

**DEVELOPMENT OF A PROBE FOR MEASURING HYDROGEN
CONCENTRATION IN THE PRESENCE OF MOIST CHLORINE**

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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
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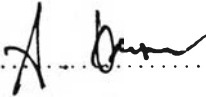
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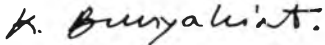
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ABSTRACT

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The presence of hydrogen gas as an impurity in chlorine gas and caustic soda generated by electrolysis of an aqueous sodium chloride solution in a Chlor-alkali plant leads to lowering plant efficiency and it can be hazardous if the hydrogen concentration exceeds 6 %. The development of an instrument for monitoring hydrogen concentration in moist chlorine gas at various locations of the Chlor-alkali plant has been performed at the Centre for Nuclear Energy Research (CNER). A series of hydrogen and chlorine permeability coefficient experiments was carried out using a test cell to identify effective coating materials for blocking chlorine, but at the same time, allowing the passage of hydrogen. It was found that Fluorodyn Caulk and Derakane Resin are the promising candidates as coating materials for blocking such chlorine.

บทคัดย่อ

นางสาวพรรณิ กิจเจริญวงศ์: การพัฒนาเครื่องมือสำหรับวัดความเข้มข้นของก๊าซไฮโดรเจนในก๊าซคลอรีนชื้น (Development of a Probe for Measuring Hydrogen Concentration in the Presence of Moist Chlorine.) อ. ที่ปรึกษา : ศ. ดร. แฟรงค์ สจ๊วต และ ผศ.ดร. ชिरศักดิ์ ฤกษ์สมบูรณ์ 105 หน้า ISBN 974-334-145-5

ก๊าซไฮโดรเจนเป็นสิ่งเจือปนในก๊าซคลอรีนและโซเดียมไฮดรอกไซด์ที่เกิดจากปฏิกิริยาอิเล็กโทรไลซิสของสารละลายเกลือหรือโซเดียมคลอไรด์ในโรงงานคลออัลคาไลน์ซึ่งทำให้ประสิทธิภาพการผลิตต่ำลง นอกจากนี้ยังเป็นอันตรายเมื่อความเข้มข้นของก๊าซไฮโดรเจนเกิน 6 % ซึ่งเป็นส่วนที่ก๊าซไฮโดรเจนระเบิดได้ ดังนั้นจึงได้มีการพัฒนาเครื่องมือเพื่อทำการวัดความเข้มข้นของก๊าซไฮโดรเจนในก๊าซคลอรีนชื้นที่ตำแหน่งต่างๆของโรงงานคลออัลคาไลน์ โดยได้ทำการทดลองและวัดค่าสัมประสิทธิ์ในการแพร่ผ่านวัสดุต่างๆของก๊าซไฮโดรเจนและก๊าซคลอรีนโดยใช้เทสต์เซลล์เพื่อที่จะหาวัสดุที่มีประสิทธิภาพในการป้องกันไม่ให้ก๊าซคลอรีนแพร่ผ่านไปได้ แต่ในขณะเดียวกันสามารถให้ก๊าซไฮโดรเจนแพร่ผ่านไปได้ จากการทดลอง พบว่าฟลูออโรไดนาคอล์ก (Fluorodyn Caulk) และ เดราเคน เรซิน (Derakane Resin) เป็นวัสดุที่มีประสิทธิภาพในการป้องกันไม่ให้ก๊าซคลอรีนแพร่ผ่านไปได้

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LIST OF SYMBOLS

a	Anolyte
A	Area of the electrode (cm^2)
$a_{\text{Fe}^{2+}}$	Activity of Fe^{2+} ion
$a_{\text{Fe}^{3+}}$	Activity of Fe^{3+} ion
$a_{\text{H}_3\text{O}^+}$	Activity of H_3O^+ ion
b	Affinity constant [cm^3 (STP) / cm^3]
B/T	Breakthrough time
c	Catholyte
C_i	Concentration of H_2 in the collection gas at time t_i , (ppm)
C_i, C_o	Concentration of the reacting substance remote from the electrode and immediately adjoining its surface, respectively.
C_{OH}	Catholyte caustic concentration (g/L)
c_s'	Langmuir capacity constant [cm^3 (STP) / cm^3]
$C_z(y)$	Concentration in grams per liter of z in medium y
d	Depleted brine
D_0, P_0, S_0	The constants , cm^2/s , [cm^3 (STP) .cm / (cm^2 .s.cmHg) , and [cm^3 (STP)] / cm^3 .cmHg) , respectively.
D_{app}	Apparent diffusivity
D_i	Diffusion coefficient of species i
E	Cell potential E which is the difference of two half cell electrode potentials at interface I and II.

E_0	A constant which is determined by calibration of the sensor with pure hydrogen gas at 1 atm.
E_b	Intramolecular activation energy
E_D	Activation energy for diffusion, cal/(gmol)
E_i	Half cell electrode potential at interface i
E_i	Intermolecular activation energy
E_i^0	Standard electrode potential
E_{II}	Half cell electrode potential at interface II
E_{II}^0	Standard electrode potential for Fe^{3+}/Fe^{2+} redox reaction
E_p	Activation energy for permeation, cal/(gmol)
F	Faraday constant (= 96,487 C/mol)
f	Feed brine
I	the current(A)
I_L	Limiting current(A)
J	The flux of species (mol.sec ⁻¹ .cm ⁻²)
k	a constant
k_g	a constant at a given temperature.($k_g = kK_g^{1/2}$)
$K_g(T)$	The equilibrium constant between hydrogen molecule in bulk gas and H-atom in Palladium
L	Specimen thickness
p	Feed brine flow rate (L/s)
P	Membrane permeability coefficient
p_{H_2}	Partial pressure of hydrogen in the contacting gas.
P_{H_2} , P_{H_2O}	Ratio of hydrogen partial pressure or water vapor pressure to the standard atmospheric pressure, respectively.

$P_i(t_i)$	Permeation rate at any time t_i , ($\text{cm}^3 \text{H}_2 \text{cm}^{-2} \text{min}^{-1}$)
q	Depleted brine flow rate (L/s)
Q	Total amount of permeate passing through the polymer from $t=0$ to $t=t$ [$\text{cm}^3 \text{(STP)}/\text{cm}^2$]
R	Gas constant
$R(T, x_H = 0)$	Resistance of the pure palladium wire
$R(T, x_H)$	Resistance of a palladium wire containing hydrogen at temperature T
S^{-1}	Henry's Law sorption coefficient
S	Segment length
T	Absolute temperature (K)
x_H	Mole fraction of hydrogen atom in palladium
Z	The number of electrons per mol
η_{NaOH}	Caustic efficiency for membrane cells
η_{Cl_2}	Chlorine efficiency for membrane cells
δ	Thickness of the diffusion layer
θ	Diffusion time lag
ε	Porosity
$\rho(x_H)$	Ratio of the resistance $R(T, x_H)$ of a palladium wire containing hydrogen at temperature T , to the resistance of the pure palladium wire $R(T, x_H = 0)$
σ_c	Average diameter of the high polymer molecule
α_{ij}	Selectivity which is the ratio of the permeability coefficient of component i and component j
σ_p	Penetrant molecule diameter