

碩士學位論文

WTRF LPCE 工程의 三重水素
除染係數에 대한 設計 및 運轉變數의
影響에 관한 研究



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A Study on the Effects of the Design and Operating
Variables on the Detritiation Factor of
the WTRF LPCE Process

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(Supervised by Professor Bum-Jin Chung)

A thesis submitted in partial fulfillment of the requirement for the
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This thesis has been examined and approved.

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Nomenclature

A_T	Tritium activity at time t (Bq/kg)
A_0	Initial tritium activity (Bq/kg)
λ	Tritium decay constant (s^{-1})
L	D_2O replacement rate = D_2O loss rate (kg/s)
M	Total D_2O circulating mass (kg)
N_r	Tritium concentration in replacement D_2O
R	Reaction rate, $CN_D\phi\sigma a$
C	Mass fraction of D_2O in core
N_D	Deuterium concentration in system (atoms of D/kg)
ϕ	Thermal neutron flux (n/cm^2s)
σ	Deuterium thermal neutron capture cross section (cm^2)
a	Station capacity factor
t	Station operating time (s)
L	LPCE system D_2O feed flow rate (mole/hr)
L_{in}	LPCE system internal D_2O feed flow rate (mole/hr)
D	LPCE system D_2 flow rate (mole/hr)
V	Internal vapor flow rate (mole/hr)
T	Temperature ($^{\circ}C$)
P	Pressure (kPa)
DF_{CD}	Detritiation factor of the cryogenic distillation system
η_c	Efficiency of a catalyst bed

N_s	Number of theoretical stages in a hydrophilic bed
N_{sec}	Total number of sections within the LPCE columns
z	Tritium mole fraction in D_2O liquid (mole/kg)
x	Tritium mole fraction in D_2 (mole/kg)
y	Tritium mole fraction in D_2O vapor prior to a hydrophilic bed (mole/kg)
y'	Tritium mole fraction in D_2O vapor after a hydrophilic bed (mole/kg)
x_{ne}, y_{ne}, z_{ne}	Equilibrium tritium mole fraction in gas, vapor and liquid phase
α	Tritium separation factor
γ	Molar flow rate ratio



Summary

중수를 냉각재와 감속재로 사용하는 가압중수로에서, 삼중수소는 주로 중수의 중성자 포획반응으로 생성된다. 냉각재와 감속재의 삼중수소 농도는 원자로 운전 시간에 따라 증가한다. 월성 1호기의 경우, 상업운전 후 20년이 경과한 2003년 말 기준으로 냉각재와 감속재의 삼중수소농도는 각각 1.75 Ci/kg과 60.5 Ci/kg을 나타내고 있다.

월성원전은 동일부지에 가압중수로가 증가함에 따라 삼중수소가 종사자와 환경에 미치는 영향을 최소화하기 위하여 2005년 말까지 삼중수소제거설비(TRF)를 설치할 계획이다. 동 설비는 월성원전 4개호기의 감속재 삼중수소농도를 10 Ci/kg 이하로 유지하도록 설계되었다.

월성TRF의 삼중수소제거과정은 크게 세 단계로 이루어진다. 첫 번째 단계는 원료중수내에 포함되어 있는 삼중수소가 기체상태로 공급되는 중수소 분자와 교환되는 과정이다. 이러한 촉매교환과정을 액상촉매교환공정(LPCE)이라 한다. 두 번째 단계는 초저온증류공정에 의해 삼중수소의 농도를 높여 삼중수소(T_2)의 흐름을 만들고, 마지막 세 번째 단계에서는 장기보관을 위하여 제거된 삼중수소를 티타늄과 반응시켜 안정한 금속 삼중수소화물을 형성하게 된다. 여기서 삼중수소제거효율은 중수중의 삼중수소 분리를 담당하는 LPCE공정의 온도, 압력, 촉매 효율 등 설계 및 운전변수에 영향을 받는다.

본 연구에서는 LPCE공정의 설계 및 운전변수가 삼중수소 제거효율에 미치는 영향을 알아보았다. 이론적 고찰을 통하여 삼중수소제거효율에 큰 영향이 있는 변수로 온도, 압력, 촉매 효율, 친수층 이론단수, 초저온증류공정의 성능, 반응단수를 선택하였다. 수소동위원소교환반응의 물질수지관계식을 유도하여 LPCE공정을 모사할 수 있는 컴퓨터 프로그램을 개발하였다.

정상운전조건에서의 LPCE공정의 탈삼중수소율은 47로써, 설계요구조진인 35를 만족하는 것으로 나타났다. 또한 설계 및 운전변수를 변화시키면서 삼중수소제거효율을 해석한 결과 LPCE공정의 탈삼중수소율은 압력을 제외한 다른

변수가 증가할 때에 같이 증가하는 것으로 나타났다. 특히, 온도는 촉매의 삼중수소 분리계수와 공정내 중수증기유량을 동시에 변화시켜 타 변수보다 삼중수소 제거효율에 미치는 영향이 더 큰 것을 알 수 있었다.

본 연구의 결과는 월성TRF를 운영할 때, LPCE공정의 삼중수소제거효율을 극대화하는데 활용될 것이다. 또한 본 연구결과를 활용하면 특정계통 또는 기기가 요구된 성능을 발휘하지 못하여 발생하는 전체설비 성능저하에 대한 원인을 효과적으로 파악할 수 있을 것이다.



I. Introduction

1. Tritium

Tritium is the heaviest and only radioactive isotope of hydrogen, which has one proton and two neutrons. It decays to an isotope of helium, releasing a beta particle which has a half-life of 12.32 years (decay rate of 5.626% per year). The maximum beta particles emitted during decay have energies up to 18.6 keV. The average energy emitted per decay is 5.7 keV. Gaseous T₂ at room temperature tends to form HT by a reaction with gaseous hydrogen if present. The vaporized tritium, HTO, is formed easily and is the most commonly encountered form of tritium in the environment (Sinclair, 1979).



2. Health effects

A beta particle with energy of less than 70 keV cannot penetrate the dead outer layer of the skin. The maximum range of beta particles emitted by tritium is about 6 μm in tissue. Therefore, tritium does not pose an external radiation hazard, but it poses an internal hazard, when taken into the body (Sinclair, 1979).

Tritium may enter the body by inhalation, absorption through the skin, and ingestion. The first two are the most frequent forms of intake in the workplace. After intake, tritiated water can replace ordinary water in human cells, approximately 70% of the soft tissue in the human body is water. Once in living cells, tritium can replace hydrogen in the organic molecules in the body. Despite tritium's low

radiotoxicity in a gaseous form and its tendency to pass out of the body rather rapidly as water, its health effects are important due to its property of being chemically identical to hydrogen (Zerriffi, 1996). Once distributed, 97% of tritium taken in remains as HTO, while 3% is converted to organically bound tritium (OBT). HTO is retained with a biological half-life of 10 days, and OBT is retained with the biological half-life of carbon, which is 40 days. The dose to adults resulting from an intake of HTO, based on the HTO model, is 2.0×10^{-11} Sv/Bq, is recommended in the guide for intakes of tritiated water (CNSC, 2003). High internal dosage of tritium in the body is possibly associated with leukemia, blood disorders, and testicular cancer. One major concern is that incorporation of tritium into DNA may result in undesirable genetic or somatic effects (Sinclair, 1979).

3. Tritium in the environment



Tritium is generated naturally by a reaction between the cosmic rays oxygen and the nitrogen, hence; tritium is produced artificially by a nuclear reactor, nuclear detonation or other industrial facilities, such as a fuel reprocessing plant. Tritium had been an ubiquitous contaminant produced by atomic energy programs. The worldwide inventory of natural tritium due to cosmic ray interactions is estimated to be 70 MCi; corresponding to a production rate of 4 MCi/yr. The average concentration of tritium in environmental waters due to a natural tritium production in the atmosphere by cosmic rays is 3.2 to 16 pCi/kg. Tritium is produced copiously by the nuclear weapons tests that took place in the atmosphere in the 1950s and 1960s. However, it has diminished substantially as a result of the limited nuclear test ban agreement, thus, tritium production by nuclear power reactors has been increasing rapidly and will in time become the dominant source (Sinclair, 1979).

4. Tritium production in NPPs

Tritium is produced both by nuclear fission and by neutron activation reactions such as ${}^2\text{H}(n, \gamma)\text{T}$, ${}^3\text{He}(n, p)\text{T}$, ${}^6\text{Li}(n, \alpha)\text{T}$, ${}^{10}\text{Be}(n, 2\alpha)\text{T}$, etc. In light water reactor, tritium is mainly generated by a ternary fission in a nuclear fuel and by neutron reactions with light elements such as boron and lithium in the control rods or poison in a coolant. On the other hand, the use of heavy water as a moderator and heat transport media in Pressurized Heavy Water Reactors (PHWRs) permits a greater burnup of the natural uranium oxide fuel, but results in the production of tritium by a neutron activation of the deuterium to a degree far in excess of that produced in a fuel (Sinclair, 1979). The amount of tritium generated in a PHWR by a neutron capture reaction of deuterium in heavy water exceeds that in a LWR by almost 100 times (Kwak and Chung, 1997).



5. Tritium in the Wolsong NPPs

Tritium activity of CANDU-6 plants, a typical PHWR with heavy water of about 500 tons in the coolant and moderator system, is a function of the reactor power level and the irradiation time. The tritium concentration can be estimated by the following equation by assuming there is no mixing between the coolant and the moderator and a tritium displacement. The tritium activity is given by

$$A_T = A_0 e^{-(\lambda + L/M)t} + \left(\frac{MR + LN_r}{M + L/\lambda} \right) (1 - e^{-(\lambda + L/M)t}) \quad (1.1)$$

The equilibrium tritium activity in the coolant and the moderator is 1.95 Ci/kg, 88.0 Ci/kg respectively (KEPCO, 1995).

Most of the tritium remains in the moderator and heat transport media, not in the fuel, and has a potential for a release to the environment by leakages from the equipments. It can be expected that the amount of tritium released to the environment increases with the age of plant and any additional units in operation. Tritium inventory of the heavy water systems increase with the operating time of the plant as in Fig. 1, however the environmental release rate is dependent not only on the operating time but also on the management of the system, for example, an improvement of the system or use of leaktightness equipments. There have been lots of efforts to reduce the tritium release to the environment from the Wolsong unit 1 since the mid 1990s by improving the systems and optimizing the operating procedures. But the presence of highly active tritium in the systems has been a potential danger to the employees and the environment. The tritium release rate to the environment of the Wolsong NPPs is shown in Fig. 2. In addition, the tritium environment release rate corresponds to the radiation dose rate of the workers as in Fig. 3.

