Journal of the Korean Nuclear Society
Volume 28, Number 4, pp. 415~423, August 1996

Optimum Design of the Wolsong Tritium Removal Facility

Do Hee Ahn, Han Soo Lee, and Hong Suk Chung
Korea Atomic Energy Research Institue
150 Dukjin-dong, Yusong-gu, Taejon, Korea

Myung-Jae Song and Soon-Hwan Son
Korea Electric Power Research Institute
103-16 Munji-dong, Yusong-gu, Taejon, Korea

(Received March 27, 1996)

Abstract

Tritium removal from tritiated heavy water in a PHWR is the most effective way in reducing workers' internal dose and radioactivity emissions from Wolsong NPP. The optimum design of the Wolsong TRF (Tritium Removal Facility) was carried out using an approximate short-cut method with an assumption that the TRF, designed to extract 8 MCi per year of elemental tritium from a heavy water feedstream, uses Liquid Phase Catalytic Exchange (LPCE) front-end process and Cryogenic Distillation (CD) process.

1. Introduction

The use of heavy water as both a moderator and heat transport medium in the pressurized heavy water reactor (PHWR) results in the continuous exposure of large volumes of deuterium oxide to neutron flux. Substantial quantities of tritium are produced by neutron activation of deuterium in the reactor core and subsequently tritium concentration in heavy water systems tends to increase with the age of the reactor to equilibrium values[1-4]. Radioactivity emissions and workers' internal radiation doses are primarily caused by tritiated heavy water escaping from equipment in these systems[1, 2].

Improving the leaktightness of these systems is an effective way in reducing emissions and internal dose but is not a long-term solution. As the tritium is built up in the systems, spills of heavy water may result in unacceptable acute radiation doses to workers and cause the power plant to exceed tritium emission targets. The tritium concentration in the moderator heavy water may be too high at the end of the station's life for heavy water reuse or disposal. The cost of disposal or long-term storage of such highly tritiated heavy water will be extremely high due to the volume of heavy water.

Tritium removal from the moderator system is the most effective in reducing the overall radiological impact of a PHWR. The Darlington TRF was built in 1987 and has been serving all twelve Pickering and Darlington reactors[2]. This plant is designed to extract approximately 15 MCi of tritium from tritiated heavy water at a product purity of greater than 99%. Target of maximum tritium concentration is 10 Ci/kg-D_2O for the moderator system and 0.5 Ci/kg-D_2O for the heat transport system, respectively, to keep occupational dose and environmental emissions low for Canadian PHWR's. There is also a potential

use of the recovered tritium.

After approximately 12 years of operation of the Wolsong NPP without a TRF, tritium concentrations in moderator and heat transport systems had reached to the values of 38.5 Ci/kg-D_2O and 1.56 Ci/kg-D_2O, respectively, by 1994[1]. Three additional PHWR's will be operable at Wolsong by the year 1999. Consequently, tritium inventory and emissions will increase with the age of reactor. In order to reduce the overall radiological impact of the Wolsong NPP's as low as reasonably achievable (ALARA), the TRF which can serve to all four reactors should be installed. It is desirable that the TRF be designed to extract 8 MCi per year of elemental tritium from heavy water using Liquid Phase Catalytic Exchange (LPCE) front-end process and Cryogenic Distillation (CD) process and installed up to 2006 [1, 5-8].

There are much works to be done for the development of the wetproofed catalyst used in the LPCE process[9-12] and for the optimal design of the LPCE process itself[13]. No optimum design work of the integrated TRF using LPCE and CD processes has been published. In this work, A mathematical model for the simplified TRF process was suggested using the approximate short-cut method which is commonly used to define roughly the optimum specifications with a minimum of tedious and extensive calculations in contrast with the rigorous method and the optimum design of the TRF to minimize tritium inventory was carried out as the first phase of the project to design and construct the Wolsong TRF.

