Development of Water Detritiation Process Using the Hydrophobic Platinum Catalyst

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ABSTRACT

Radioactive emissions and occupational doses by tritium are mainly caused by tritiated water escaping from equipment in the nuclear industry. Improving the leak-tightness of equipment is effective in reducing emissions and internal dose but is not a long-term solution. Water detritiation was consider to be the most effective tritium control option since tritium is removed right from the source. The WTRF (Wolsong Tritium Removal Facility) is under construction now with the completion date of June, 2006 in Korea. It is designed to remove tritium from tritiated heavy water in each of the existing four CANDU units at Wolsong site. We developed a hydrophobic platinum catalyst (Pt/SDBC catalyst) that would be used at the LPCE (Liquid Phase Catalytic Exchange) column in the WTRF. The catalytic rate constants of the newly developed catalyst for the deuterium exchange reaction between water vapor and hydrogen gas were measured in a recycle reactor. The catalytic rate constants of the Pt/SDBC catalyst decreased with reaction time and were much greater than that required, 2.0×10^{-4} mol (D_2)/s/g(pellet) in the design of the WTRF. Tritium removal efficiency of the WTRF, which is important for a safe and reliable operation of the facility, depends on the design and operating variables. A theoretical model based on the design and operating variables of the LPCE process was set up, and the equations between the parameters were derived. Numerical calculation result from a computer program shows steep increase of the detritiation factor of the LPCE process with respect to temperature increase and mild increase with respect to pressure decrease. The other parametric study shows that the calculated detritiation factors increase as the catalyst efficiency, number of theoretical stages of hydrophilic packing, the detritiation factor of cryogenic distillation system and the total number of sections increase. We also proceeded with the experiments for the hydrogen isotopic exchange reaction in a trickle bed reactor packed with a mixture of hydrophobic catalyst and hydrophilic packing to improve liquid distribution and vapor/liquid transfer area. The overall rate constant $K_y a$ $(m^3(STP)s^{-1}m^{-3})$ increased as the increase of the hydrogen flow rate in the range of 0.4 to 1.6 m/s at STP.

INTRODUCTION

Tritium is mainly produced through neutron capture by the deuterium atom in heavy water (D_2O) which is used as the moderator and coolant in PHWRs. Most of the tritium exists as a form of DTO in the heavy water, and its amounts build up due to greater generation rates than decay rates. Since tritium is a radioactive hydrogen isotope, the higher concentration of DTO means a higher radiation level. The recovery of tritium from the heavy water is one of the most important processes not only because tritium is a very precious element for fusion reaction but also because the radiation hazard from tritium can be reduced. The amount of tritium generated in a PHWR exceeds that in a LWR by almost 100 times. For Wolsong Unit 1, CANDU reactor, the estimated

equilibrium tritium activities in the coolant and moderator are 72.15 GBq/kg (1.95 Ci/kg), 3.256 TBq/kg (88 Ci/kg), respectively [1]. After 20 years operation, the tritium activities are estimated to reach about 2.22 TBq/kg in moderator, and 65.12 GBq/kg in coolant by the end of 2003.

Korea has 4 units of CANDU at Wolsong site; the tritium inventory is estimated to reach about 1.63×10^{18} Bq by 2005. During the licensing review of Wolsong Unit 2-4, the WTRF was recommended by the regulatory body and is now under construction with a completion date of June, 2006. The WTRF is designed to maintain the tritium activity in the moderator to about 0.37 TBq/kg [2] and it will take about 4-5 years to reduce the tritium concentration.

Water detritiation process is made up of three parts (transfer, enrichment and storage). The first part involves the transfer of tritium from a water molecule to a gas molecule. The LPCE and CECE (Combined Electrolysis Catalytic Exchange) with a hydrophobic catalyst are very effective methods to transfer small quantities of tritium from light or heavy waste water streams because of its high separation factor and mild operating conditions. The hydrophobic Pt/ SDBC catalyst has been developed in Korea for the LPCE column of the WTRF. The isotopic exchange reaction between hydrogen and water on platinum supported catalysts provides a useful step for separating the hydrogen isotopes such as deuterium and tritium [3]. Although platinum supported catalysts on various oxides are well known as active catalysts for this process, they come to lose their activity gradually, presumably owing to the condensed water in the capillary [4]. Therefore, the development of suitable wet-proofing catalysts is essential for a satisfactory reaction process. SDBC was of particular interest since it has a negligible water adsorptivity and practically no capability for activating the water molecule and a platinum catalyst supported on SDBC presents a high activity even with a gas saturated with water vapor [5].