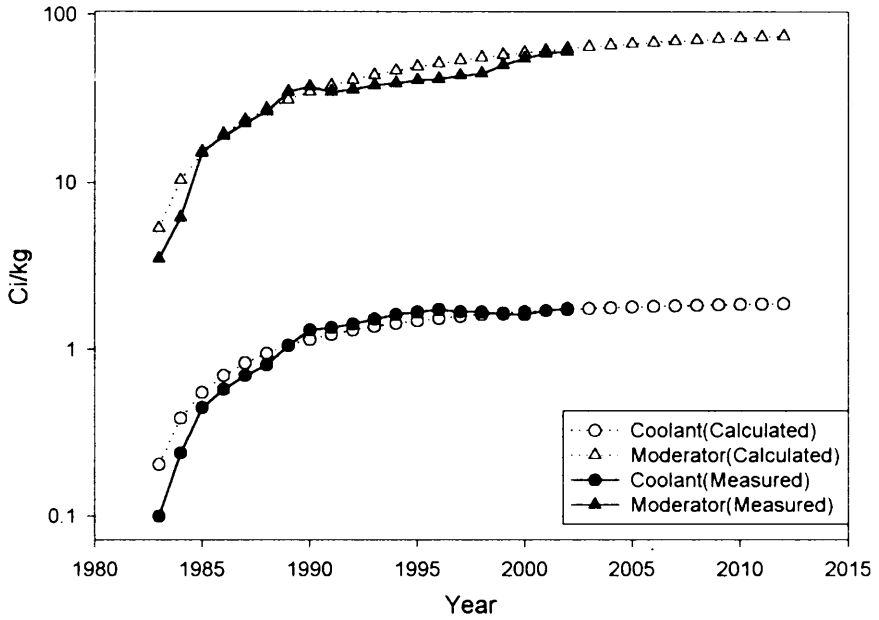


Figure 1. Tritium activities in the Wolsong unit 1.

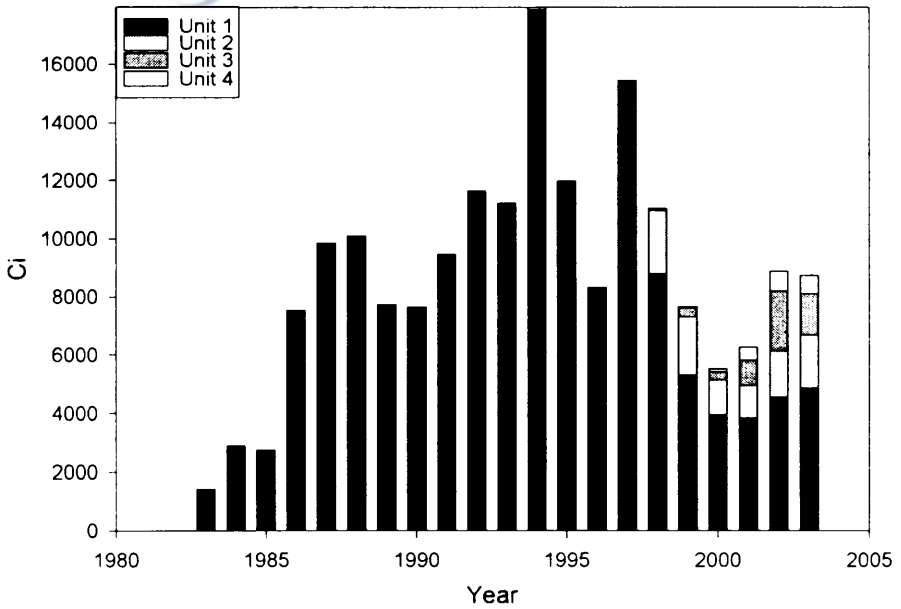


Figure 2. The tritium release rate to the environment from the Wolsong NPPs.

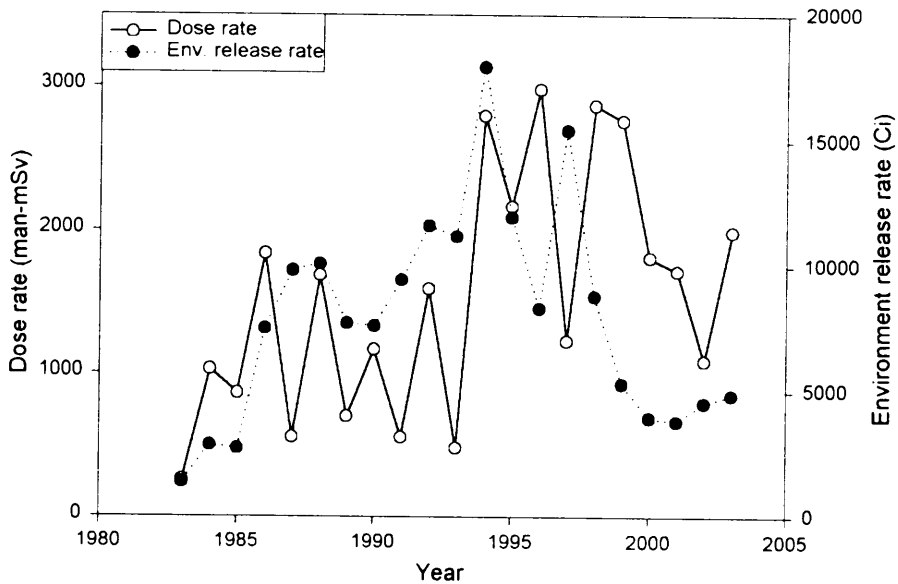


Figure 3. Radiation dose rate of workers vs. the environment release rate of the Wolsong unit 1.



The presence of tritium in the heavy water systems of the CANDU plants is a major source of the radiation doses to the operating personnel and the environment. For preventing radiation hazards, a tritium reduction or removal from the systems was suggested in the early 1970s. Canada, the developing country of the CANDU reactor, has been operating the Darlington tritium removal facility since 1988. Korea, which has 4 units of CANDU at the Wolsong site, is now constructing the Wolsong tritium removal facility (WTRF). The tritium inventory of the Wolsong NPPs will reach about 44.1 MCi by 2005, and it will decrease with the WTRF operation at about 10 MCi by 2013. The WTRF is designed to maintain the tritium activity in the moderator to about 10 Ci/kg (KHNP, 2001). However, the tritium removal efficiency of the WTRF depends heavily on the design and operating variables such as the operating temperature and pressure, catalyst efficiency, etc. Therefore, it is necessary to investigate their relations for a safe and reliable operation of the facility between the those variables and the performance of the WTRF.

II. Wolsong Tritium Removal Facility (WTRF)

1. General description of the WTRF

Wolsong unit 1 is the second nuclear power plant in Korea after Kori unit 1, and it started its commercial operation on April 22, 1983. At that time, there was not enough consideration given to the tritium hazards, even to the operating personnel. During the safety inspection of the Wolsong unit 1 by the regulatory agency in 1986, it was recommended that the Korea Hydro and Nuclear Power company (KHNP) establish a long-term plan for exceeding the tritium activity criterion in the heat transport media by 2 Ci/kg.

For the increased potential of a radiation hazard from the tritium accumulation at the Wolsong site caused by the operation of more units, the government, i.e. 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 on the workers and the environment from the Wolsong NPPs to as low as reasonably achievable (ALARA), as a condition to the construction permit of the Wolsong unit 3 and 4. In regards to this, the KHNP submitted the construction plan of the WTRF to the government, and the WTRF project was launched and as a result the specific tritium handling technologies and systems were developed and designed.

The WTRF is currently under construction with the completion date of the end of 2005. It is designed to remove tritium from the tritiated heavy water in each of the existing four CANDU units at the Wolsong site. A general design and performance specification for the WTRF is given in Table 1. This design specification allows to maintain the Wolsong four units moderator concentration at

about 10Ci/kg, when operated on a 24h/day basis and at the specified availability factor (KHNP, 2001).

Table 1. General design parameters of the WTRF.

D ₂ O feed isotopic mole %	≥ 99.8% D ₂ O (99.82 wt% D ₂ O)
D ₂ O feed tritium concentration	10-60 Ci/kg
D ₂ O processing rate	100 kg/hr
Minimum tritium extraction efficiency per pass	97% (detritiation factor of 35)
Tritium by-product	≥ 99.0% T ₂
Service life	40 years
Availability	80%

The WTRF operating mode varies with the heavy water feed tritium concentrations of units 1-4 at the beginning of operations. For the Wolsong unit 1, it will take about 4-5 years to reduce the tritium concentration to under 10 Ci/kg for the moderator as the WTRF is expected to process the tritiated heavy water with a feed rate of 20 kg/hr for each unit. The estimated amount of the removed tritium is expected to be 2,576 atomic mole-T by 2013 (Song et al., 2003).

The total tritium inventory of the Wolsong units 1-4 and the environment release rate will be decreased exponentially with the operation of the WTRF. They will reach an equilibrium level after a 7-year operation as shown in Fig. 4. It was assumed that the reactor service life is 30 years.

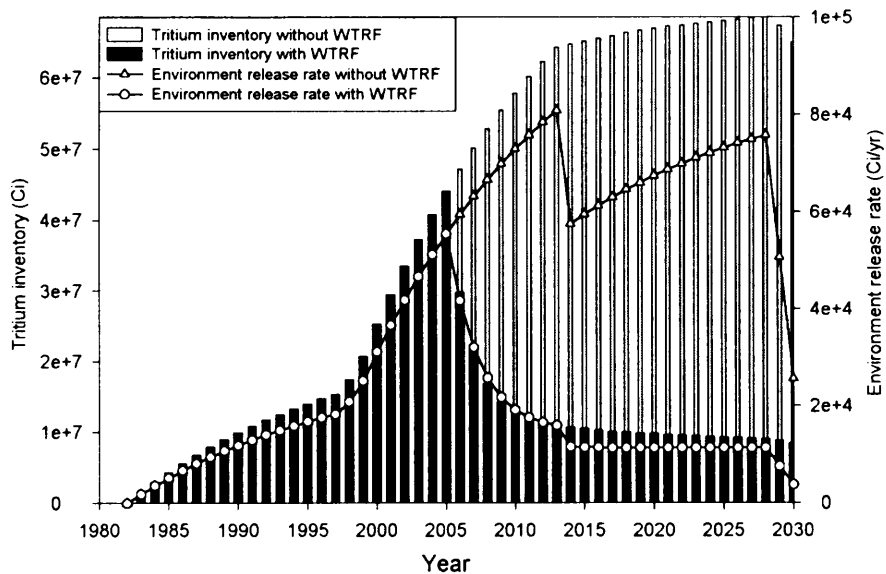


Figure 4. The change of the tritium inventory and the environment release rate.

The detritiation process of the WTRF is made up of three parts as shown in Fig. 5. The LPCE system is adapted to the facility for a tritium separation from the heavy water feed. Except for the LPCE system, however, the overall design is based on the AECL's experience with detritiation and tritium handling technologies, developed and proven over the past decades. The first part involves the transfer of tritium from a heavy water molecule to a deuterium molecule by hydrogen isotopic exchange reaction over a catalyst. This process is termed as a Liquid Phase Catalytic Exchange (LPCE). The second part of the process is the enrichment stage. This stage concentrates the tritium by a 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 a secure, long-term storage (Paek et al., 2002).

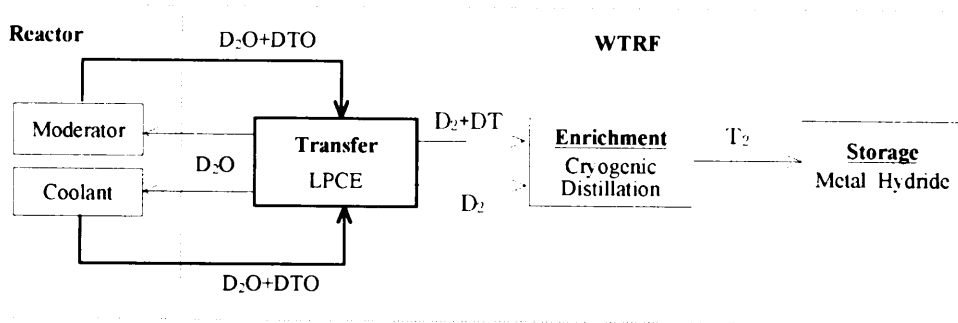


Figure 5. Detritiation process in the WTRF.