2. Theoretical Analysis

2.1. A Flow Diagram of the TRF

A flow diagram of the plant is shown in Fig. 1. The tritiated heavy water containing of 10 Ci/kg-D_2O from reactor trickles down through a LPCE column while deuterium gas from the first CD column flows upwards. Tritium transfers from heavy water to deuterium in the LPCE column and the tritium concentration in the return D_2O stream to reactors is 0.28 Ci/kg-D_2O. The cryogenic unit contains three distillation columns in series where tritium is concentrated to 99% T_2 in the final column. Tritium gas drawn off in the column is immobilized on titanium metal as a

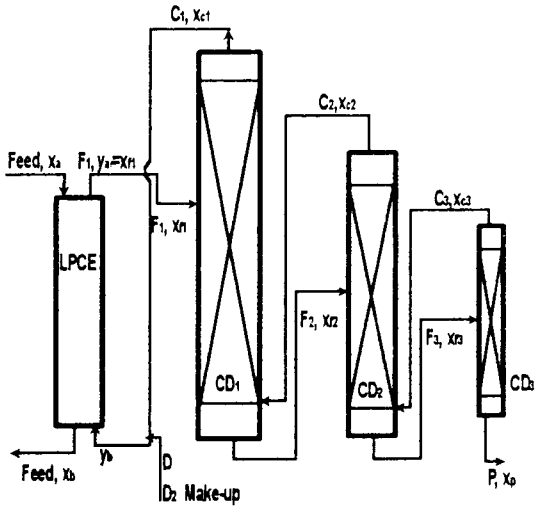

Fig. 1. A Flow Diagram of the TRF

Table 1. Design Conditions of the TRF

	Process variables	Symbol	Value
	Temperature		60℃
	Pressure		1atm
	Tritium conc.		
	Feed. stream	x_a	10Ci/kg-D_2O
LPCE	Return stream	x_b	0. 28Ci/kg-D_2O
	Mass transfer coefficient	Kya	$2.4s^{-1}$
	Superficial velocity	F	1m/s
	Separation factor	α	1.538
	Feed rate	Feed	5760mole/hr
	Temperature		24K
	Pressure		1atm
	Tritium conc. of product stream	x_p	99%
CD	Vapour pressure		
	D_2	P_{T2}	554.8mmHg
	DT	P_{DT}	680.6mmHg
	T_2	P_{D2}	838.4mmHg
	HETP	HETP	0.3m

tritide.

The design conditions for the TRF are illustrated in Table 1. The operating temperatures of the LPCE and CD columns are 60°C and 24K respectively as shown in Table 1.

2.2. A Mathematical Model

The following assumptions are made in establishing a mathematical model for the TRF.

- All streams contain three components of D_2, DT, and T_2 which are in chemical equilibrium except for two liquid streams in the LPCE column which contain two components of D_2O and DTO.
- The internal flow rates of gas and liquid are constant in each column.
- The head products of the second and third CD columns return to the bottom reboilers of the first and the second CD columns each.

The following material-balance equations can be written in terms of the variables set in Fig. 1.

$$\text{Feed} + D = \text{Feed} + P \tag{1}$$

$$F1 = C1 + P \tag{2}$$

$$F2 = C2 + P \tag{3}$$

$$F3 = C3 + P \tag{4}$$

$$\text{Feed} \cdot x_a + 0 = \text{Feed} \cdot x_b + P \cdot x_p \tag{5}$$

$$F1 \cdot x_{f1} = C1 \cdot x_{c1} + P \cdot x_p \tag{6}$$

$$F2 \cdot x_{f2} = C2 \cdot x_{c2} + P \cdot x_p \tag{7}$$

$$F3 \cdot x_{f3} = C3 \cdot x_{c3} + P \cdot x_p \tag{8}$$

where x designates tritium atomic fraction in each stream.

Since each gas stream is composed of D_2, DT, and T_2 which are in equilibrium of the isotopic exchange reaction ($D_2 + T_2 = 2DT$), the equilibrium constant K which is a function of the temperature can be expressed by

$$X_2^2 = K \cdot X_1 \cdot X_3 \tag{9}$$

where X_1, X_2, X_3 denote mole fractions of D_2, DT, and T_2, respectively[14]. Tritium atomic fraction x is defined as follows.

$$x = X_2/2 + X_3 \tag{10}$$

Therefore, mole fractions can be calculated from Eqs.(9) and (10) in each stream if the temperature and tritium atomic fraction are known.

The height of the LPCE column Z_L is obtained using the following NTU-HTU (Number of a Transfer Unit-Height of a Transfer Unit) equation[15-17],

$$Z_L = HTU \cdot NTU = \frac{F}{K_y a} \int_{y_a}^{y_b} \frac{dy}{y - y^*}$$

$$= \frac{F}{K_y a} \frac{y_b - y_a}{(y - y^*)_{lm}} \tag{11}$$

where F is the superficial gas velocity, K_ya is the overall mass transfer coefficient, y and y^* are the tritium atomic fractions in the deuterium stream and in equilibrium with the bulk concentration in the heavy water stream respectively, and subscript lm stands for logarithmic mean.

