Journal of the Korean Nuclear Society
Volum 18, Number 2, June 1986

Analysis of Steady and Unsteady State Behavior in Heavy Water Distillation Process

Kwang Rag Kim, Hong Suck Chung, Ki Woung Sung and Yong Eak Kim
Korea Advanced Energy Research Institute

Kun Jae Lee
Korea Advanced Institute of Science and Technology

(Received March 29, 1986)

중수증류공정의 정상 및 비정상상태 거동해석

김광락 · 정흥석 · 성기웅 · 김용익
한국에너지연구소

이건재
한국과학기술원

(1986. 3. 29 접수)

Abstract

The steady and unsteady state models were established for the performance analysis and design of heavy water distillation columns packed with corrugated wire mesh. After the steady state model was derived with pressure drops, separated D_2O concentration and temperature profiles and pressure gradients in the column were obtained by solving MESH equations with equation tearing method. For the analysis of unsteady state behavior, the equilibrium stage transient model deduced from modifying the Cohen's ideal cascade equation was used to predict the concentration change of heavy water with time. These models were in good agreement with the experimental results of heavy water distillation at total reflux. And the newly developed packing material turned out to be very efficient separation device for very small HETP, pressure drop and holdup.

요 약

새로이 개발된 망상구조 충전탑에서의 중수증류성능해석 및 설계를 위한 정상 및 비정상상태 모델을 수립하였다. 정상상태 모델은 MESH 방정식에 각단의 압력강하를 고려하여 설정하고, Equation Tearing방법으로 그해를 구하여 중수증류탑내의 농도, 온도 및 압력구배를 얻었다.

비정상상태 거동해석을 위하여 Cohen의 이상단 모델을 수정한 평형단 전이모델을 세웠으며, 그 모델식의 해석적 해를 구함으로써 시간에 따른 중수 농축과정을 예측할 수 있게 되었다.

설정된 모델들은 전환류 중수증류탑에서의 실험결과와 매우 잘 일치하였으며 개발된 충전물은 높은 이론단수에 낮은 압력강하, 저체류량을 갖는 우수한 중수농축용 충전물임이 확인되었다.

Nomenclature

B	bottom product flow rate(kgmol/hr)
C	number of component
D	top product flow rate(kgmol/hr)
F	feed flow rate(kgmol/hr)
Fs	F-factor($U_G\sqrt{\rho_G}$) (m/sec $\sqrt{kg/m^3}$)
g	gas load(kg/m^2/sec)
H	enthalpy of D_2O-H_2O mixture(kcal/kgmol)
H	liquid phase holdup(kgmol/m)
h	vapor phase holdup(kgmol/m)
HETP	height equivalent to a theoretical plate(m)
K	vapor-liquid equilibrum ratio
L	liquid flow rate (kgmol/hr)
N	number of equilibrium stages
NTSM	number of theoretical stages per meter(m^{-1})
P	perssure(mmHg, torr.)
T	mass transfer rate at phase interface (kgmol/m/sec)
T	temperature(°K)
U	superficial gas velocity(m/sec)
U	liquid flow rate(m^3/m^2/hr)
V	vapor flow rate(kgmol/hr)
V'	vapor flow rate(kgmol/sec)
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase
Z	total height of packed section(m)
z	height of packing from the bottom (m)
z	mole fraction of feed stream

Subscripts

B	bottoms
D	distillate
F	feed
G	gas
i	at phase interface
i, j	particular component i in a stream leaving stage j
L	liquid phase
o	infinite reservoir condition
R	reboiler
V	vapor phase
z	height of packing from bottom

Greek symbol

α	separation factor

1. Introduction

The accurate description of the steady and unsteady state phenomena for the heavy water separation from natural water is an essential task in the design and analysis of heavy water distillation towers.