Tritium removal efficiency of the WTRF, which is important for a safe and reliable operation of the facility, depends on the design and operating variables such as the operating temperature and pressure, catalyst efficiency, number of stages a hydrophilic bed, etc [2]. In order to assess the influences of such variables to the detritiation factor, a computer program was developed and the change of detritiation factor of the LPCE system was simulated varying those operating and design variables. The selected variables are the operating temperature and pressure, catalyst efficiency, number of stages in a hydrophilic bed, detritiation factor of cryogenic distillation system and number of sections within the LPCE column.

 The catalytic columns are multiple-tube type in the WTRF, the concentric cylinder consisted of two separated catalytic bed and hydrophilic bed. The catalyst bed is installed at outside from the center of column [6]. The catalytic columns with various structures were developed. The multistage type provided better results than the trickle-bed type. However, the structure of the column is complicated. The trickle-bed type has a significant advantage in that the structure of the column is quite simple: the hydrophobic catalysts or the catalysts and hydrophilic packing are packed within the column. This structure would lead to a smaller column height than the multistage type. An experiment for the hydrogen isotope exchange reaction was also carried out in a trickle-bed reactor packed with the mixture of a hydrophobic catalyst and hydrophilic packing.

CHARACTERIZATION OF THE LPCE CATALYST IN THE WTRF

Catalyst Preparation

Several types of macroporous SDBC were synthesized and selected as support materials. SDBC was synthesized to obtain a porous structure. Toluene was used as a good solvent, and 2-ethyl-1-hexanol as a poor solvent. The specific surface area and the pore volume could be controlled by the ratio of the monomer to the solvent [7]. This polymer support has a form of a cylindrical pellet (4 mm diameter; 4mm height). The platinum precursor solution was made by dissolving hexa-chloroplatinic acid (H_2PtCl_6) in ethanol. The Pt/SDBC catalysts were prepared by pouring an appropriate volume of the platinum solution to make a slurry, and then evaporating the stirred slurry to a near-dryness in a rotary evaporator at 80°C. After the platinum was impregnated over the SDBC support, the sample was directly reduced. The standard reduction procedure was to maintain the sample at 230°C for 15 hours in flowing hydrogen after purging it with pure nitrogen at room temperature for 30 minutes.

The physical properties of the polymer supports and the Pt/SDBC catalysts, such as the BET surface area, pore volume and pore size distribution, etc., were measured by a physical adsorption of the nitrogen gas at the liquid nitrogen temperature of 77K by using Autosorb-6. The surface area of the supported platinum particles was determined by hydrogen chemisorption on the catalysts by using a conventional volumetric apparatus at 298K. The characteristics of the catalysts were given in Table 1

Table 1. Basic characteristics of the catalysts

Platinum loading (weight %)	0.80
BET surface area (m^2/g)	442
Micropore area/Total area (-)	0.42
Pt dispersion (H/Pt)	0.98
Apparent density (g/cm^3)	0.18

Recycle reactor

A recycle reactor was built for the long-term performance test of the catalyst at various temperature and gas velocities [8]. The catalyst was placed in a water-jacketed reactor. Below the reactor a water-jacketed equilibrator was located to achieve equilibration between water and vapor in the recycled hydrogen gas. A saturation section was located directly below the equilibrator. A metal bellows pump was used for the hydrogen circulation in the system. The water vapor in the circulation gas was removed with a condenser.