2. Detritiation process description of the LPCE system

The LPCE system is designed to reduce the tritium content of the tritiated heavy water feed from the moderator with a removal efficiency of 97% in a single pass (tritium concentration in the heavy water product is 1/35 of the tritium in the tritiated heavy water feed).

The tritiated heavy water feed from moderator of unit 1 has a tritium concentration of up to 60 Ci/kg. The tritiated heavy water feed is designed to be 100 kg/hr, while the internal heavy water flow of the LPCE column should be added to the condensed water returning to the top of the column. The detritiated heavy water product from the LPCE system shall be at a rated flow of 100 kg/hr.

The LPCE system consists of two packed-bed columns as in Fig. 6 and is used to remove the tritium from the tritiated heavy water to the deuterium gas phase. The heavy water is flowing in a counter current to and in direct contact with the deuterium gas in the LPCE columns.

The feed is first heated to 70 °C in the circulation heater prior to entering the top section of the first column. The heavy water is flowing downward and in contact with the flowing upward deuterium gas in the catalyst beds and mass transfer packing.

The heavy water leaving the bottom of the first column is pumped to the top of the second column. Prior to the entering the second column, the heavy water is heated and maintained at a temperature of 70 °C. The detritiated heavy water leaves at the bottom of the second column (KHNP, 2001).

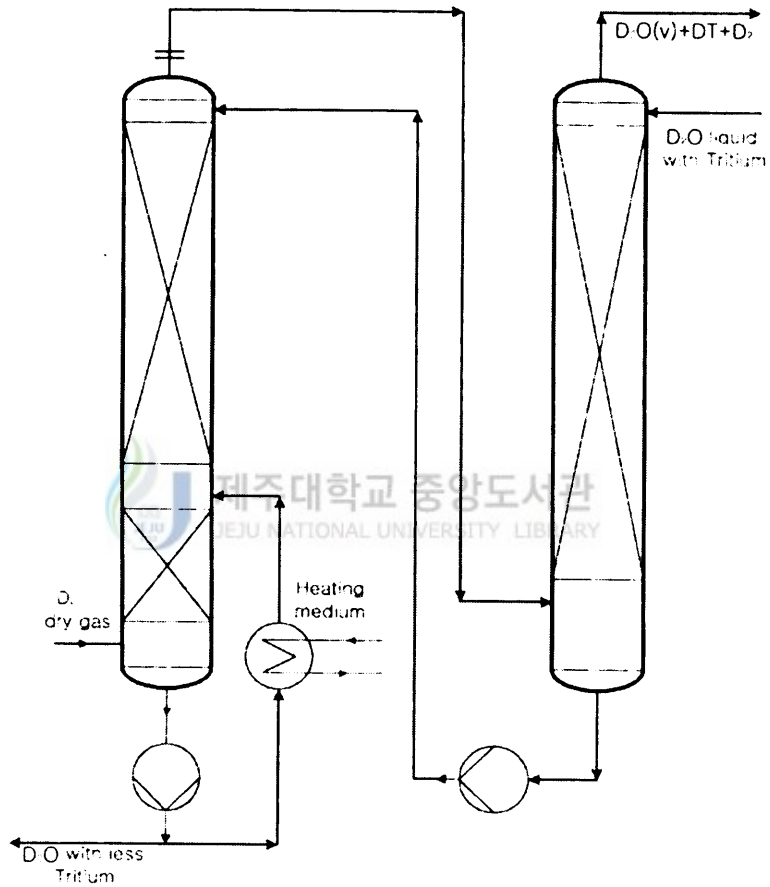
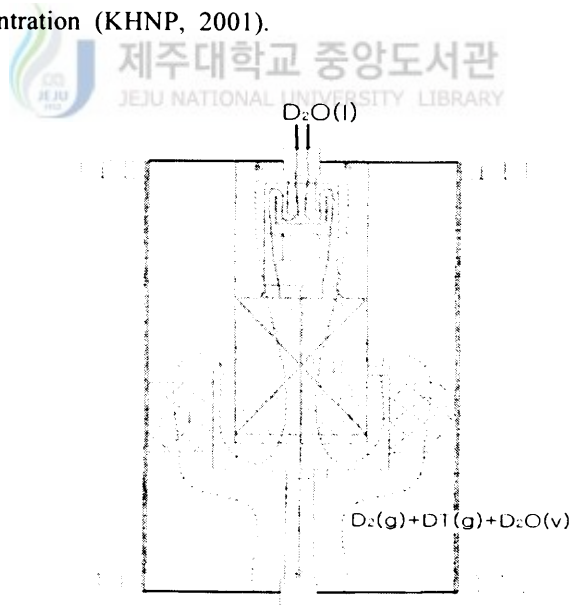


Figure 6. Flow diagram of the LPCE system.

The newly developed LPCE reaction beds are a multiple-tube type, the concentric cylinder consists of two separated catalytic bed and hydrophilic bed. The catalyst bed is installed on the outside of the center of the column as in Fig. 7 (Paek et al., 2002).

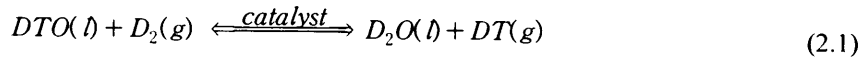
The deuterium gas enters the bottom section of the second LPCE column and is humidified with the heated circulating detritiated heavy water. The saturated heavy water vapor leaving the top of the column is condensed in the LPCE overhead condenser with chilled water. The LPCE system is designed for a heavy water feed rate of 163 kg/hr, which covers a feed of 100 kg/hr plus a condensate return of 63 kg/hr. The first column is operated at a temperature of 70 °C and a pressure of 120 kPa(a), while the second LPCE column is operated at a temperature of 70 °C and a pressure of 145 kPa(a). It is assumed that the vapor with the gas flow is a plug flow when passing through the catalyst bed. For this plug flow, the tritium of the vapor cannot be transferred to the deuterium gas over equilibrium concentration (KHNP, 2001).



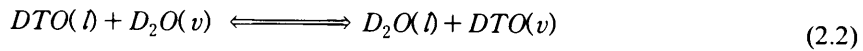
1. Catalyst bed 2. Sulzer packing (Hydrophilic bed)

Figure 7. Structure of a section of the LPCE column.

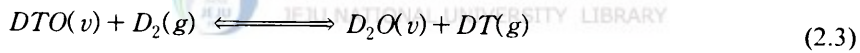
The overall mechanism of the tritium transfer from the heavy water to the deuterium gas in the LPCE system can be represented by the following equation (Paek et al., 2002).



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



The catalytic reaction of tritium in the vapor phase is shown below.



III. Modeling of the LPCE system

1. The flow of reaction materials in the LPCE system

A schematic diagram of the LPCE system is illustrated in Fig. 8. The figure 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 a hydrophobic platinum catalyst and a hydrophilic bed. The bottom section of the column contains a saturator to humidify the deuterium gas returning from the cryogenic distillation system. Tritiated heavy water is fed to the top of the column and allowed to flow downward counter-currently to a rising stream of the heavy water vapor (KHNP, 2002).

The tritiated heavy water feed flow L with a tritium mole fraction z_f is pumped to the LPCE system. This fresh feed is mixed with the condensed water, prior to it entering the top section (n -th section) of the LPCE column. Total heavy water feed flow L_{in} with a tritium mole fraction z_{n+1} enters the hydrophilic bed in the n -th section. Saturated vapor flow V with a tritium mole fraction y_n also enters the hydrophilic bed from the catalyst bed in the n -th section. Tritium is transferred from liquid water to a water vapor in the hydrophilic bed just like a distillation column for a tritiated heavy water separation. The mass transfer step involves the transfer of DTO from the liquid phase to the vapor phase.

The liquid water flow L_{in} with a tritium mole fraction z_n leaves the hydrophilic bed in the n -th section. The vapor flow V with a tritium mole fraction y_0' also leaves hydrophobic bed from the n -th section with deuterium gas. The vapor flow V

with a tritium mole fraction y_{n-1}' and the deuterium gas flow D with a tritium mole fraction x_{n-1} enter to the catalyst bed in the n -th section concurrently from the $n-1$ -th section below. After catalytic isotopic exchange reaction between the tritiated heavy water vapor and the deuterium gas, the vapor flow V with a tritium mole fraction y_n and the deuterium gas flow D with a tritium mole fraction x_n leave the catalyst bed (KHNP, 2002).

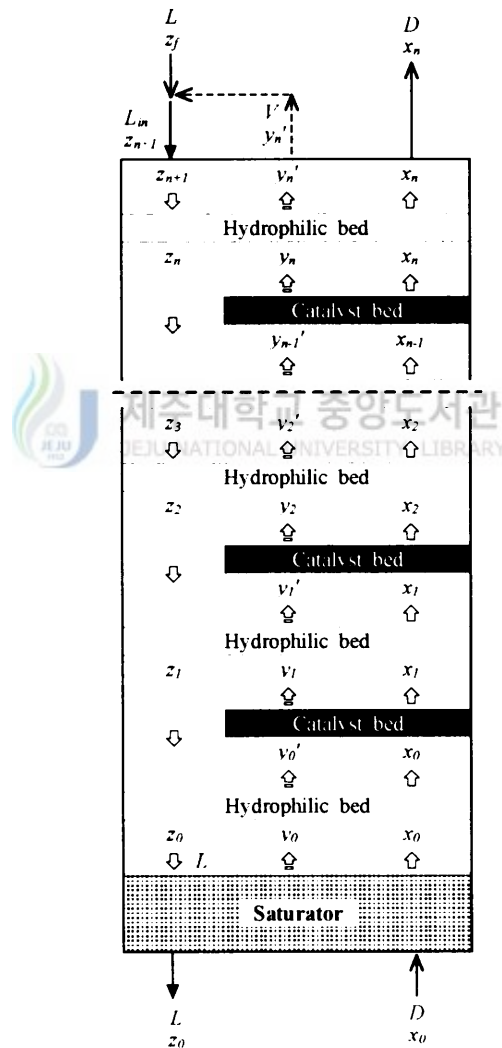


Figure 8. A schematic representation of the LPCE process with n sections.

2. The catalyst bed

Efficiency of the catalyst bed in the n-th section, η_c is defined by

$$\eta_c \equiv \frac{y_n - y_{n-1}'}{y_{ne} - y_{n-1}} = \frac{x_{n-1} - x_n}{x_{n-1} - x_{ne}} \quad (3.1)$$

where x_{ne} and y_{ne} are the equilibrium tritium concentrations between the vapor and the liquid phase, respectively (Ryohei et al., 1982). Maximum value of η_c is 1.0 when the isotope exchange reaction reaches an equilibrium at given tritium concentrations in the water vapor and the deuterium gas phase.