Since the separation factor($\alpha=1.04$), which is a yardstick for the difficulty of separation, is extremly small, a large number of theoretical stages is required for heavy water distillation (1, 2, 3, 4, 5, 6, 7, 8). Conventional steady state calculational methods for the normal distillation processes can not be employed in this case because pressure drop throughout the column must be taken into account, in addition to the mass balance, enthalpy blance and equilibrium relationships(MESH equations). Thus the pressure drop at each stage should be expressed as a function of vapor flow rate in order to obtain accurate concentration and temperature profiles and also pressure gradient of each steady state stage.

The ideal cascade theory by Cohen (9, 10, 11) has been used for the unsteady state analysis (12, 13, 14) of general isotope separation processes. But a new model taking into account of the non-ideality of the actual cascades must be developed to predict the exact time to reach equlibrium for practical heavy water distillation process.

In this work, models have been developed for the analysis of heavy water behavior in packed distillation columns not only at steady state but also at unsteady state case. The validity of the models have been examined by heavy water separation experiments performed in a pilot scale column packed with newly developed wire mesh packings. Some design data produced on the packings were also presented.

II. Theoretical Analysis

1. Analytical Solution of the Equilibrium Stage Equations for the Prediction of Unsteady State Behavior

The simple theory of ideal cascade for the isotope separation is first developed by Cohen (12). The fundamental equations by Cohen(9), Benedict(1), and London(15) are expressed by differential equations in the infinitesimal case where the separation factor is very close to unity. These theories are only applicable to the case of ideal cascade, and are not amenable to a detailed analysis of equilibrium stage such as heavy water distillation process.

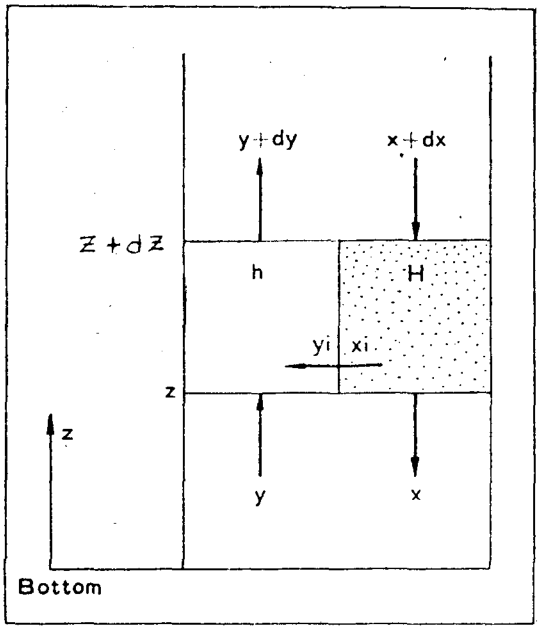

Fig. 1. Schematic Representation of a Heavy Water Cascade

So, in this paper, two sets of balance equations are derived from equilibrium relationships between flow rates and stage parameters.

The following analysis is based on a simple packed distillation system(Fig. 1). If the isotope in question is enriched in the liquid phase, the material balances in the packed column can be represented by the following equations,

for gas phase

$$h\frac{\partial y}{\partial t} = T - V'\frac{\partial y}{\partial z} \tag{1}$$

and for liquid phase

$$H\frac{\partial x}{\partial t} = -T + L\frac{\partial x}{\partial z} \tag{2}$$

Where T (kg-mole/m • sec) is the rate of transfer of isotope to the depleted phase across the interface per unit length of column assuming $dz=1$ HETP, the following equilibrium relationship can be derived.

$$y+dy=\alpha x/\{1+(\alpha-1)x\} \tag{3}$$

Since vapor phase holdup is negligilble, Eq. (1) can be reduced to

$$T=V'(dy/dz) \tag{4}$$

If $(\alpha-1)\ll 1$, Eq. (4) becomes

$$T=-k\{y(1-x)-\alpha x(1-y)\} \tag{5}$$

where, $k=V'/\text{HETP}$, $x=x_{H_2O}$, $y=y_{H_2O}$

Inserting Eq. (5) into Eqs. (1) and (2), We can get the following equations,

$$h\frac{\partial y}{\partial t}+V'\frac{\partial y}{\partial z}=-k[(y-x) -(\alpha-1)x(1-y)] \tag{6}$$

$$H\frac{\partial x}{\partial t}-L\frac{\partial x}{\partial z}=k[(y-x) -(\alpha-1)x(1-y)] \tag{7}$$

These two equations can now be combined with the assumption that $(\alpha-1)$ is very small.