The diameter φ of the LPCE column can be calculated from the following relationship between the gas flow rate F1 and the superficial gas velocity F.

$$F1 = (4/\pi) \cdot \varphi^2 \cdot F \tag{12}$$

The short-cut methods which allow determination of total number of stages as a function of reflux ratio are commonly used to study the effect of reflux on optimum design of distillation process. The following FUG (Fenske-Underwood-Gilliland) equation is one of the short-cut methods for the approximate solution of multicomponent and multistage separation problems[18, 19].

$$\frac{N - N_m}{N+1} = \tag{13}$$

$$1 - \exp\left(\frac{1 + 54.4 \frac{R - R_m}{R+1}}{11 + 117.2 \frac{R - R_m}{R+1}} \cdot \frac{\frac{R - R_m}{R+1} - 1}{\left(\frac{R - R_m}{R+1}\right)^{0.5}} \right)$$

where N and R is total number of stages and reflux ratio in a CD column respectively. The minimum number of stages Nm at total reflux can be written as

$$N_m = \frac{\ln\left[\left(\frac{X_{ci}}{X_{pi}}\right)\cdot\left(\frac{X_{pr}}{X_{cr}}\right)\right]}{\ln \alpha_i} \quad (14)$$

where c and p denote overhead and bottom stream, i is any component and r is an arbitrarily selected reference component in the definition of relative volatility α_i. Minimum reflux ratio R_m can be obtained from the following equations.

$$R_m = 1 - \sum_i \frac{\alpha_i (X_{ci})_m}{\alpha_i - \theta} \quad (15)$$

$$q = 1 - \sum_i \frac{\alpha_i \cdot X_{fi}}{\alpha_i - \theta} \quad (16)$$

where q is the thermal condition of the feed (e.g., 0 for a saturated vapor feed) and f denotes the feed.

The height of a CD column is defined as the total number of stages multiplied by HETP (Height Equivalent to a Theoretical Plate).

The diameter of the CD column can be calculated from Eq.(12) in the same manner as in the LPCE column since the vapor flow rate G can be written from the definition of the reflux ratio as follows.

$$G = (R+1)C \quad (17)$$

A computer program was developed based on the mathematical model to investigate effect of the process variables on the size of the columns.

3. Results and Discussion

3.1. Volumes of the LPCE and the First CD Columns

The tritiated deuterium stream from the LPCE column is sent to the CD system for tritium extraction. The detritiated deuterium overhead stream from the first CD column is recirculated to the LPCE column. It is important to optimize the entire TRF process and not to design the LPCE and CD processes separately. Volumes of the LPCE and the first CD columns depend on process variables such as temperatures, flow rates and tritium concentrations in these two deuterium streams. Tritium concentration in the detritiated deuterium stream y_b in Fig. 1 must fall between 0 and y_b^*(tritium concentration which is in equilibrium with the bulk concentration in the detritiated heavy water stream), while the others are input data as listed in Table 1 or can be determined from the data. Fig. 2 shows effect of y_b on volumes of the LPCE and the first CD columns under the condition that the tritium enrichment factor is constant in the first CD column. Volume of the LPCE column increases while that of the first CD column decreases with increase of y_b and consequently total volume of the LPCE and the first CD columns shows a minimum at 0. 3 of y_b/y_b^* as shown in Fig. 2.

3.2. Tritium Inventory in CD Columns

The unique design feature of this CD system is to minimize tritium inventory in the TRF for safety reasons. Total tritium inventory T_{hold} in three CD columns can be expressed as follows.

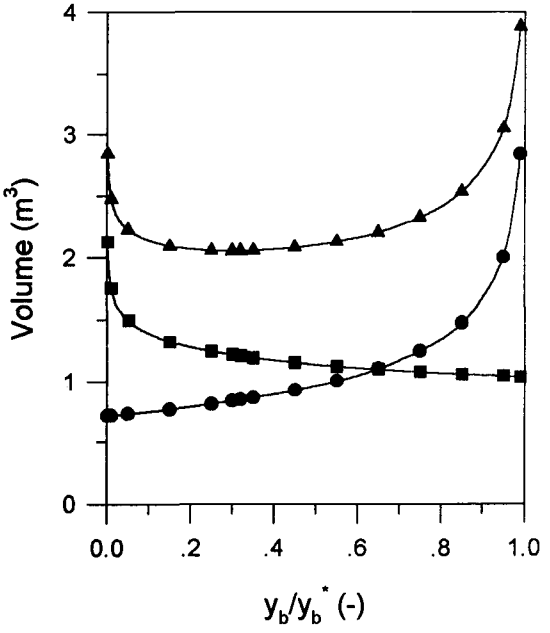

Fig. 2. Effect of y_b on Volumes of the LPCE and the First CD Columns (LPCE : ●, first CD : ■, total : ▲)