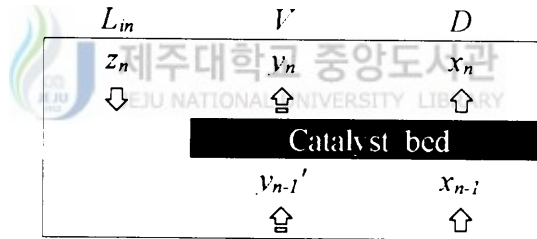


Figure 9. Reaction materials flow diagram in a catalyst bed.

The separation factor α_g , between the water vapor and the deuterium gas is defined in terms of the tritium to deuterium atom ratios in the two species at an equilibrium. At low tritium concentrations, α_g is equal to Eq. (3.2).

$$\alpha_g = \frac{y_{ne}}{x_{ne}} \quad (3.2)$$

Equation (3.1) combined with Eq. (3.2) gives the following Eq. (3.3).

$$y_n = \alpha_g x_n + (1 - \eta_c)(y_{n-1}' - \alpha_g x_{n-1}) \quad (3.3)$$

From a component material balance for tritium in the catalyst bed in section n ,

$$y_n = \gamma_g (x_{n-1} - x_n) + y_{n-1}' \quad (3.4)$$

$$x_n = x_{n-1} - \frac{y_n - y_{n-1}'}{\gamma_g} \quad (3.5)$$

where γ_g is defined by a molar flow rate ratio of deuterium gas to a water vapor and equal to a partial pressure ratio, that is, $\gamma_g \equiv D/V = P_{D_2}/P_{D_2O}$. The deuterium gas of the molar flow rate D returning from the cryogenic distillation system is saturated with heavy water vapor at a temperature of 70 °C and a pressure of 145 kPa(a), which is nominal operating conditions of the saturator at the bottom section of the column. The operating pressure of the saturator P_{sys} is the sum of the partial pressures, that is, $P_{sys} = P_{D_2} + P_{D_2O}$. Then, γ_g can be expressed by

$$\gamma_g \equiv D/V = P_{D_2}/P_{D_2O} = (P_{sys} - P_{D_2O})/P_{D_2O} \quad (3.6)$$

The partial pressure of the heavy water P_{D_2O} (kPa), can be obtained by the following regressed equation which is a function of the temperature in degrees Kelvin, T (Van Hook, 1967).

$$P_{D_2O} = 10^{[7.01448 - (1544.32 + 124209/T)/T]} \quad (3.7)$$

From Eqs. (3.3) and (3.5), the tritium mole fraction of the deuterium gas stream leaving the catalyst bed from the n -th section, x_n is (KHNP, 2002)

$$x_n = \left(1 - \frac{\eta_c \alpha_g}{\alpha_g + \gamma_g}\right) x_{n-1} + \left(\frac{\eta_c}{\alpha_g + \gamma_g}\right) y_{n-1} \quad (3.8)$$

From Eqs. (3.4) and (3.8), the tritium mole fraction of the heavy water vapor stream leaving the catalyst bed from the n-th section, y_n is

$$y_n = \left(\frac{\alpha_g \gamma_g \eta_c}{\alpha_g + \gamma_g}\right) x_{n-1} + \left(1 - \frac{\gamma_g \eta_c}{\alpha_g + \gamma_g}\right) y_{n-1} \quad (3.9)$$

3. The hydrophilic bed

The number of theoretical stages per bed (N_s) is introduced, for estimating the performance of the hydrophilic bed, instead of the tritium extraction efficiency of a bed. This is suggested by the hydrophilic bed manufacturer as an item of the performance estimation, because the efficiency is usually over 100% in a counter-current vapor-liquid separation. With an assumption of a straight equilibrium and operating lines, N_s can be expressed by the following equation when tritium mole fraction of the heavy water vapor streams entering the bottom and leaving the top of the hydrophilic bed are y_{in} and y_{out} , respectively (Ling, 1971). N_s is not necessarily an integer but a real number.

$$\frac{y_{in} - y_{out}}{y_{in} - y_{out}^*} = \frac{(L/mV) - (L/mV)^{N_s+1}}{1 - (L/mV)^{N_s+1}} \quad (3.10)$$

Here, y_{out}^* is the tritium concentrations in the vapor phase which would be in equilibrium with the liquid phase, L and V are the molar flow rates of the liquid

and vapor stream, m is the slope of the equilibrium line equals to a tritium concentration ratio of the vapor to the liquid phase at an equilibrium which is one of the parameters that represents the characteristics of the hydrophilic bed. The slope of the equilibrium line is steep at a high efficient bed.

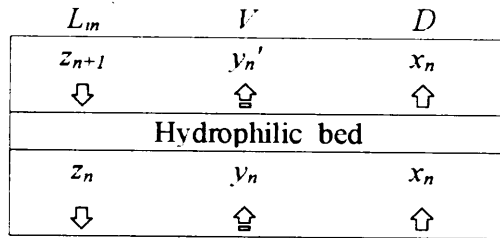


Figure 10. Reaction materials flow diagram in a hydrophilic bed.

The separation factor α_r between the liquid and the vapor is defined in terms of the tritium to deuterium atom ratio in the two species at an equilibrium. At low tritium concentrations, α_r is equal to Eq. (3.11) for the mass transfer step in section n .

$$\alpha_r \equiv \frac{z_{ne}}{y_{ne}} = \frac{1}{m} \quad (3.11)$$

The above-mentioned separation factors α_r and α_g , are functions of the temperature in degrees Kelvin T only, and given empirically as follows (KHNP, 2002).

$$\alpha_r = \exp(0.066076 - 61.03/T + 14198.4/T^2) \quad (3.12)$$

$$\alpha_g = \exp(0.772 - 676.3/T + 277052/T - 3.1803 \times 10^7/T^3 + 5.0868 \times 10^8/T^4) \quad (3.13)$$

Eq. (3.10) combined with Eq. (3.11) gives the following Eq. (3.14) where γ_l is defined by a molar flow rate ratio of the vapor to the liquid in the column, that is, $\gamma_l = V/L_{in}$.

$$\frac{y_n - y_n'}{y_n - z_{n+1}/\alpha_v} = \frac{\alpha_v/\gamma_l - (\alpha_v/\gamma_l)^{N_s - 1}}{1 - (\alpha_v/\gamma_l)^{N_s + 1}} \quad (3.14)$$

From a component material balance for tritium in the hydrophilic bed,

$$y_n' = y_n - \frac{z_n - z_{n+1}}{\gamma_l} \quad (3.15)$$

When x_{n-1} , y_{n-1}' , z_n are given, x_n , y_n , z_{n+1} , y_n' can be calculated using Eqs. (3.8), (3.9), (3.14) and (3.15). Therefore, the tritium concentrations in all the sections can be calculated in a serial order with the assumption that the operating temperature and pressure, efficiency of the catalyst bed, and the number of theoretical stages per hydrophilic bed are constant in all the sections.

4. Algorithm of the calculation

The detritiation factor of the LPCE system ($DF = z_f/z_0$) and the tritium concentrations x_i , y_i , z_{i+1} , y_i' in an arbitrary section i can be calculated using Eqs. (3.8), (3.9), (3.14) and (3.15) when the flow rate L of the heavy water feed, the tritium mole fraction of the feed water stream z_f , the flow rate of the deuterium stream D , 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} , the efficiency of the catalyst bed η_c , the number of theoretical stages per hydrophilic bed N_s , and the total number of sections N_{sec} are given. The calculation procedures are summarized as follows;

- a) Tritium concentration of the heavy water product z_0 is assumed. z_0 should be less than z_f .
- b) Tritium concentration of the vapor stream leaving the saturator at the bottom of the column y_0' is calculated by a definition of the separation factor α_v .

$$y_0' = z_0 / \alpha_v \quad (3.16)$$

- c) Tritium concentration of the liquid stream leaving the first section z_1 is calculated using the material balance.

$$z_1 = \frac{L \times z_0 + V \times y_0'}{L_{in}} \quad (3.17)$$

- d) Tritium concentration of the deuterium gas stream entering the first section x_0 is assumed. x_0 should be less than $y_0' / \alpha_g = (z_0 / \alpha_v) / \alpha_g$ for the tritium transfer from the heavy water vapor to the deuterium stream.
- e) Tritium concentrations x_1, y_1, z_2, y_1' are calculated by means of Eqs. (3.8), (3.9), (3.14) and (3.15). In the same way, x_2, y_2, z_3, y_2' are calculated and then x_i, y_i, z_{i+1}, y_i' in section i are obtained in a serial order.
- f) If section i is the top of the column, the vapor stream is condensed and mixed with the fresh feed. The calculated value of the tritium concentration of the fresh feed $z_{f,cal}$ can be obtained by a mass balance.

$$z_{f,cal} = \frac{L_{in} \times z_{i+1} + V \times y_i'}{L} \quad (3.18)$$

If the value of $z_{f,cal}$ is greater than that of z_f , i is equal to the number of total sections in the column n .

- g) If the following convergence criterion is satisfied, the calculated values of x_n , y_n , z_{n+1} , y_n' are considered to be a solution set for the assumed value of x_0 .

$$|x_n - x_0 \times DF_{CD}| < \epsilon, \quad 0 < \epsilon \ll 1 \quad (3.19)$$

Steps a) through g) are carried out repeatedly by changing the value of z_0 and x_0 until the calculated value of the number of total sections for the assumed value of z_0 equals the input value N_{sec} . This iteration is performed by using the half-interval method, where z_0 and x_0 are the iterative values.



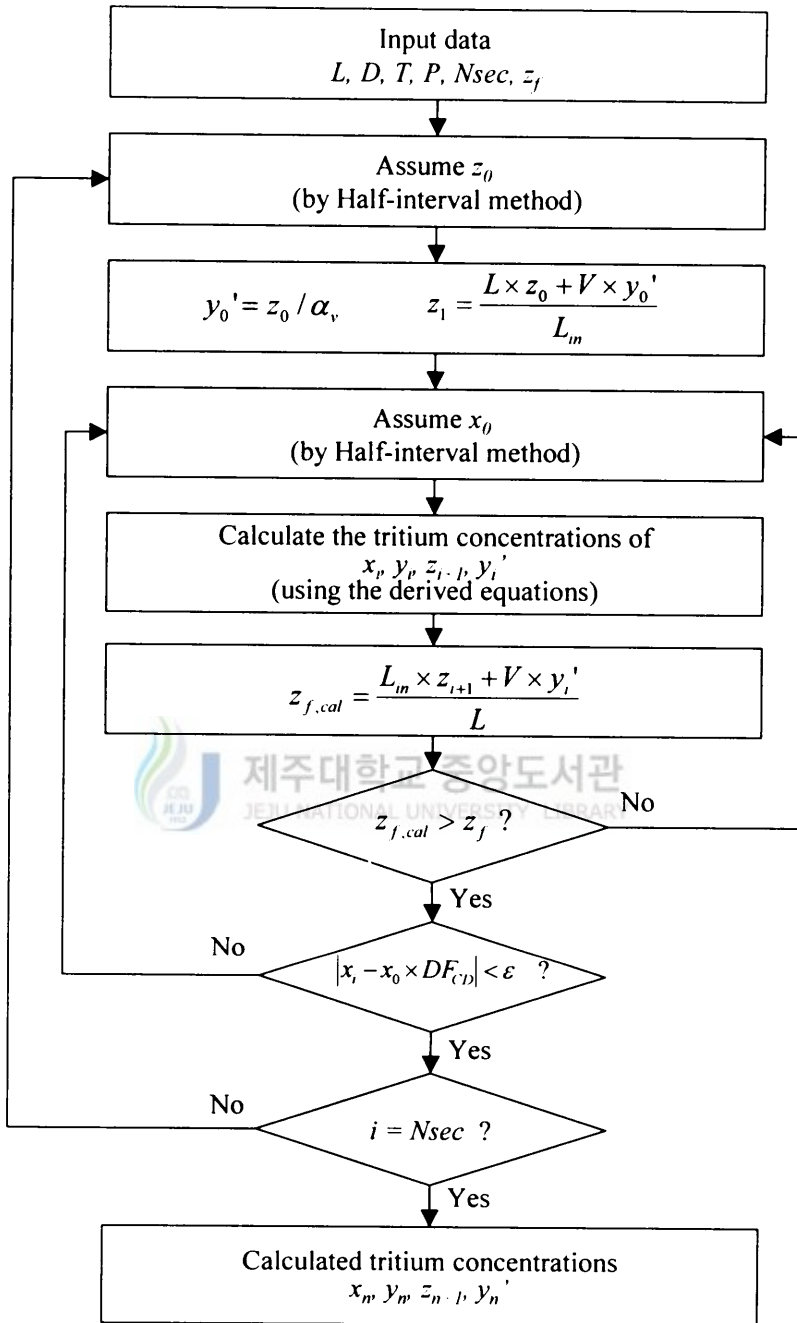


Figure 11. Algorithm of the calculation of the tritium concentrations.