Noting that the operator $\partial/\partial t$ is proportional to $(\alpha-1)^2$ and $\partial/\partial z$ is of the order of $(\alpha-1)$, (9)

$$H\frac{\partial y}{\partial t}=-\frac{\partial}{\partial z}\left[\frac{L\cdot V'}{k}\frac{\partial y}{\partial z} -L(\alpha-1)y(1-y)+D\cdot y\right] \tag{8}$$

or

$$H\frac{\partial x}{\partial t}=(L\cdot\mathrm{HETP})\frac{\partial^2 x}{\partial z^2}$$
$$-\frac{\partial}{\partial z}[D\cdot x+V'(\alpha-1)x(1-x)] \qquad (9)$$

for dilute solution of D_2O(reassuming $x=x_{D,0}$ $\ll 1$), Eq. (9) can be rearranged to

$$\lambda\frac{\partial x}{\partial t}=\frac{\partial^2 x}{\partial z^2}-2\epsilon(1+\phi)\frac{\partial x}{\partial z} \qquad (10)$$

where $\lambda=H/L\cdot\mathrm{HETP}$

$\epsilon=-V'(\alpha-1)/2\ L\cdot\mathrm{HETP}$

$\phi=-D/V'(\alpha-1)$

For the case of a column operated under total reflux, i.e. no production, $D=0 \rightarrow \phi=0$, with the concentration at the bottom maintained at x_0.

The boundary conditions for the total reflux operation with infinite bottom reservoir are

$z=0 \rightarrow x=x_0$

$z=Z \rightarrow \partial x/\partial z=2\epsilon x$

$t=0 \rightarrow x=x_0$

The most expeditious method of solving Eq. (10) under these boundary conditions is the use of the Laplace transformation method. The concentration at the top of the column varies with time in the following form when we neglect the higher transient terms, (9)

$$\frac{x(Z,t)}{x_0}=e^{2\epsilon Z}+\frac{2\epsilon e^{p_1 t}}{\left[\frac{\lambda Z}{2}+\frac{\lambda}{2\gamma_1{}^2}(\epsilon Z-1)\epsilon\right]P_1} \qquad (11)$$

Now P_1 is given by

$$P_1=-\frac{(\gamma_1 Z)^2+(\epsilon Z)^2}{\lambda Z^2} \qquad (12)$$

and $\gamma_1 Z$ is the smallest root of

$$\tan Z=\gamma Z/\epsilon Z. \qquad (13)$$

This equation always holds when the leading transient term dominates after $t=\gamma Z^2/10$.

2. Analysis for Steady State Behavior

The development of a new computer code has been carried out to simulate the process analysis of pilot experimental column. This code includes the packing characteristics and other factors such as material balance, component balance, phase equilibrium data, vapor pressure data and pressure drop. Then the equations tearing method is applied to a main calculational loop.