Premixed H_2/D_2 gas was converted to HD gas through a Pt catalyst. HD gas was used as a spike gas for activity measurement. The concentration of HD gas was measured with a gas chromatography. Gas samples from the inlet and outlet of the reactor were dried by passing through molecular sieve tubes. De-mineralized water de-aerated through a vacuum column was used as feed water, and Total Organic Carbon (TOC) of the feed water was controlled to maintain below 0.5 ppm to avoid the adsorption of organic material onto the active sites of the catalysts. The volume of the reactor, 27.3 L, was determined by measuring both the volume of hydrogen gas and the change of the pressure in the reactor. The mass of catalysts loaded in the reactor is 19.01g. The diameter and height of the catalyst bed are 5.5 cm and 4.5 cm,

respectively. The apparent density of catalyst in the reactor is 0.18 g/mL. The temperature of the reactor was controlled to maintain at 60°C using water-jackets around the reactor and equilibrator, a feed water heater, and a circulation water heater. After evacuating the system several times, the hydrogen gas was injected and started to circulate the system with the bellows pump, which gave the recycle flow rate of around 64 LPM. The recycle hydrogen gas was saturated with water vapor passing through the equilibrator. A circulation water pump circulated the water in the saturator, and a feed water pump supplied water for the saturator. The reactor pressure was controlled to maintain at 135 kPa (abs) by a water column. After reaching a reaction temperature of 60°C, the spike gas was switched from H_2 gas to HD gas. The injection rate of HD gas was controlled to 0.2 LPM with a mass flow controller, and the concentration of HD gas was around 22 mole D_2 %. The concentration of HD gas from the inlet and outlet port was measured every ten minutes for around 3 hours. After reaching steady state, the concentration of HD gas was measured ten times again with an interval of 30 seconds. The average of the latter ten measurements was used for the calculation of catalytic rate constants.

Catalytic reaction constants

The catalytic rate constants of the Pt/SDBC catalyst were measured as a function of reaction time. The concentration of HD gas in the gas samples at the inlet and outlet reached a steady state about 100 minutes after injection. After 200 minutes of HD gas injection, we measured the HD concentrations of inlet and outlet gas samples. Fig. 1 showed the average HD concentrations from the inlet and outlet gas samples increased with time. It seemed to be due to the deactivation of the catalyst. The catalytic rate constant in Fig.1 was calculated. The wide gap between HD concentration of outlet and equilibrium concentration meant the low catalytic rate constant. The outlet concentration almost approached the equilibrium concentration in early time. The catalyst showed very high initial catalytic rate constants of around 1.0×10^{-3} mol (D_2)/s/g(pellet). The catalytic rate constants decreased with time. These catalytic rate constants were much greater than that required, 2.0×10^{-4} mol (D_2)/s/g(pellet) in the design of the WTRF.
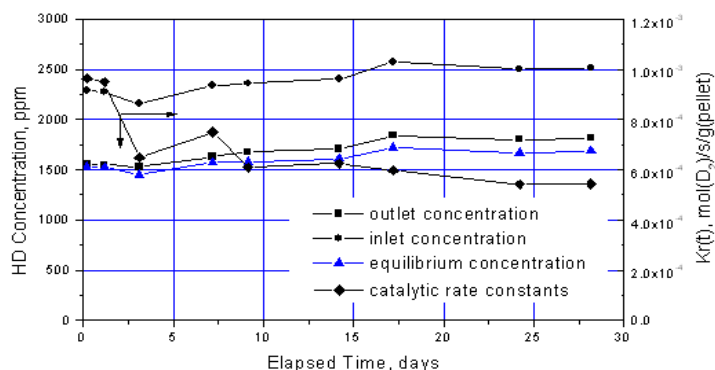

Fig. 1. HD concentrations at outlet and inlet of the catalyst bed and calculated equilibrium concentrations and catalytic rate constants

ANAYSIS OF THE LPCE PROCESS IN THE WTRF

Description of the LPCE Process

Wolsong Unit 1 is the second nuclear power plant in Korea after Kori Unit 1, had started commercial operation on April 22, 1983. At that time, there was not enough consideration for the tritium hazards even to the operating personnel. During the safety inspection of Wolsong Unit 1 by regulatory agency in 1986, it was recommended Korea Hydro and Nuclear Power company (KHNP) to establish the long-term plan for exceeding the tritium activity criterion in the heat transport media 2 Ci/kg. For the increased potential of radiation hazard from tritium accumulation at Wolsong site caused by the operating of more units, the government, the Ministry of Science and Technology, requested the KHNP to submit a master plan for reducing the tritium inventory and environmental emission, in order to reduce the overall radiological impact to workers and environment from the Wolsong NPPs as low as reasonably achievable (ALARA), as a condition of the construction permit of Wolsong Units 3 and 4. In regards to that, the KHNP submitted the construction plan of the WTRF to the government, and the WTRF project was launched and the specific tritium handling technologies and systems were developed and designed.