IV. Results and Discussions

In order to investigate the performance of the LPCE system, a computer program was developed based upon the relations between operating and design parameters derived from the mass transfer, catalytic reaction and material balance equations at a steady state. The computer program uses an algorithm that solves the equations step by step and was developed in the FORTRAN language and executed in a double precision as attached in the Appendix.

A parametric study was performed using the computer program to investigate the effects of the design and operating parameters on the detritiation factor of the LPCE system. The design and operating variables were selected in the process of establishing a model for the LPCE system, as they need to be seriously considered from the point of view of the system's performance. The selected design and operating variables were the operating temperature, pressure, catalyst efficiency, number of theoretical stages in a hydrophilic bed, detritiation factor of the cryogenic distillation system and the number of sections of the LPCE column.

The nominal values of the design and operating parameters which were varied in the study, are summarized in Table 2.

Table 2. Nominal operating conditions of the LPCE system

Design and operating parameters	Nominal value
Number of sections in the LPCE columns	55
D ₂ O feed flow rate	100 kg/hr = 5 kmole/hr
D ₂ O feed tritium concentration	10 Ci/kg
D ₂ flow rate	10 kmole/hr
Detritiation factor of the CD system	50
Efficiency of a catalyst bed	0.9
Number of theoretical stages in a hydrophilic bed	2.0
LPCE column operating temperature	343 K = 70 °C
LPCE column operating pressure	145 kPa

Fig. 12 shows the expected tritium atomic mole fraction for each reaction material in a nominal operation of the LPCE system. The detritiation factor of the LPCE system is calculated to be about 47.

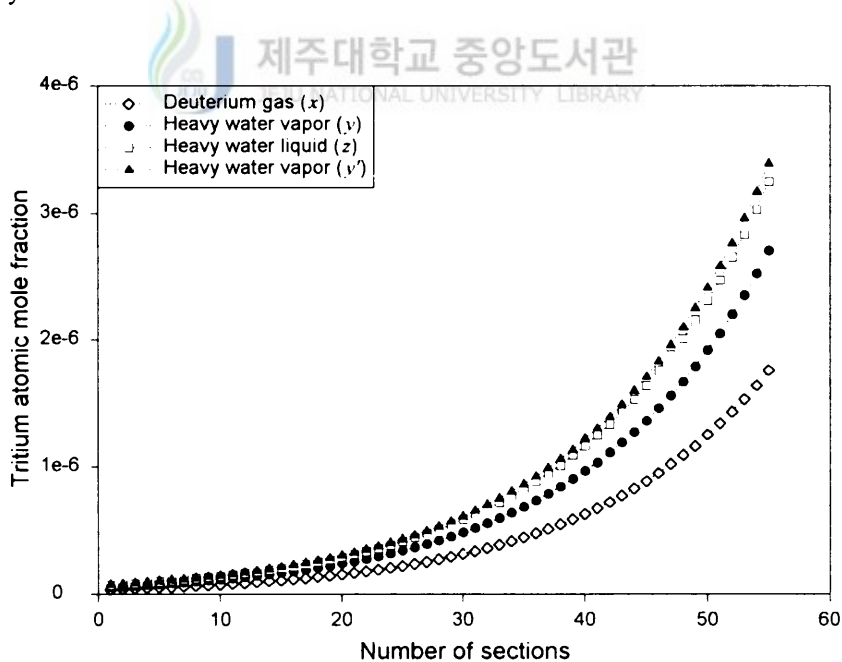


Figure 12. Tritium concentration profiles of each reaction material in the LPCE column.

1. The effects of the temperature

The effect of the operating temperature on the detritiation factor of LPCE system is presented in Fig. 13. The nominal value of the temperature is chosen as 70 °C as designed. During a normal operation of the WTRF, the temperature may fluctuate. Thus in this study the temperature range was arbitrarily selected to be from 55 °C to 75 °C, which includes the temperature variation envelop.

As shown in Fig. 13, the detritiation factor shows a near proportionality to the temperature variation. The curve fitting result for the range of the variation is

$$DF(T) = 1.85T - 81.87, \quad 55 \text{ } ^\circ\text{C} \leq T \leq 75 \text{ } ^\circ\text{C} \quad (4.1)$$

The tritium separation factor (α) and the molar flow rate ratio (γ) are affected by a variation of the temperature. The tritium separation factor is decreased with a temperature increase, and the increasing temperature induced an increasing internal molar flow rate of the vapor. These are activating the tritium transferring from the tritiated feed water to the deuterium gas.

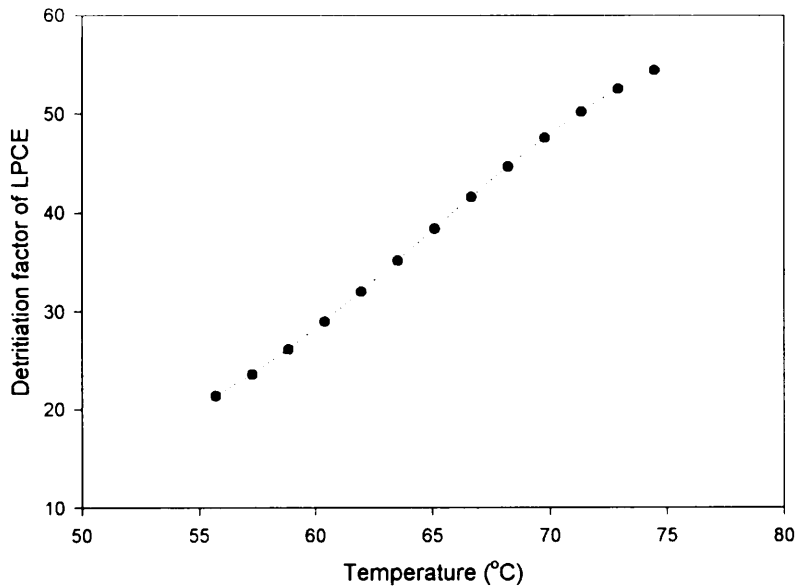


Figure 13. The detritiation factor of the LPCE system as a function of the operating temperature.



2. The effects of the pressure

The operating pressure affects on the detritiation factor of the LPCE system. Fig. 14 shows the variations of the detritiation factor with a system pressure change. The system pressure is expected to be 145 kPa of an absolute pressure at a nominal operating condition, to cover the pressure drop in the LPCE system. However, the system pressure can be changed by the operating conditions. The system pressure range was arbitrarily selected to be from 110 kPa to 200 kPa.

The detritiation factor is in an inverse proportion to the pressure increase as shown in Fig. 14. The curve fitting result for the range of variation is

$$DF(P) = -0.233P + 83.63, \quad 110 \text{ kPa} \leq P \leq 200 \text{ kPa} \quad (4.2)$$

The change of the pressure affects the molar flow rate of the heavy water vapor. If the pressure is decreased, the heavy water vapor flow rate is increased. The variation of the molar flow rate (V) occurs at the molar flow rate ratio (γ) of the isotopic exchange materials in the LPCE column. Heavy water vapor is a media of the tritium transferring from the tritiated heavy water feed to the deuterium gas.

The increased vapor flow rate can remove more tritium from the heavy water feed. This results in the increasing of detritiation factor of LPCE.

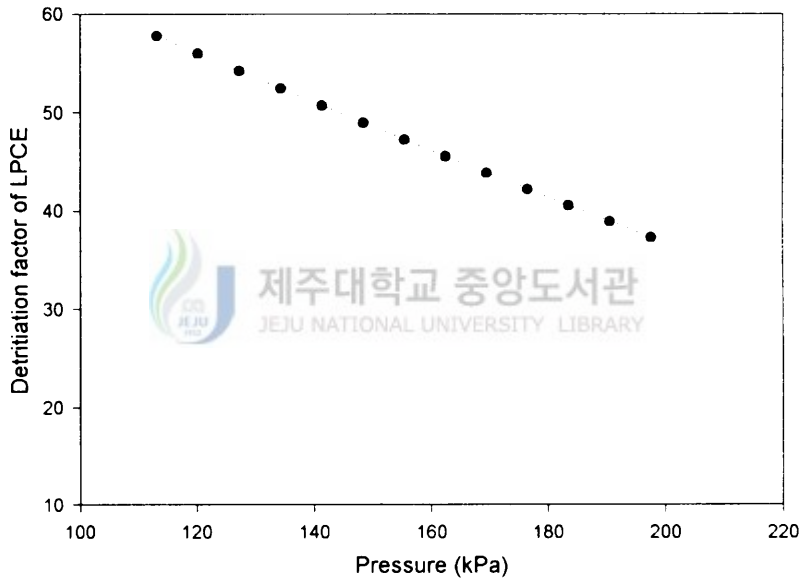


Figure 14. The detritiation factor of the LPCE system as a function of the operating pressure.

3. The effects of the catalyst efficiency

A hydrophobic platinum catalyst supported on the styrene-divinyl-benzene copolymer is adopted for the tritium transferring from the heavy water vapor to the deuterium gas by catalytic exchange reaction. The definition of the catalyst efficiency is the ratio of the tritium concentration of the heavy water vapor to the deuterium gas at the exit of one section of the catalyst bed of one section. The catalyst efficiency is affected by the temperature variations, because an increased temperature accelerates the tritium separative reaction velocity between the heavy water vapor and the deuterium gas. Also, it depends on the flow rate of the reactional materials, and the physical shape of the catalyst bed such as the height. The catalyst efficiency is difficult to calculate by a combination of some other parameters. In this study, the catalyst efficiency was considered to be an independent variable.

The catalyst efficiency is observed at over 0.9 in the experiment of the pilot plant. However, a deterioration of the catalyst can occur from the WTRF operating time and the environment. The range of the catalyst efficiency was arbitrary selected to be from 0.6 to 1.