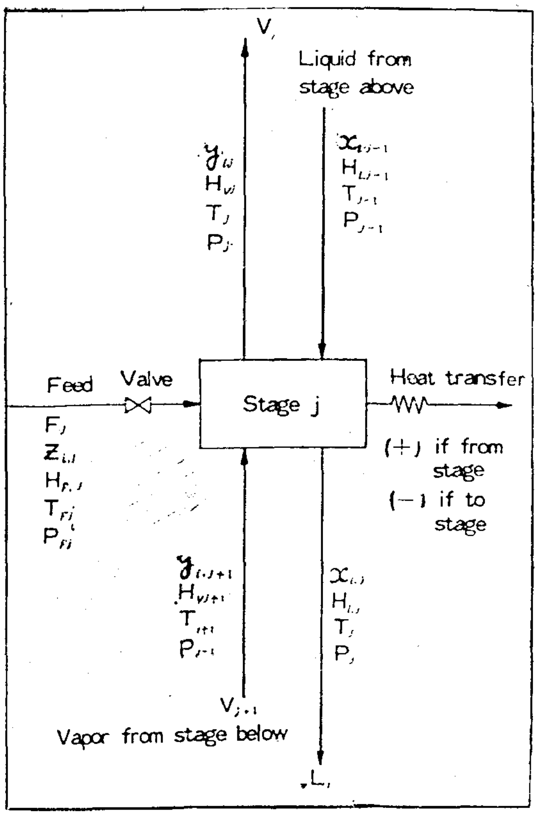

Fig. 2. General Equilium Stage

Consider a general, continuous, steady state vapor-liquid separator which consists of many stages, arranged in a countercurrent type cascade (16, 17). Assume that the phase equilibrium is achieved at each stage and that no chemical reaction occurs.

Equation tearing method (18, 19) is known as an adequate numerical procedure for the description of the multistage column such as water distillation process. Associated with each general theoretical stage are the following indexed equations, so called MESH equations, expressed in terms of the variable set in Fig.2.

1) M-equation: Material balance for each component

$$M_{i,j}=L_{j-1}\ x_{i,j-1}+V_{j+1}\ y_{i,j+1}+F_j\ z_{i,j}$$
$$-L_j\ x_{i,j}-V_j\ y_{i,j}=0 \qquad (14)$$

The constituents of H_2O, HDO and D_2O can be assumed as binary system (D_2O-H_2O) according to Urey (20) and others(21, 22).

The assumptions are:

a. Liquid and vapor phases form ideal solution.

b. The vapor pressure HDO is the geometric mean of the vapor pressure of H_2O and D_2O.

c. The distribution coefficient of the following reaction has the value of 4.0

$H_2O+D_2O\rightleftharpoons 2HDO$, $Ke=4$

2) E-equation: Phase equilibrum relationship for each component

$$E_{i,j}=y_{i,j}-K_{i,j}\ x_{i,j}=0 \qquad (15)$$

where K is the phase equilibrium ratio.

3) S-equation: Mole fraction summation

$$(Sx)=\sum_{i=1}^{c} x_{i,j}-1.0=0 \qquad (16)$$

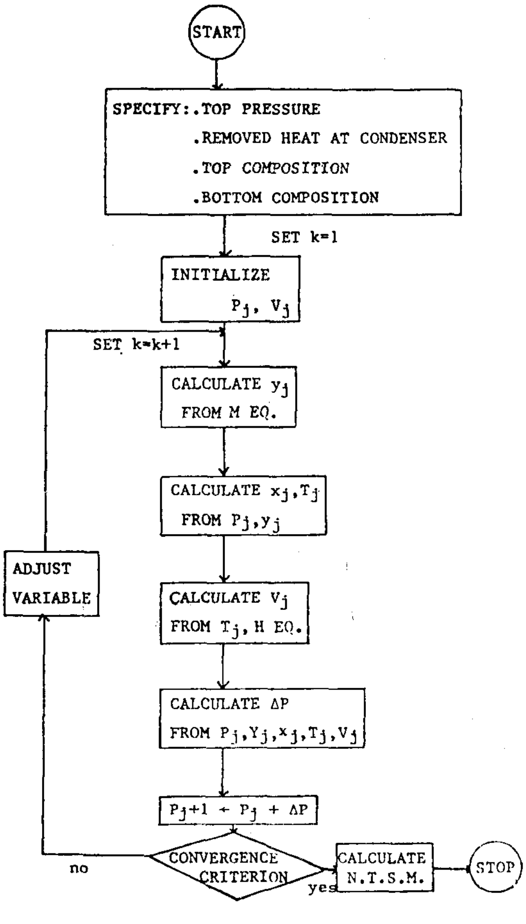

Fig. 3. Flow chart for iteration.