The WTRF is under construction now with the completion date of June, 2006. It is designed to remove tritium from tritiated heavy water in each of the existing four CANDU units at Wolsong site. A general design and performance specification for the WTRF is given in Table 2. This design specification allows to maintain the Wolsong four units moderator concentration at about 10 Ci/kg, when operated on a 24 h/day basis and at the specified availability factor [2].

Table 2. General parameters for the WTRF

D_2O feed isotopic	≥99.8 mol% D_2O
D_2O feed tritium concentration	10-60 Ci/kg
D_2O processing rate	100 kg/h
Minimum tritium extraction efficiency per pass	97%
Tritium by-product	≥ 99.0 mol% T_2
Service life	40 years
Availability	80%

The detritiation process of the WTRF is made up of three parts. The first part involves the transfer of tritium from a heavy water molecule to a deuterium molecule. The second part of the process is the enrichment stage. This stage concentrates the tritium by Cryogenic Distillation (CD) of the D_2/DT mixture, to produce streams of pure D_2 and T_2. The third part of the process is the measurement and packaging of the concentrated T_2 for secure, long-term storage. The LPCE system is designed to reduce the tritium content of tritiated heavy water feed from the moderator with a removal efficiency of 97% in a single pass (equivalent to the detritiation factor 35).

The overall mechanism of tritium transfer from the heavy water to the deuterium gas in the LPCE system can be represented by the following equations [4].

$$DTO(l) + D_2(g) \Leftrightarrow D_2O(l) + DT(g) \qquad \text{(Eq. 1)}$$

The reaction mechanism consists of two steps, mass transfer and catalytic reaction. The mass transfer step involves the transfer of DTO from the liquid phase to the vapor phase as below,

$$DTO(l)+D_2O(v)\Leftrightarrow D_2O(l)+DTO(v) \qquad\qquad \text{(Eq. 2)}$$
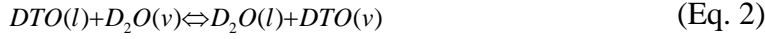
The catalytic reaction of tritium in the vapor phase is

$$DTO(v)+D_2(g)\Leftrightarrow D_2O(v)+DT(g) \qquad\qquad \text{(Eq. 3)}$$

Modeling of the LPCE system

Fig. 2 shows n sections arranged in a counter-current cascade, where the sections are numbered up from the bottom and each section contains a catalyst bed using the hydrophobic platinum catalyst and a hydrophilic bed. Tritiated heavy water is fed to the top of the column and allowed to flow downward counter-currently to a rising stream of deuterium gas [2]. A saturator is installed to humidify the deuterium gas at the bottom of column with flow rate of V, and a condenser is installed to condensate the heavy water vapor at the top of column. Tritiated heavy water is fed to the top of column and the detritiated heavy water product is discharged at the bottom with flow rate of L. The internal liquid flow rate (L_{in}) is the sum of the feed water and the condensed vapor. The deuterium gas is entered from the cryogenic distillation system through the bottom section of column with flow rate of D.

The deuterium gas is flowing upward contacting the vapor in a catalyst bed. The tritium mole fraction in deuterium gas stream (x_n) and heavy water vapor stream (y_n) leaving the n-th catalyst bed are [9]

$$x_n = \left(1-\frac{\eta_c\alpha_g}{\alpha_g+\gamma_g}\right)x_{n-1}+\left(\frac{\eta_c}{\alpha_g+\gamma_g}\right)y_{n-1}' \quad\text{and} \qquad \text{(Eq. 4)}$$

$$y_n = \left(\frac{\eta_c\alpha_g\gamma_g}{\alpha_g+\gamma_g}\right)x_{n-1}+\left(1-\frac{\gamma_g\eta_c}{\alpha_g+\gamma_g}\right)y_{n-1}'. \qquad \text{(Eq. 5)}$$