The detritiation factor is proportionally increased by an increase of the catalyst bed efficiency as in Fig. 15. The curve fitting result for the range of the variation is

$$DF(\eta_c) = 0.572\eta_c + 30.476, \quad 0.6 \leq \eta_c \leq 1 \quad (4.3)$$

The tritium is naturally transferred between the heavy water vapor and the deuterium gas by the hydrogen isotopic exchange reaction. The catalyst activates the exchange reaction, therefore, a high catalyst efficiency can transfer more tritium.

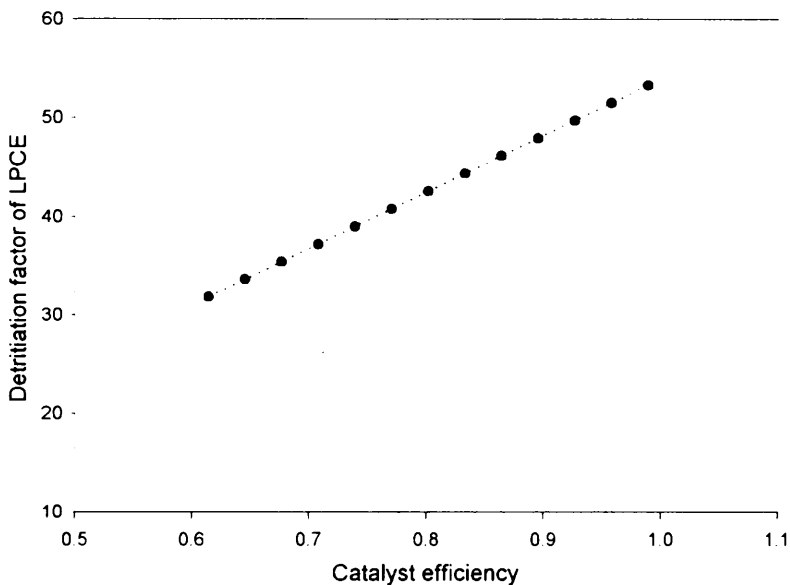


Figure 15. The detritiation factor of the LPCE system as a function of the efficiency of a catalyst bed.



4. The effects of the number of theoretical stages in a hydrophilic bed

The heavy water is flowing down and in contact with the flowing upward heavy water vapor in the hydrophilic bed. The hydrophilic bed consists of the packing of the Sulzer Ltd., which is generally used in heavy water manufacturing plants or an upgrader.

The number of theoretical stages is introduced for the Sulzer packing, instead of the efficiency of the bed. The tritium can be transferred from the heavy water feed to the heavy water vapor at over 100% under the condition of a counter current flow between the liquid and the vapor. The definition of N_s is the ratio of the real

tritium concentration and the theoretical equilibrium tritium concentration per bed. N_s depends on the flow rate of the reaction materials and other parameters, however, N_s is difficult to calculate using these parameters, like the catalyst efficiency. Thus, N_s was considered as an independent variable in this study, and the observed N_s is over 2 in the pilot plant. But a deterioration of the hydrophilic bed can occur from the WTRF operating time and the environment. The range of N_s was arbitrary selected to be from 1 to 3.

The detritiation factor is proportional to the second order of a logarithmic function of N_s as shown in Fig. 16. The curve fitting result for the range of the variation is

$$DF(N_s) = -7.86[\ln(N_s)]^2 + 23.14 \ln(N_s) + 36.38, \quad 1 \leq N_s \leq 3 \quad (4.4)$$

The hydrophilic bed activates the transferring reactions between the heavy water feed and the vapor, therefore, a high N_s of the hydrophilic bed can transfer more tritium.

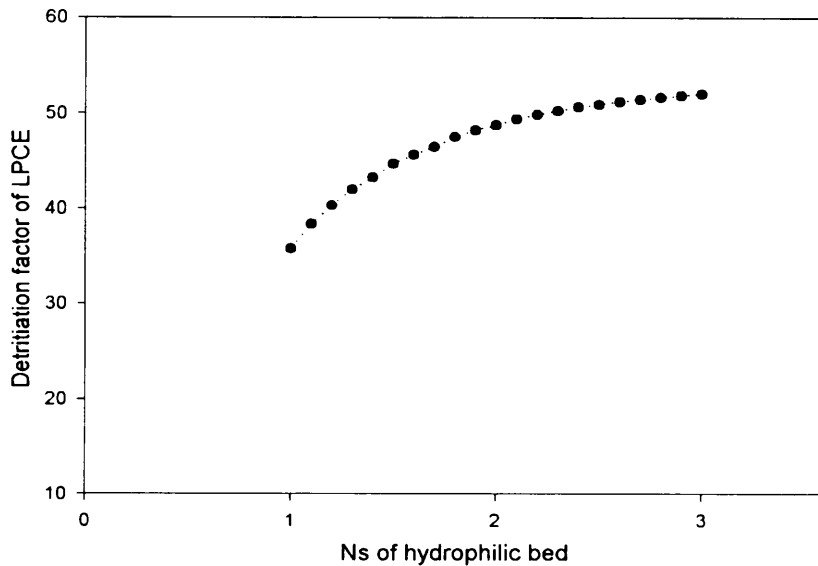
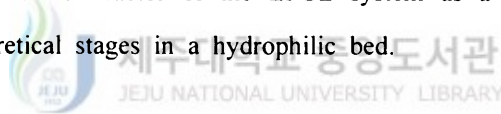


Figure 16. The detritiation factor of the LPCE system as a function of the number of theoretical stages in a hydrophilic bed.



5. The effects of the detritiation factor of the cryogenic distillation system

Deuterium gas is designed to circulate through the LPCE system and the cryogenic distillation system. The tritiated deuterium gas stream enters the cryogenic distillation system, and the detritiated deuterium gas is supplied to the LPCE system. The initial tritium concentration of the supplied deuterium gas to the LPCE columns is important for the performance of the system, since it is the material for the hydrogen isotopic exchange reaction.

The cryogenic distillation system is designed to meet a detritiation factor of over 50. The performance degradation can be caused by the operating environment or

system installation problems, even if the performance has been proved by the AECL's experiences. The range of the detritiation factor of the cryogenic distillation system is arbitrary selected to be from 30 to 60.

The detritiation factor is proportional to the detritiation factor of the cryogenic distillation system as shown in Fig. 17. The curve fitting result for the range of the variation is

$$DF(DF_{CD}) = 0.821DF_{CD} + 6.49, \quad 30 \leq DF_{CD} \leq 60 \quad (4.5)$$

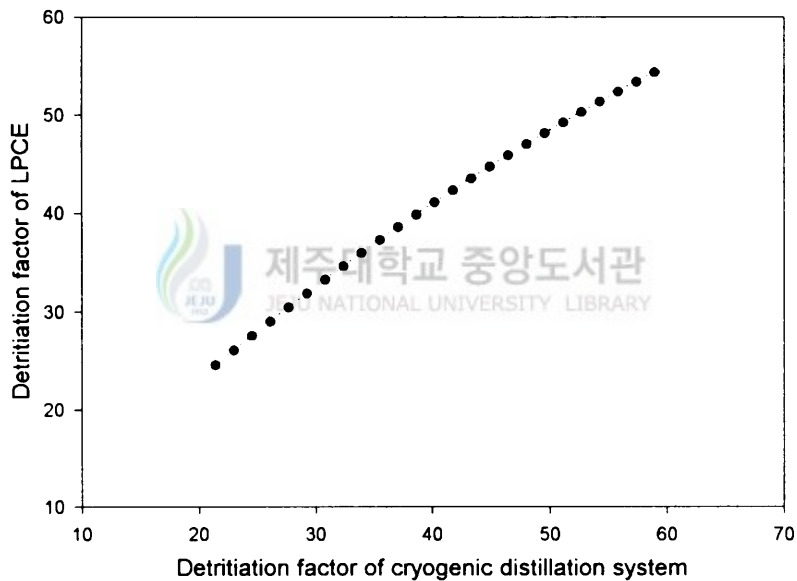


Figure 17. The detritiation factor of the LPCE system as a function of the detritiation factor of the cryogenic distillation system.

6. The effects of the number of sections within the LPCE column

The LPCE column is designed to consist of 55 sections that have a design margin to ensure the performance, i.e. the detritiation factor of 35. The correspondent sections to satisfy the required detritiation factor of 35 are calculated to about 44 sections under a nominal operating condition.

Even though, there is little possibility for manufacturing or installation defects on the LPCE sections, it can be considered that the LPCE system operates with the minimum sections satisfying the required performance. The variance of the total number of sections is arbitrary selected to be from 40 to 55.

The detritiation factor is increased linearly if sections are added, as shown in Fig. 18. The curve fitting result is

$$DF(Nsec) = 1.104Nsec - 12.9, \quad 40 \leq Nsec \leq 55 \quad (4.6)$$

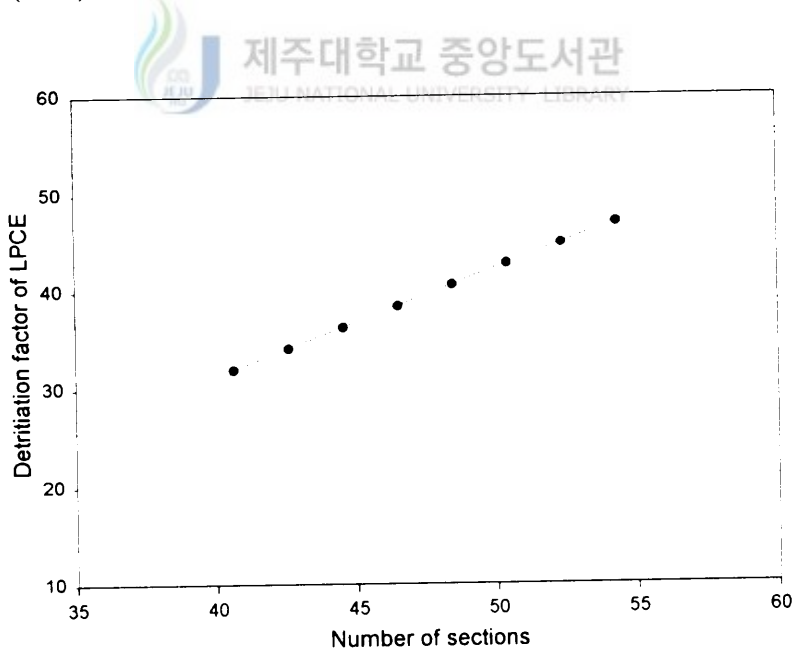


Figure 18. The detritiation factor of the LPCE system as a function of the total number of sections.

7. Assessment of the performance degradation

Prior to declaring the WTRF in-service, a performance verification test will be conducted to confirm that the WTRF process meets the design specifications including those for safety. The LPCE process will be confirmed to be capable of a 97% tritium removal from up to 60 Ci/kg of the tritiated heavy water feed at a flow rate of 100 kg/hr. If the detritiation factor of the LPCE system under nominal operating conditions does not meet the design specification during the performance test, it should be identified as to which one causes the degradation among the components. When it is assumed that the measured detritiation factor of the LPCE system is, for example, 30 under nominal operating conditions and the degradation is caused by only one design parameter with nominal values of the other parameters, it is calculated from the computer program that the efficiency of a catalyst bed is 0.61, the number of theoretical stages in a hydrophilic bed is 0.82, or the detritiation factor of the cryogenic distillation system is 28 approximately. The above parameters were selected to be verified for their performance, because they have a relatively high uncertainty for their performance, in comparison with the other variables.