4) H-equation: Energy balance

$$H_j=L_{j-1}\ H_{Lj-1}+V_{j+1}\ H_{Vj+1}+F_j\ H_{Fj}-L_jH_{Lj}-V_jH_{Vj}=0 \qquad (17)$$

and total material balance is given by

$$L_j=V_{j+1}+\sum_{j=1}^{j}F_j-V_1 \qquad (18)$$

In addition to these equations we have the pressure drop relationships obtained experiments.

5) Pressure drop relatioship

$$P_j=P_{j+1}-\Delta P \qquad (19)$$

where ΔP is pressure drop per HETP.

In this study, it is systematically analyzed by a number of tearing technique for solving the MESH equations with the given pressure drop relationship.

The algorithms are shown in Fig.3.

III. Experiment

1. Description of Distillation Column

Fig. 4 shows the schematic diagram of the pilot system where the various separation characteristics of the corrugated wire mesh packing were measured. The column has a diameter of 0.1m and filled with 4m height of packing material. Four unit columns of each 1m height was combined by flanges. The reboiler has a capacity of 40 liters and the coil type condenser has an external surface of 3.1m^2 made of copper. With the vacuum pump and vacuum regulator, the operating pressure can be set around 10^{-2}mm of mercury absolute. The pressure drop was measured with a U-tube filled with a high boiling-point organic mixture and checked with an accurate membrane manometer.

An orifice type distributor was installed at the top of each unit column in an uniformly distributed 37 points with each hole cross section of 8.04×10^{-6}m^2. To determine the NTSM, the column was operated at total reflux. Each time the equilibrium condition was reached, samples were taken from the five sampling points and

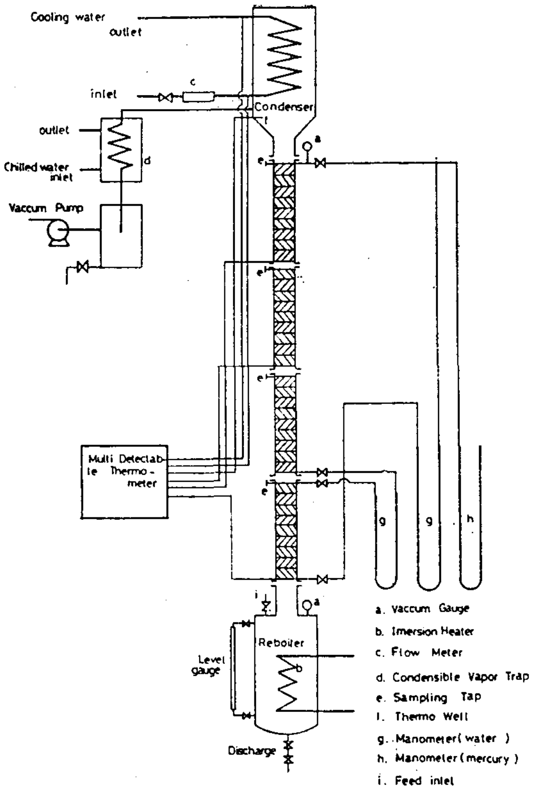

Fig. 4. Schematic Diagram of The Experimental Pilot System.

analyzed by Infrared Spectrophotometer(23, 24).

A feed that contains about 5,000ppm $\{D/(D+H)\}$ was distilled over the various range of operating pressure and flow rates. The vapor flow rate was calculated by the cooling water consumption.

2. Description of Corrugated Wire Mesh Packing

Corrugated wire mesh packing has a regular structure. Its surface, however, consists of thin sheets with wire mesh, and the hydraulic diameter of the crimps is comparatively large. The packing is made in the form of cylindrical elements which fill the entire cross section of the column. Adjacent packing bodies are then rotated by 90° in series.