The heavy water is flowing downward and in contact with the vapor flowing upward in a hydrophilic bed. The tritium mole fraction of heavy water feed stream (z_{n+1}) and vapor stream (y_n') leaving the hydrophilic bed are [9]

$$z_{n+1} = \frac{[\alpha_v/\gamma_l-(\alpha_v/\gamma_l)^{Ns}]y_n-z_n/\gamma_l}{[\alpha_v/\gamma_l-(\alpha_v/\gamma_l)^{Ns}]/\alpha_v-1/\gamma_l} \quad\text{and} \qquad \text{(Eq. 6)}$$

$$y_n' = y_n - \frac{z_n-z_{n+1}}{\gamma_l} \qquad\qquad \text{(Eq. 7)}$$

The tritium separation factor between the vapor and gas (α_g) and the separation factor between liquid and vapor (α_v) defined in terms of the tritium to deuterium atom ratio in the two species at equilibrium, are functions of Kelvin temperature. γ_g and γ_l are the ratios of molar flow rate between vapor and liquid and between vapor and liquid, respectively. The partial pressure of heavy water P_{D_2O} (kPa), can be obtained by the following regressed equation [9].

$$P_{D_2O} = 10^{[7.01448-(1544.32+124209/T)/T]} \qquad\qquad \text{(Eq. 8)}$$

The η_c of a catalyst bed and the number of theoretical stages (Ns) in a hydrophilic bed are defined as

$$\eta_C \equiv \frac{x_{n-1} - x_n}{x_{n-1} - x_{ne}}, \qquad Ns \equiv \frac{y_n' - y_n}{y_n' - y_{ne}} \qquad\qquad \text{(Eq. 9)}$$

respectively, where the suffix e, denotes equilibrium.

Numerical calculation

The detritiation factor of LPCE system and tritium concentrations x_i, y_i, z_{i+1}, y_i' in an arbitrary section i can be calculated using the Eqs. (4-7) when the flow rate of heavy water feed, the tritium mole fraction of feed water stream (z_f), the flow rate of deuterium stream, the detritiation factor of the cryogenic distillation process ($DF_{CD}=x_n/x_0$), the operating temperature (T), the operating pressure of the saturator (P_{sys}), efficiency of the catalyst bed (η_c), number of theoretical stages (Ns) per hydrophilic bed, total number of section ($Nsec$) are given.
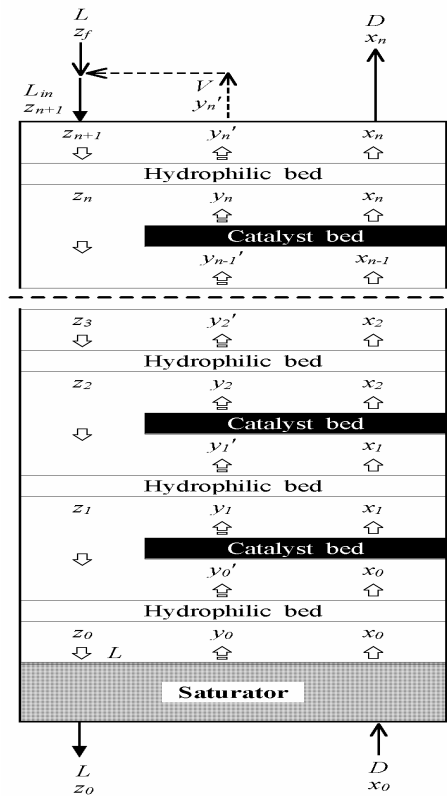

Fig. 2. Schematic diagram of the LPCE process

The temperature affects on the tritium separation factor and the molar flow rate of vapor, while the pressure only affects on the molar flow rate of vapor. The increased temperature induces a decrease of separation factor and an increase of internal heavy water vapor flow rate. Also, the vapor flow rate is increased with decrease of the pressure. They are influencing the tritium transfer from the tritiated feed water to deuterium gas. Thus, the tritium separation factor (α) and molar flow rate ratio (γ) are affected by the variation of temperature and pressure.