Fig. 19 and Fig. 20 represent the tritium concentration profiles of the deuterium gas and the heavy water vapor phases in the LPCE column for different design parameters with 30 for the detritiation factor. Two tritium concentration profiles of the deuterium gas phase for a low efficiency of a catalyst bed and a small number of theoretical stages in a hydrophilic bed are nearly the same but distinguishable from that for a low detritiation factor of the cryogenic distillation system as shown in Fig. 19. On the other hand, three tritium concentration profiles of the heavy water vapor phase for low efficiency of a catalyst bed, small number of theoretical stages in a hydrophilic bed, or a low detritiation factor of the cryogenic distillation system are different from each other as shown in Fig. 20.

It appears from these results that the cause of the performance degradation can be cleared by comparing the measured tritium concentration profiles of the heavy water vapor phase with the calculated profiles. The measured tritium concentration profile is obtained by analyzing the heavy water vapor samples. Every fifth section has a sampling line for the gas and vapor streams in the LPCE column.

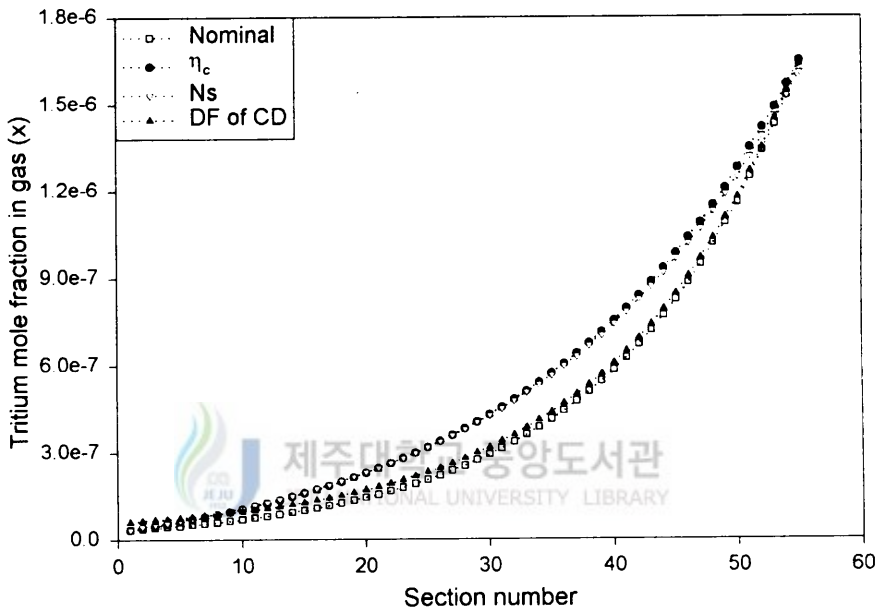


Figure 19. Tritium concentration profiles of the deuterium gas phase in the LPCE column for different design parameters.

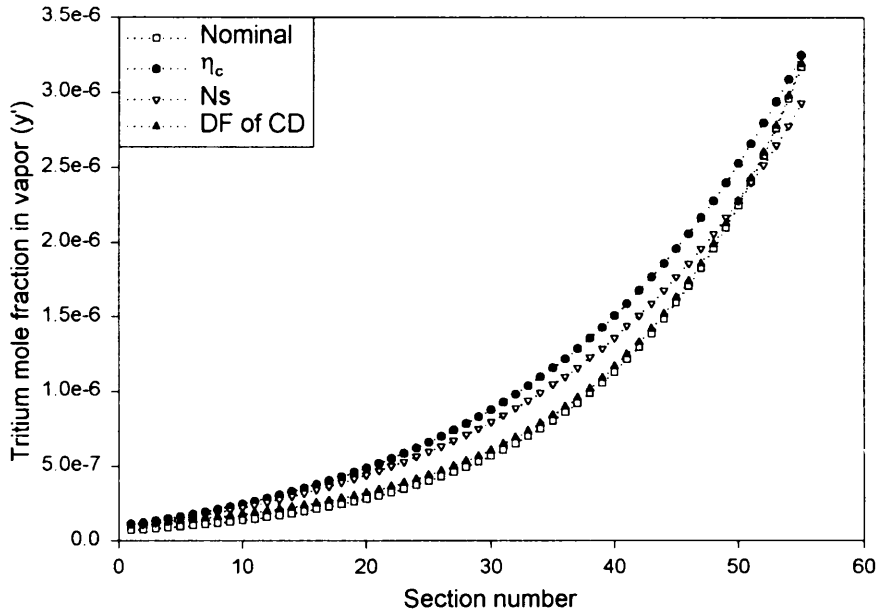


Figure 20. Tritium concentration profiles of the heavy water vapor phase in the LPCE column for different design parameters.



V. Conclusions

A WTRF is under construction at the Wolsong site in order to remove the tritium generated from 4 CANDU NPPs. The function of the WTRF is to remove the tritium from the coolant and the moderator, immobilize the tritium, store it safely on site and return the detritiated heavy water to the reactors. The performance parameters specified for the WTRF are to process 100 kg/hr of tritiated moderator heavy water feed whose tritium concentration is limited to 60 Ci/kg and to remove 97% (detritiation factor of 35) of the tritium per pass.

The most important system which determines the performance of the WTRF is the LPCE system. Design and operating variables of the LPCE system affect the detritiation factor of the WTRF. A theoretical model is suggested for the analysis of the LPCE system. The design and operating variables were selected during the procedures for establishing the model of the LPCE system, that need to be seriously considered from the point of view of the system performance. The selected design and operating variables were the operating temperature, pressure, efficiency of catalyst bed, number of theoretical stages in a hydrophilic bed, detritiation factor of the cryogenic distillation system and the number of sections within the LPCE columns.

The relations between the operating and design parameters were derived from the mass transfer, catalytic reaction and material balance equations at a steady state. A computer program was developed by using the derived equations among the parameters relations and an algorithm that solves the equations step by step.

The LPCE system was proven to have a design margin to ensure a performance reliability that meets the WTRF design specification. The calculated detritiation factor of the WTRF LPCE system is 47 at a nominal condition, which is higher by about 30%, than the 35, which is the requirement value.

The detritiation factor of the LPCE system was increased by increasing the operating temperature, catalyst efficiency, the number of theoretical stages in a hydrophilic bed, the detritiation factor of the cryogenic distillation system, and the total number of sections within the LPCE columns, and by decreasing the LPCE column operating pressure, respectively. The following is a summary of the effects of the above mentioned variables on the performance of the LPCE system.

- a) The temperature affects the separation factor and molar flow rate ratio, the detritiation factor is increased with the temperature increase.
- b) The pressure affects the molar flow rate ratio, and the detritiation factor is increased by decreasing the pressure.
- c) Catalyst efficiency is related to the tritium transferring performance of the catalyst bed from the heavy water vapor to the deuterium gas. The increase in the catalyst efficiency induced an increase of the detritiation factor.
- d) Number of theoretical stages in a hydrophilic bed is a parameter of the tritium transferring performance of the hydrophilic bed from the heavy water feed to the vapor, the detritiation factor is increased with an increase of the number of theoretical stages.
- e) The performance of the cryogenic distillation system affects the initial tritium concentration in the deuterium gas which enters the LPCE column as a reaction material, the purity of the deuterium gas is important for the detritiation factor of the LPCE column.
- f) The total number of sections was considered from the point of an installation of the LPCE sections, the detritiation factor is increased by adding more reaction sections.

The variables worthy of attention are temperature and pressure, because they are relatively easy to vary and have an effect on almost all the components and the other parameters such as the catalyst, saturator, vapor flow rate, separation factor, etc. Also, the temperature has a relatively strong effect on the detritiation factor of the

system, because the temperature affects both the molar flow rate of the vapor and the tritium separation factor. Based upon these results, the operating nominal condition can be re-set to maximize the detritiation factor of the WTRF under a safe operation of the facility.

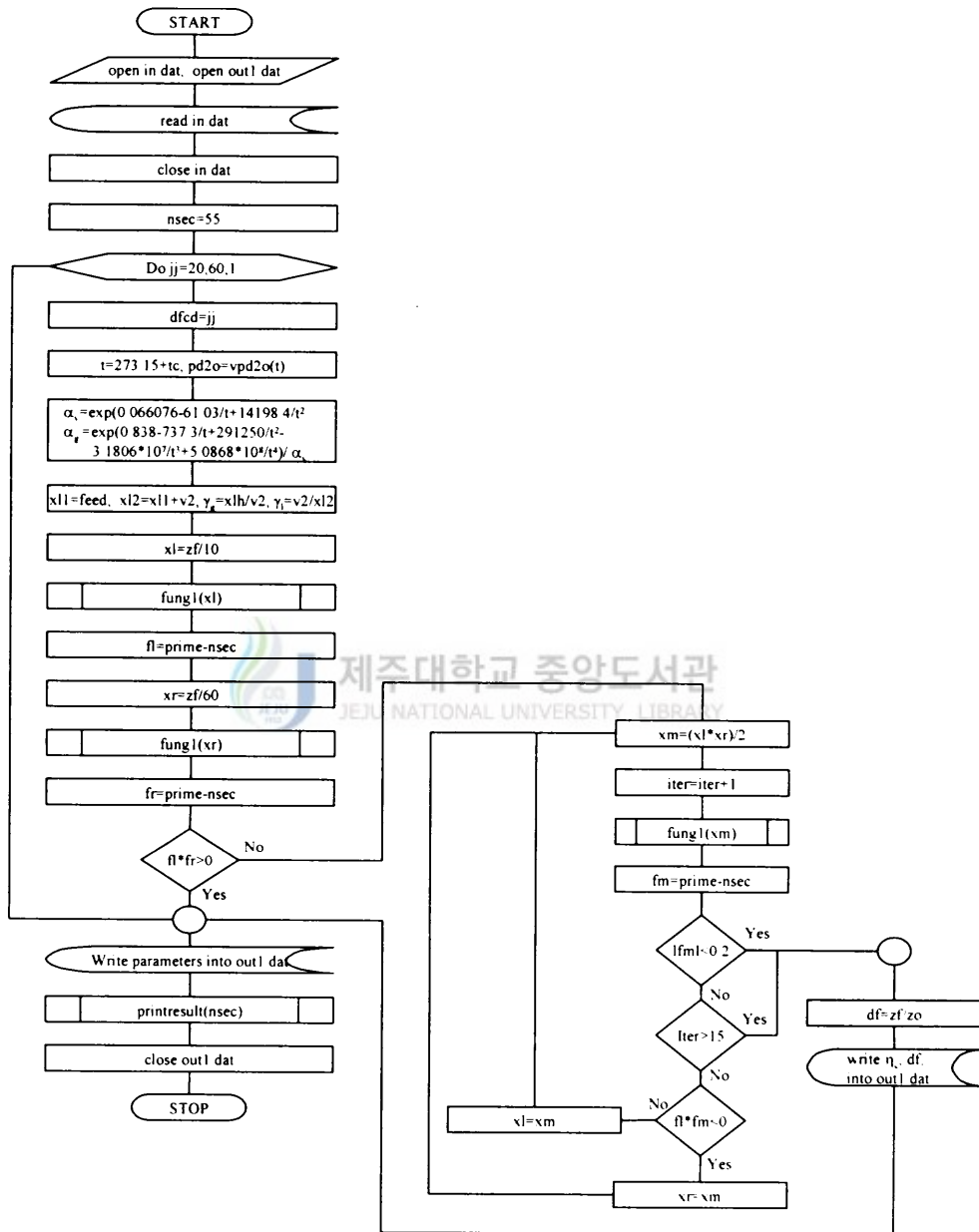
A method of clearing a performance degradation of the facility was studied. A performance degradation can be mainly caused by a low efficiency of a catalyst bed, a small number of theoretical stages in a hydrophilic bed, or a low detritiation factor of the cryogenic distillation system. Tritium concentration profiles of the heavy water vapor phase, which are calculated for three low-grade design variables by the computer program, are different from each other, while those of the deuterium phase are not distinguishable. Therefore, the cause of the performance degradation can be cleared by comparing the measured tritium concentration profiles of the heavy water vapor phase with the calculated profiles by the computer program. These results can be used as operating references for the LPCE system.