$$T_{hold} \propto \Sigma Vol_j \cdot (x_{cj}+x_{pj})/2 \quad (18)$$

where Vol_j is volume of the j-th column, x is the tritium atomic fraction, c and p designate head and bottom product respectively.

If tritium concentrations of top and bottom products are specified in each CD column, tritium inventory shows its minimum when volume of each CD column is minimized

There are three streams (i.e., feed, top product and bottom product) in a typical distillation column. Besides the conditions of the three streams, reflux ratio defined as the ratio of mass of liquid returned to the top section of a column to the mass of the top product determines the size of a column. Total number of equilibrium stages proportional to the height of a column depends on the reflux ratio whose minimum can be calculated from compositions of the three streams and the thermal condition of the feed. Fig. 3 shows effect of the reflux ratio on the size of a column which is given by the FUG equation[18, 19] for a given feed and specified separation. Diameter of a column increases while height of a column decreases steeply at the vicinity of minimum reflux ratio with increase of reflux ratio and accordingly the optimum reflux ratio to minimize volume of a column exists as shown in Fig. 3. The optimum reflux ratio corresponds to minimum tritium inventory in a column for a given average tritium concentration.

The CD system in the Darlington TRF is separated into two parts : the larger low tritium/high deuterium-containing (LTC) system and the smaller high tritium/low deuterium-containing (HTC) system [2]. During shutdowns, the HTC is isolated from the LTC, thereby mixing of the HTC and the LTC systems is avoided. The first CD column belongs to the LTC system while the others do to the HTC system. The tritium enrichment in the first CD column, which is defined as the ratio of tritium concentration in bottom product to that in feed and corresponds to x_{f2}/x_{f1} in Fig. 1, has been limited to a factor of 20-25 for safety reasons in the CRNL Tritium Extraction Plant[2].

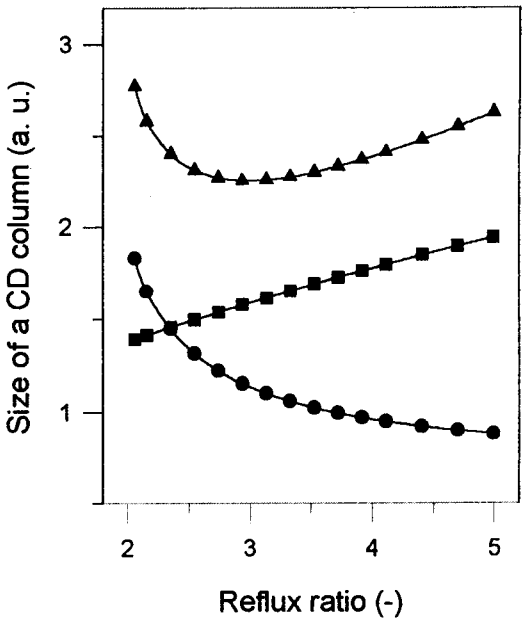

Fig. 3. Effect of Reflux Ratio on the Size of a CD Column (volume : ▲, diameter : ■, total no. of stages : ●)

Fig. 4 shows tritium inventory as a function of tritium concentration in the feed of the third CD column which is denoted by x_{f3} in Fig. 1 assuming that the tritium enrichment factor of the first column is equal to 25. The minimum of the total tritium inventory in three CD columns occurs at 0.026 of x_{f3} as shown in Fig. 4. With increasing x_{f3}, tritium inventory in the third column is decreased due to the decrease in the diameter of the column, while that in the second column is increased due to the increase in the height of the column and average tritium concentration, and that in the first column is kept constant.