The characteristic data of corrugated wire mesh packing are summarized in Table 1. The angle of inclination is 45° to the column axis.

Table 1. Characteristics of Packing

Material	SUS304
Mesh size	60
Packing diameter	1.83cm
Packing height	2.5cm
Size length	4.95mm
Corrugation angle	46°
Inclination angle	45°
Turning of succesive assembly	90°
Density of packing	0.20g/cm^3
Voidage	96.6%
Geometrical surface area	8.4cm^2/cm^3

The trickling surface features many holes and fine grooves. The holes promote turbulence in liquid phase, whereas due to capillary action the grooves cause the liquid to spread over the whole surface area. As a result, uniform plug flow of the liquid is obtained. In addition, strong lateral mixing in the vapor phase compensates the effect of a small maldistribution in the liquid flow.

IV. Results and Discussion

1. Hydrodynamics

1) Pressure drop

∘ Air-water pressure drop tests

In the distillation tests at total reflux, the maximum liquid load was 43.2m^3/m$^2\cdot$hr at atomspheric pressure and with a F-factor of 3. In order to obtain data at higher liquid loads we conducted some experiments in a 0.1m diameter column with air-water system. The liquid load was changed from zero to 60m^3/m$^2\cdot$hr, while the gas velocity was varied from 0.4m/s to its flooding velocity. The results are plotted in Fig. 5, where pressure drop for various liquid loads is shown as a function of the F-factor. At a low F-factor, the pressure drop is proportional to the air velocity. At a higher F-factor, the holdup increases and the open cross section therefore becomes smaller. Hence the pressure drop increases steadily until the slope becomes