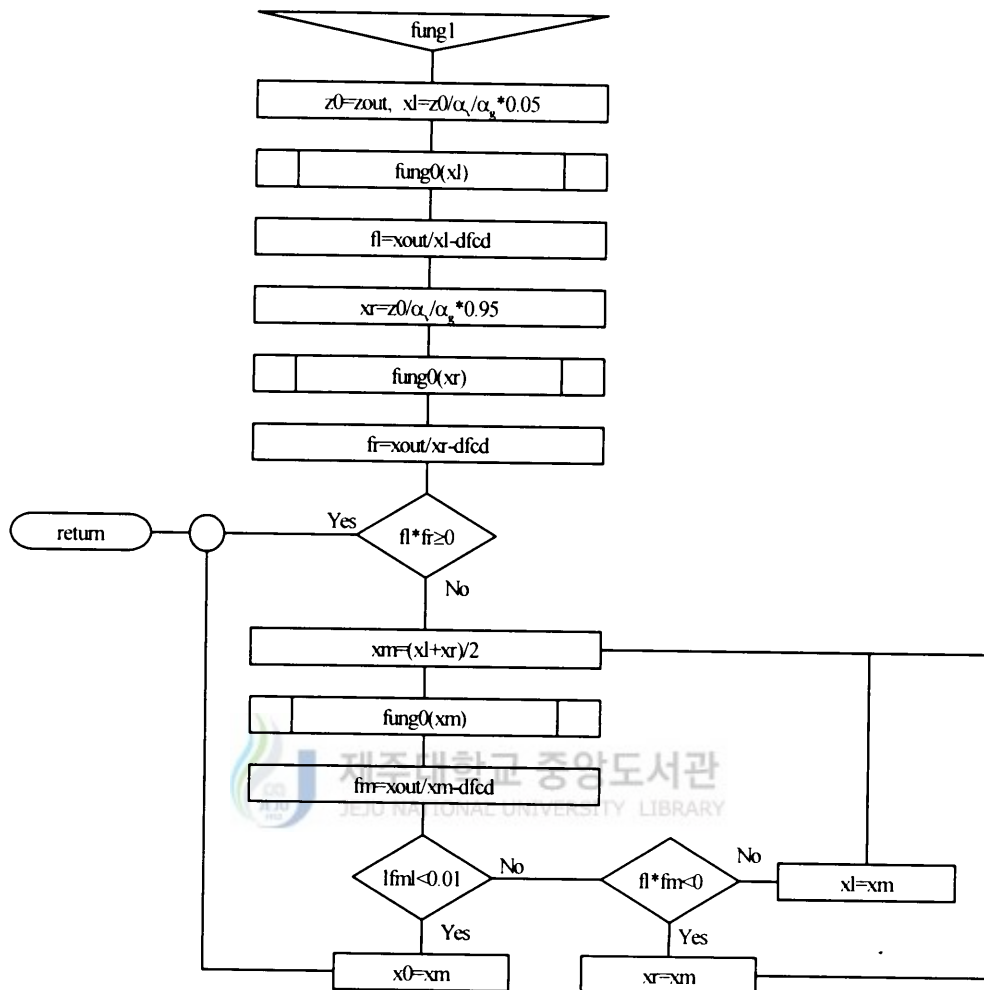
The operating temperature and pressure affects the heavy water vapor flow rate and the separation factor among the reaction materials, therefore, their gradient on the inside of the LPCE column becomes important factor for a more realistic approach. The catalyst efficiency and the N_s were considered as independent variables in this study. However, the temperature or other variables could affect η_c and N_s . Therefore, their terms can be replaced with a combination of terms of other parameters and the temperature, if the relations of the temperature and catalyst efficiency were defined. This would be more realistic way to assess the detritiation processes of the LPCE system.

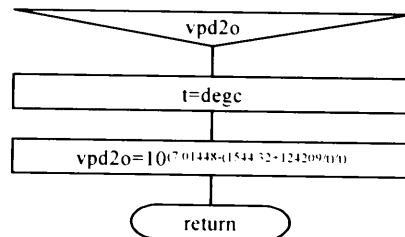
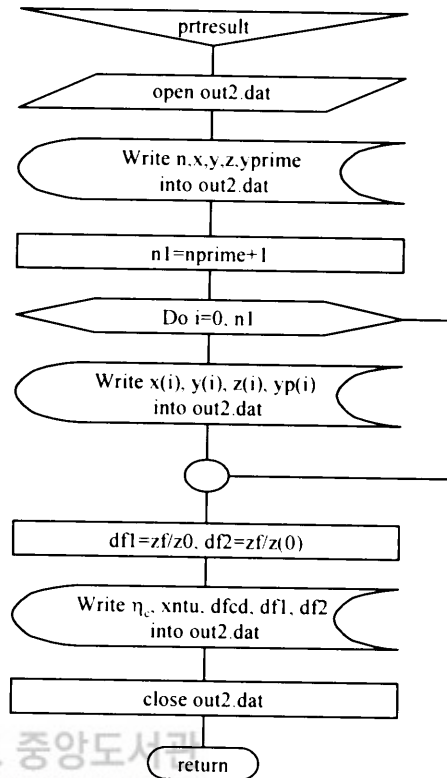
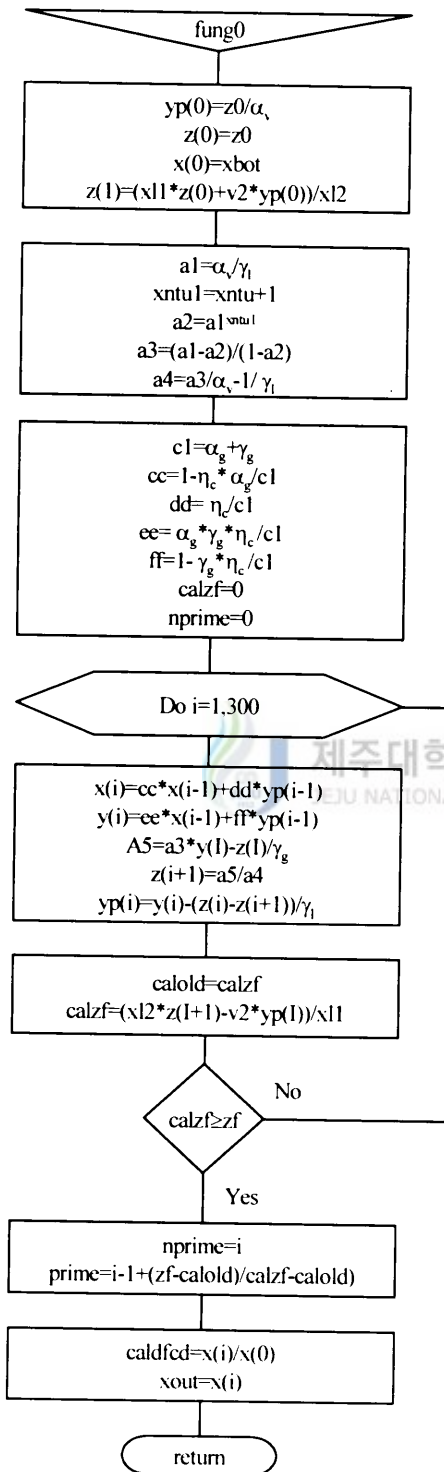
References

- CNSC, 2003, Radiobioassay for Intakes of Tritium, The CNSC Working Group on Internal Dosimetry, pp.1~7.
- KEPCO, 1996, Wolsong # 2,3,4 Final Safety Analysis Report, Chapter 11.3., pp.11.3-1~11.3-7.
- KHNP, 2001, Safety Analysis Report, Wolsong Tritium Removal Facility, pp.1~150.
- KHNP, 2002, Development of Tritium Removal Technology (I) Phase 2, 141 pp.
- Kwak, S. W., Chung, B. J., 1997, An Assessment on the Contribution of ^3He to the Tritium Generation in the CANDU PHWR, The Journal of the Korean Association for Radiation Protection, 22(2), 119~125.
- Ling, C. J., 1971, Separation processes, McGraw-Hill Book Company, New York, pp.390~396.
- Paek, S. W., Ahn, D. H., Lee, H. and Chung, H., 2002, Tritium Activities in Korea, Fusion Science and Technology, Vol. 41, 329~333.
- Ryohei, N. et al., 1982, Separation the isotopes of tritium and deuterium, Japan Scientific Societies Press, Tokyo, pp.3~12.
- Sinclair, W. K., 1979, Tritium in the Environment, National Council on Radiation and Measurement Report, NCRP No. 62. pp.1~66.
- Song, S. K., Lee, S. J., Lee, S. K., and Shon, S. H., 2003, Prediction of Tritium Release from Wolsong unit during the WTRF Operation, Proceedings of the Korean Radioactive Waste Society Conference 2003, pp.484~490.
- Van Hook, W. A., 1967, Vapor pressures of the isotopic waters and ices, The Journal of Physical Chemistry, Vol. 72, No. 4, 1234~1244.
- Zerriffi, H., 1996, Tritium: The Environmental, Health, Budgetary, and Strategic Effects of the Department of Energy's Decision to Produce Tritium (online), Available at: <http://www.ieer.org/reports/tritium.html>, Assessed Aug. 12, 2004.

Appendix: Flow charts of the computer program







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멀리서 공부하는데 많은 도움을 준 김지훈 선생, 구윤희 선생, 고영주 누나, 이경진 형에게 그 동안의 도움과 격려에 감사드리며, 원자력안전연구실 김형석, 고상혁, 강두혁 등 연구실 후배들도 앞날에 큰 발전이 있기를 기원합니다.

직장과 학업을 같이할 수 있도록 여러 가지로 배려해주시고, 원자력에 대하여 깊이 있게 이해할 수 있도록 도와주신 과학기술부 이영준 실장님과 월성주재관실 동료여러분께 감사드립니다.

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석사과정을 시작하는 해에 태어난 우리 천사 세연이, 그 동안 공부한다고, 일한다고 많이 놀아주지도 못했는데 건강하고, 정말 해맑게 커주는 것 같아 고맙습니다. 그 동안 싫은 표정 짓지 않고 묵묵히 참고 견디며, 밝은 미소와 말들로 항상 제 곁에서 힘이 되어준 아내 허미선에게 이 논문으로 그 동안의 미안함과 감사, 그리고 사랑을 전합니다.