดประกอบด้วย เหล็กกล้าชนิด A106B (โครเมียม 0.03%), เหล็กกล้าควินแซน (โครเมียม 0.33%), เหล็กกล้าที่มีองค์ประกอบของโครเมียม 2.5% กับ โมลิบดีนัม 1.0% และ เหล็กกล้าไร้สนิม ชนิด 304 (โครเมียม 19.1%) โดยจากผลการศึกษาการกระจายตัวของธาตุองค์ประกอบและ แผนภาพการแทรกสอดของอิเล็กตรอนที่ระดับความลึกต่างๆกัน พบว่าฟิล์มออกไซด์มีลักษณะการเรียงตัวแบบสองชั้นประกอบด้วย ฟิล์มออกไซด์ชั้นนอกที่มีธาตุเหล็กเป็นองค์ประกอบหลักปกคลุมอยู่บนฟิล์มออกไซด์ชั้นในซึ่งสามารถตรวจพบธาตุโครเมียม ได้ในชั้นนี้โดยฟิล์มออกไซด์ทั้งสองชั้นมีโครงสร้างแบบ spinel นอกจากนี้ยังพบว่า เหล็กกล้าที่มีปริมาณโครเมียมมากจะมีขนาดอนุภาคของฟิล์มออกไซด์เล็กและความหนาแน่นในการจัดเรียงตัวสูง ส่วนการศึกษาลักษณะทางเคมีไฟฟ้าที่อุณหภูมิห้อง พบว่าเหล็กกล้าที่มีธาตุโครเมียมเป็นองค์ประกอบมากจะให้ค่าความหนาแน่นของกระแสแอโนดิกในเส้นโค้งโพลาริเซชันต่ำ สำหรับผลการห่าษาโดยเทคนิคอิเล็กโตรเคมีคอลอิมพีแดนซ์ พบว่าค่าอิมพีแดนซ์ที่ได้มีลักษณะเช่นเดียวกันกับวงจรไฟฟ้าที่ประกอบด้วยตัวเก็บประจุสองตัว โดยเหล็กกล้าที่มีโครเมียมเป็นองค์ประกอบมากจะมีค่าความต้านทานของฟิล์มออกไซด์ ( $R_f$ ) และความต้านทานในการถ่ายเทประจุ ( $R_c$ ) สูงกว่าเหล็กกล้าที่มีโครเมียมน้อย

## ACKNOWLEDGEMENTS

I would like to express my deep gratitude to Dr. Frank R. Steward and Dr. Thirasak Rirksomboon, my supervisors. Without them, I would not have an opportunity to carry out research at University of New Brunswick, Canada. I would like to thank them for their valuable advice, knowledge and support.

I would like to express sincere gratitude to Dr. Y.F. Cheng for his truthfully help and every suggestions.

I would like to thank staff of the Centre for Nuclear Energy Research (CNER).

I am grateful for the partial scholarship and partial funding of the thesis work provided by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

I would to thank Ms. Sudprathana Tetanun, my best and very important friend for her encouragement, understanding and comfort when the times got rough.

Many thanks are due to my friends in Fredericton, Canada and in Thailand for the valuable encouragement.

Last but not least, I would like to deeply thank my parents for the important support, love and everything throughout this work.

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**ABBREVIATIONS**

|                  |   |
|------------------|---|
| Ag               | Silver                                    |
| CANDU            | Canada Deuterium Uranium                  |
| Cr               | Chromium                                  |
| C                | Carbon                                    |
| Co               | Cobalt                                    |
| D <sub>2</sub> O | Heavy water                               |
| CE               | Counter electrode                         |
| ECP              | Electrochemical corrosion potential       |
| EDXA             | Energy dispersive X-ray analysis          |
| EIS              | Electrochemical impedance spectroscopy    |
| FAC              | Flow-assisted corrosion                   |
| Fe               | Iron                                      |
| FRA              | Frequency response analyzer               |
| Ga               | Gallium                                   |
| HWC              | Hydrogen water condition                  |
| Mn               | Manganese                                 |
| Nb               | Niobium                                   |
| Ni               | Nickel                                    |
| NWC              | Normal water condition                    |
| O                | Oxygen                                    |
| Ox               | Oxidized species                          |
| PHTS             | Primary heat transfer system              |
| Pt               | Platinum                                  |
| RE               | Reference electrode                       |
| Re               | Reduced species                           |
| SEM              | Scanning electron microscope              |
| STEM             | Scanning transmission electron microscope |
| TEM              | Transmission electron microscope          |
| UO <sub>2</sub>  | Natural uranium                           |
| V                | Vanadium                                  |

|    |                   |
|----|-------------------|
| WE | Working electrode |
| Zr | Zirconium         |

## LIST OF SYMBOLS

|                                |   |
|--------------------------------|---|
| A                              | Exposed area                              |
| a                              | Atomic weight                             |
| E                              | Potential                                 |
| E'                             | Real part of potential                    |
| E''                            | Imaginary of potential                    |
| I'                             | Real part of current                      |
| I''                            | Imaginary part of current                 |
| E <sub>corr</sub>              | Corrosion potential                       |
| E <sub>oc</sub>                | Open circuit potential                    |
| F                              | Faraday's constant (96,480 coulombs/mole) |
| f                              | Frequency                                 |
| Fe <sub>3</sub> O <sub>4</sub> | Magnetite                                 |
| I                              | Current                                   |
| I <sub>o</sub>                 | Exchange current density                  |
| i <sub>o</sub>                 | Exchange current density                  |
| m                              | Mass reacted                              |
| n                              | Moles of transferred electron             |
| r                              | Reaction rate                             |
| r <sub>f</sub>                 | Forward reaction rate                     |
| r <sub>r</sub>                 | Reverse reaction rate                     |
| t                              | Reaction time                             |
| Z                              | Impedance                                 |
| Z'                             | Real part of impedance                    |
| Z''                            | Imaginary part of impedance               |
| R                              | Resistance                                |
| C                              | Capacitance                               |
| R <sub>f</sub>                 | Film resistance                           |
| R <sub>ct</sub>                | Charge transfer resistance                |
| R <sub>s</sub>                 | Solution resistance                       |
| C <sub>f</sub>                 | Film capacitance                          |

|                                |                                |
|--------------------------------|--------------------------------|
| $C_{dl}$                       | Double layer capacitance       |
| $R$                            | Gas constant                   |
| $T$                            | Absolute Temperature           |
| $\epsilon_0$                   | $8.85 \times 10^{-14}$ F/cm    |
| $\epsilon$                     | Dielectric constant            |
| $d$                            | Coating thickness              |
| $V$                            | Volt                           |
| $\gamma\text{-Fe}_2\text{O}_3$ | Maghemite                      |
| $\alpha\text{-Fe}_2\text{O}_3$ | Hematite                       |
| $\eta$                         | Over-potential or Over-voltage |
| $\Phi$                         | Phase angle shift              |
| $\omega$                       | Angular velocity               |