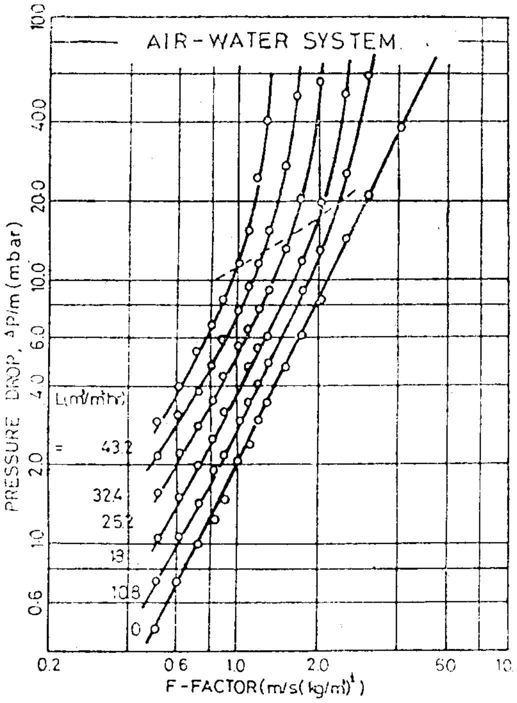

Fig. 5. **Pressure Drop for Different F-factor and Liquid Load.**

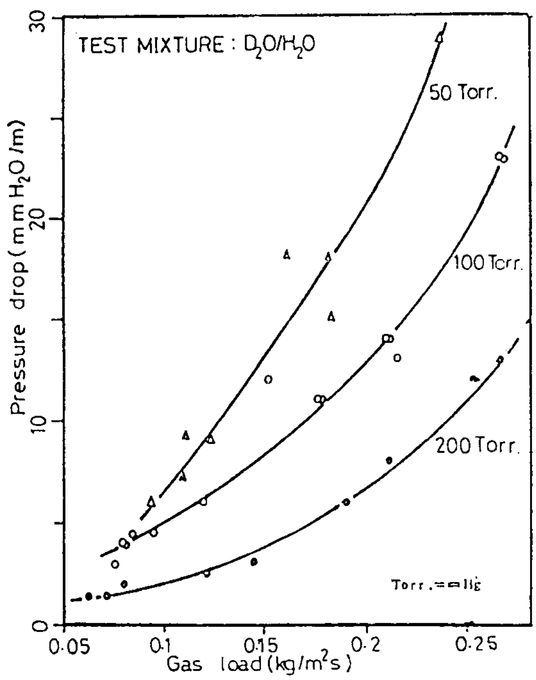

Fig. 6. **Pressure Drop for Different Gas Load and Head Pressure.**

infinite and the flooding point is reached. When the gas stream starts to blow droplets from the upper end of the packing, small amounts of liquid can be observed pulsating within the packed bed mainly in the contact area between the packing elements for the different liquid loads. This zone is shown by a dotted line (upper loading).

The pressure drop per unit height of packed bed, across the dry and irrigated packings under loading, was correlated by empirical equations similar to those suggested by Billet et al.[25]

For dry packing:

$$\Delta P_0/Z = 2.043(U_G\sqrt{\rho_G})^{2.09} \qquad (20)$$

For irrigated packing:

$$\Delta P/Z = 0.258(\Delta P_0/z)\,U_G^{-0.85}\cdot U_L^{0.35} \qquad (21)$$

$(\Delta P$: mbar)

Constants were evaluated after linearization of the respective equations by regression analysis.

∘ Steam-water pressure drop tests

Pressure drop is an important quantity for the analysis of distillation columns. However, since it decreases continuously with decreasing load, it does not play any dominating role for the performance analysis of corrugated wire mesh packing, and turns out to be about half of that for 1 inch Raschig ring.[26] The pressure drop of the corrugated wire mesh packing has such a low value that its measured value was 10 to 60% flooding point (Fig. 6).

2) Liquid holdup

The holdup in the fractionation equipment becomes a primary concern in batch and superfractionation distillations. In our experiment, it is an important factor affecting the sharpness of separations and time to reach equilibrium respectively. Experimental holdup data were obtained in a pilot test using level gauge. This information is summarized graphically in Fig. 7. The typical holdup has been estimated to be 5% at vapor load value of 0.26kg/m²·s.

3) Heavy Water Distillation

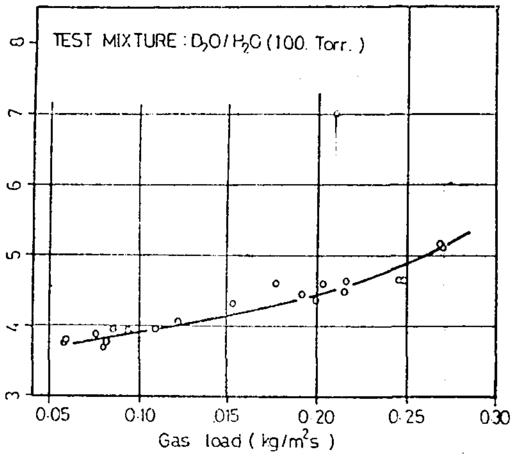

Fig. 7. Liquid Holdup for Different Gas Load.

- Unsteady state analysis

Distillation process continued until equilibrium condition is reached. Liquid samples were withdrawn at each 30 minutes intervals. These samples were analyzed by Infrared Spectrophotometer, which was standardized for every sample.

Particular examples of the solutions given by Eq. (10) may be used in the experiments. The most special case of the experiment, namely $D=0$ and $\phi=0$, has been considered in detail. This is the case of column operated under total reflux (no production) with the concentration at bottom maintained constant. The operating conditions are shown in Table 2.