The optimum x_{f3} to minimize the total tritium inventory in three CD columns and the minimum value of the tritium inventory as a function of the tritium enrichment factor of the first column are shown in Fig. 5 and Fig. 6, respectively. As the tritium enrichment factor increases from 10 to 50, so does the optimum x_{f3} as shown in Fig. 5 and the tritium inventory in the second and the third columns de-

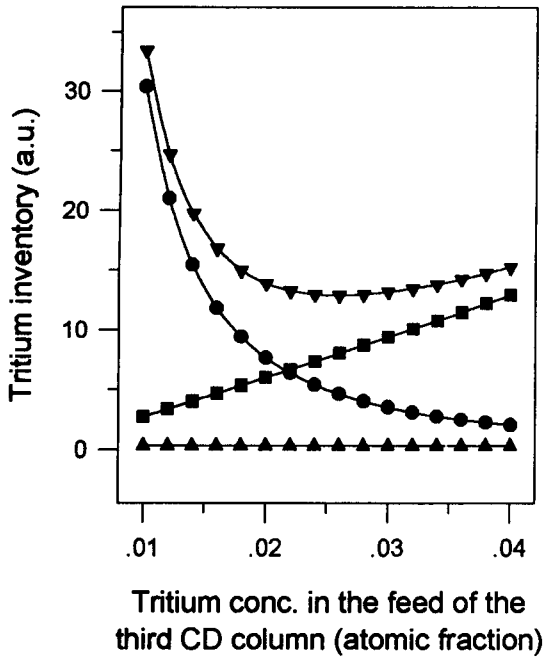

Fig. 4. Tritium Inventory as a Function of Tritium Concentration of the Feed in the Third CD Column (total: ●, 1st: ▼, 2nd: ▲, 3rd: ■)

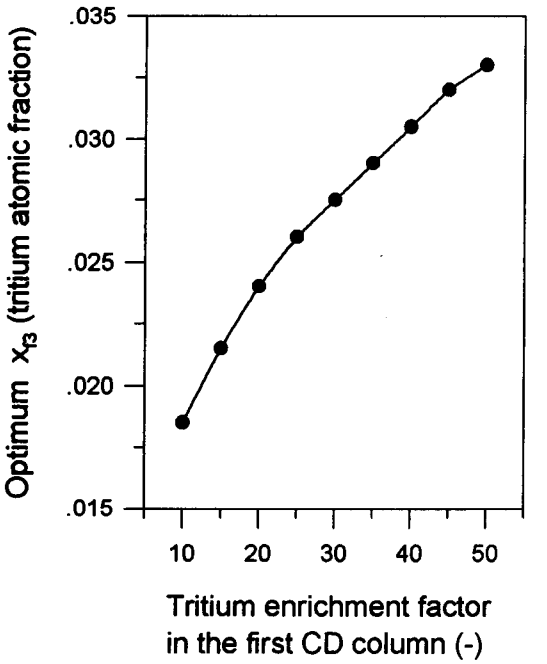

Fig. 5. Optimum Tritium Concentration in the Feed of the Third CD Column as a Function of Tritium Enrichment Factor in the First CD Column

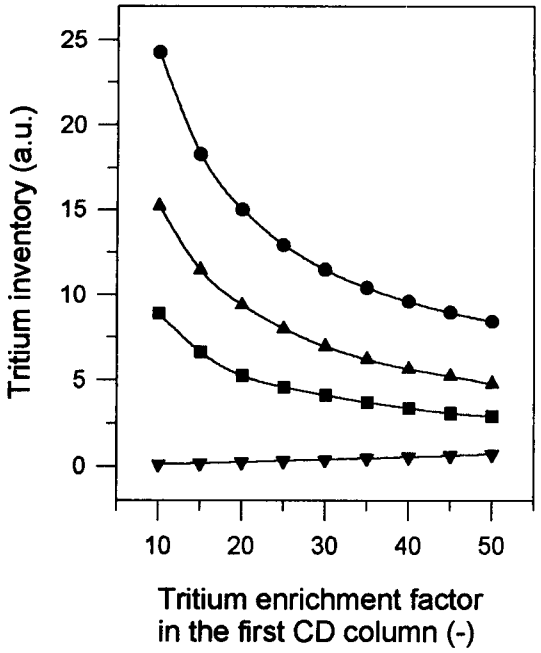

Fig. 6. Tritium Inventory as a Function of Tritium Enrichment Factor in the First CD Column (total: ●, 1st: ▼, 2nd: ▲, 3rd: ■)

crease respectively while that in the first column increases as shown in Fig. 6. Since the former is much higher than the latter, the total tritium inventory in the CD system decreases with increase of the tritium enrichment factor in the first column.