Fig. 3 shows steep increase of detritiation factor with respect to temperature increase and mild increase with respect to pressure decrease. Because the pressure variation is only affecting to the molar flow rate of vapor, on the other hand, the temperature variation is affecting to the both molar flow rate of vapor and tritium separation factor.

The parametric study shows that the calculated detritiation factors increase as the catalyst efficiency, number of theoretical stages of hydrophilic packing, the detritiation factor of cryogenic distillation system and the total number of sections increase.
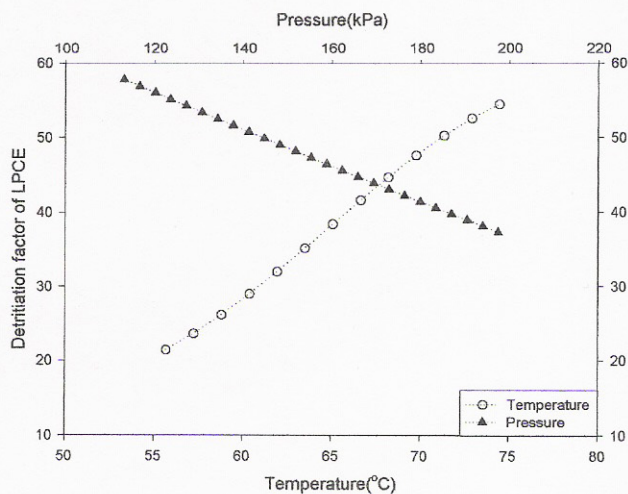

Fig. 3. The DF of the LPCE process as functions of temperature and pressure.

A TRICKLE BED PACKED WITH THE Pt/SDBC COMPLEX

Catalytic columns of trickle bed type filled with mixture of the Pt/SDBC catalyst with hydrophilic packing which is abbreviated to Pt/SDBC complex were developed. An experimental apparatus was built for the performance test of the Pt/SDBC complex at various temperatures and gas velocities. The catalyst bed was a cylindrical column 3 cm in diameter by 40 cm in length. A non-catalytic packed equilibrator was located below the catalyst bed to achieve an equilibration between the vapor in the hydrogen entering the bed and the liquid water leaving the bed. It operated on a recirculating gas once-through water principle. A metal bellows pump was used for the hydrogen circulation in the system. The water vapor in the circulation gas was removed with a condenser. The catalyst under study was packed wet into the bed and the water was injected at the top through a liquid distributor and allowed to flow by gravity through the packing. Hydrogen gas which had been passed through the bed and the gas samples was drawn off from the inlet and outlet of the bed. The concentration of the HD gas was analyzed with a gas chromatography. In order to maintain the column pressure, hydrogen was bled into the loop ahead of the gas circulator. HD gas was used as a spike gas for the catalyst performance. The temperature of the reactor was controlled by using water-jackets around the reactor and an equilibrator, a feed water heater, and a circulation water heater. After evacuating the system several times, the hydrogen gas was injected into the system and it began to circulate through the system with the use of the bellows pump, which provided a recycle flow rate of around 60 LPM.

Many tests have been carried out for the activity of the catalyst, Kya. In all the tests carried out, the liquid flow rate of the column was maintained as constant (120ml/min). The activities of the catalyst, Kya, were measured for several days. Deuterium mol fractions of the inlet and outlet gas samples reached a steady state at about 100 minutes after an injection. After 200 minutes from the injection, the gas samples were analyzed. The steady state deuterium mol fractions from the inlet and outlet gas samples increased with time due to a deactivation of the catalyst. The decline in the catalysts performance could be a result of a catalyst poisoning by some foreign material or a slow condensation of the water in the pores of the catalyst particle. The effect of a water uptake is to slow down the pore diffusion of the reactants and the products and cause a reduction in the internal and direct transfer rates.

Fig. 4 shows the effect of the hydrogen gas flow on the overall rate constant for the Pt/SDBC complex. Kya increased with the hydrogen flow rates in the range of 0.4 to 1.6 m/s at STP. This flow dependency indicates that an external resistance plays an important role in the exchange process. The variation in the flow dependency may be due in part to an increase in the liquid holdup at the higher flows. As a result of the liquid holdup in the bed, the water distribution, and thereby Kya will likely be improved.
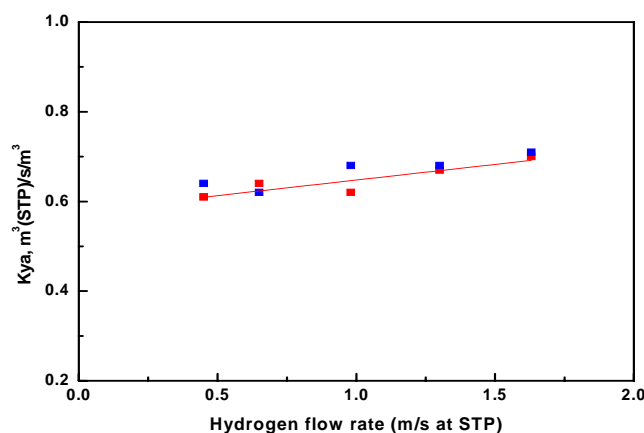

Fig. 4. Effect of the hydrogen gas flow rate on the overall rate constant of the Pt/SDBC complex

CONCLUSION

The Pt/SDBC catalyst was developed for The WTRF designed to remove tritium from tritiated heavy water in each of the existing four CANDU units at Wolsong site. The catalytic rate constants of the catalyst for the deuterium exchange reaction between water vapor and hydrogen gas decreased with time and were much greater than that required, 2.0×10^{-4} mol (D_2)/s/g(pellet) in the design of the WTRF. In order to investigate the influence of the design and operating variables to the performance of the WTRF, the LPCE process was modeled. Important design and operating variables were identified and a computer program was developed based upon the relations between the operating and design parameters derived from the mass transfer, catalytic reaction and material balance equations at a steady state. Numerical calculation result from the computer program shows steep increase of the detritiation factor of the LPCE process with respect to temperature increase and mild increase with respect to pressure decrease. The other

parametric study shows that the calculated detritiation factors increase as the catalyst efficiency, number of theoretical stages of hydrophilic packing, the detritiation factor of cryogenic distillation system and the total number of sections increase. We also proceeded with the experiments for the hydrogen isotopic exchange reaction in a trickle bed reactor packed with a mixture of hydrophobic catalyst and hydrophilic packing to improve liquid distribution and vapor/liquid transfer area. The overall rate constant $K_y a$ (m^3(STP)$s^{-1}m^{-3}$ increased as the increase of the hydrogen flow rate.

ACKNOWLEDGEMENT

REFERENCES

1. KHNP, 2001, *Safety Analysis Report, Wolsong Tritium Removal Facility.*
2. KEPCO, 1996, *Wolsong # 2,3,4 Final Safety Analysis Report*, Chapter 11.3.
3. Urey, H.C. (1955). *Production of Heavy Water.* McGraw Hill. New York. p.261.
4. Rolston, J.H. and Goodale J. W. (1972). Isotopic Exchange between Hydrogen and Water Vapor over Supported Metal Catalysts. Part I. Kinetics of the Exchange. *Can. J. Chem.* 50:1900-1906.
5. Izawa, H., Isomura S. and Nakane R. (1979). Gaseous Exchange Reaction of Deuterium between Hydrogen and Water on Hydrophobic Catalyst Supporting Platinum. *J. Nucl. Sci. Tech.* 16(10):741-749
6. Paek, S., Ahn, D.H., Lee, H. and Chung, H. (2002). Tritium Activities in Korea. Fusion Science and Technology 41:329-333.
7. Kang, H. S., Lee, H., Kim, K.R., Ahn, D. H., Paek, S., Lee, S. H. and Chung, H. (1999). Effect of Solvent on Pore Characteristics of Styrene-Divinylbenzene Copolymer. Polymer. 23(3):368-375.
8. Suppiah, S., Lee, H. and Kutchcoskie, K.J., 1998, *Characterization and Performance Testing of KAERI/KEPRI Catalysts for Hydrogen Isotope Exchange*, AECL-RC-2082.
9. KHNP, 2002, *Development of Tritium Removal Technology (I) phase 2*.