It thus appears that the optimum CD system in the TRF is designed to minimize the total tritium inventory after the tritium enrichment factor in the first column whose volume is much larger than any other column is determined from the viewpoint of airborne tritium control in the LTC system.

4. Conclusion

A mathematical model for the simplified TRF process was suggested using an approximate short-cut method. Optimum design of the Wolsong TRF which extracts 8 MCi per year of tritium from tritiated heavy water stream was carried out to minimize total tritium inventory with assuming that the tritium enrichment

Table 2. Optimum Design Data for the TRF

1. LPCE column
   - Diameter : 29.7cm
   - Height : 12.1m
   - Volume : 839liters
   - y_b/y_b^* : 0.3
2. CD columns
   - Enrichment factor in the first column : 25
   - Size and reflux ratio

	1st	2nd	3rd
Diameter(cm)	16	3.2	0.43
Height(m)	18	21	19
Reflux ratio(−)	3.0	3.0	0.58

- Material balance

Stream	mole/hr	Tritium atomic fraction
F1	9144.8932	2.151E-6
C1	9144.8735	1.902E-8
F2	416.9455	5.378E-5
C2	416.9258	7.016E-6
F3	16.7872	0.0260
C3	16.7675	0.0249
P	0.0197	0.99

factor of the first column is equal to 25. Table 2 lists the optimum design data including size of each column and tritium concentration in each stream. As described in the previous sections, optimum value of y_b/y_b^* is 0.3 to minimize total volume of the LPCE and the first CD columns and tritium concentration in the feed of the third column is 0.026 (tritium atomic fraction) to minimize total tritium inventory in three CD columns.

These optimum design data obtained roughly by a short-cut method will be investigated more exactly with a rigorous method in the basic design step of the Wolsong TRF.

References

1. M.J. Song et al., *Development of Wetproofed Catalyst and Catalytic Exchange Process for Tritium Extraction*, KEPRI-93N-J02 (1995)
2. W.J. Holtslander, T.E. Harrison and D.A. Spagnolo, *Fusion Eng. and Design*, **12**, 357 (1990)
3. A. H. Dombra et al., *Management of Tritium at Nuclear Facility*, Technical Reports Series No. 234, IAEA, Vienna (1984)
4. M. Galley et al., *Heavy Water and Tritium Management*, The Third CANDU Technology Course, KAERI-NTC (1985)
5. Y.E. Kim et al., *A Study on the Hydrogen Isotopes Separation Technologies*, KAERI/RR-469/85 (1985)
6. M. Shimizu, *Separation of Deuterium and Tritium*, p. 219, Kakai Press Center, Tokyo (1982)
7. G. Vasaru, *Tritium Isotope Separation*, p. 61, CRC Press, Baca Raton (1993)
8. D.R.P. Thatcher et al., *Instit. Chem. Symp. Series* 87, 159 (1985)
9. W.H. Stevens, *Process and Catalyst for Enriching a Fluid with Hydrogen Isotopes*, Canadian Patent 907, 292 (1972)
10. J.H. Rolston et al., *Process for the Exchange of Hydrogen Isotopes between Streams of Gaseous Hydrogen and Liquid Water*, U.S. Patent 4, 025, 560 (1977)
11. J.P. Butler, J.D. Hartog and F.W.R. Molson, *Process for the Exchange of Hydrogen Isotopes Using a Catalyst Packed Bed Assembly*, U.S. Patent 4, 126, 667
12. H.A. Langwala, S.E. Wanke and F.D. Otto, *Can. J. of Chem. Eng.*, **72**, 296 (1994)
13. M. Shimizu et al, *J. of Nucl. Sci. and Tech.*, **17**, 448 (1980)
14. D.C. Souers et al., *A Simple Model of D_2-DT-T_2 Equilibrium at Cryogenic Temperature*, UCRL-51681 (1974)
15. W.L. MaCabe, J.C. Smith and P. Harriott, *Unit Operation of Chemical Engineering*, 4th ed., McGraw-Hill, New York (1992)
16. J.H. Bae et al., *J. of Kor. Nucl. Soc.*, **27**, 121 (1995)
17. H.K. Rae, ACS Symposium Series 68, 163 (1978)

18. R.H. Perry and D. W. Green, Perry's Chemical Engineers' Handbook, 6th ed., p. 19−37, McGraw-Hill, New York (1992)

19. M.V. Winkle, Distillation, p. 286, McGraw-Hill, New York (1967)