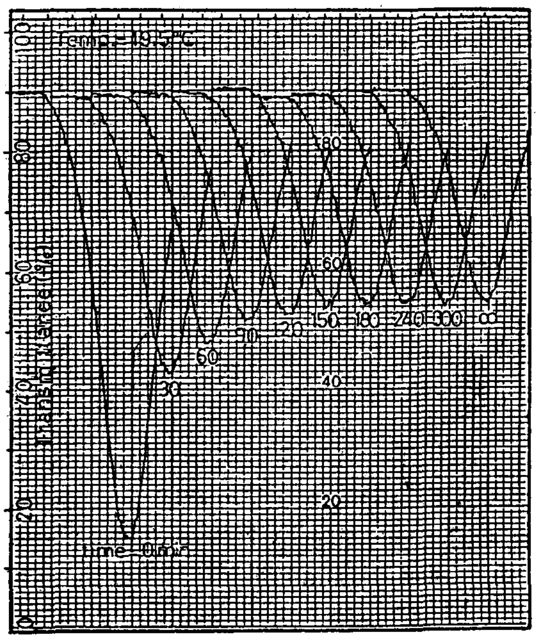

Fig. 8. Time to Reach the Steady Operation at Total Reflux (IR curve).

Table 2. Operating Conditions

column head pressure	100mmHg
gas load	0.27kg/m²·s
top concentration (x_D)	$3.1044\times10^{-3}\{D/(D+H)$ mole fraction$\}$
bottom concentration (x_0)	$4.6052\times10^{-3}\{D/(D+H)$ mole fraction$\}$

In this condition, the dynamic behavoir of column is shown on the Infrared Spectrophotometer curve (Fig. 8).

From Eq. (10), when $D=0$ and $\phi=0$, ϵ is given by

$$\epsilon=-(\alpha-1)/2\cdot\mathrm{HETP} \qquad (22)$$

For this case, Eq. (10) becomes for $t\to\infty$

$$Z=-\frac{2\cdot\mathrm{HETP}}{\alpha-1}\tanh^{-1}\left[\frac{x_D-x_0}{x_D+x_0-2x_Dx_0}\right] \qquad (23)$$

In this operation, $\alpha=1.056$, $Z=4$m and HETP=0.5658m. From the Eq. (12) and Eq. (13), $\lambda=333.1$ and $\gamma_1=0.4218$. Accordingly Eq. (10) takes the form

$$x(t)=4.6052\times10^{-3}\ \{0.67031 + 0.253\exp(-5.417\times10^{-4}t)\} \qquad (24)$$

Thus the unsteady state equation (Eq. 24)

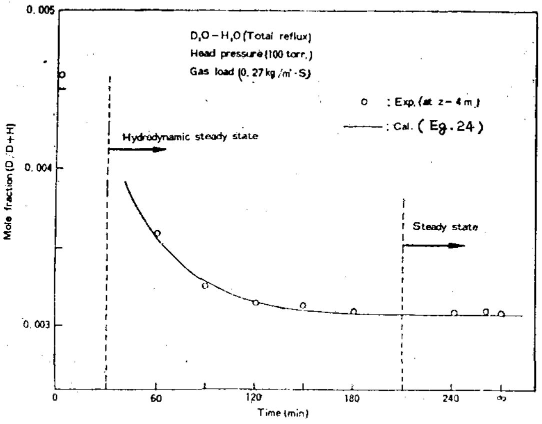

Fig. 9. Time to Reach the Steady Operation at Total Reflux

shows good agreement with the experimental results (Fig. 9). Finally this model may be applied to predict initial operation of a large scale water distillation process and heavy water upgrader(27).

○ Steady state analysis

The column behavior at steady state was observed and calculated by using a computer program (Fig. 10). Fig. 11 shows the effect of operating pressure and vapor flow rate on NTSM values.

In all cases, the overall NTSM value is estimated to be about 2.7. It is not influenced by the vapor flow rate under the present experimental conditions. The significant conclusion drawn from the fact of the constant NTSM is that the equilibrium stage model is well suited for prediction of the actual column behavior, and the present computer aided simulation allows us to predict the column performance even in the case where the packed column is higher and the column is operated under various different conditions.

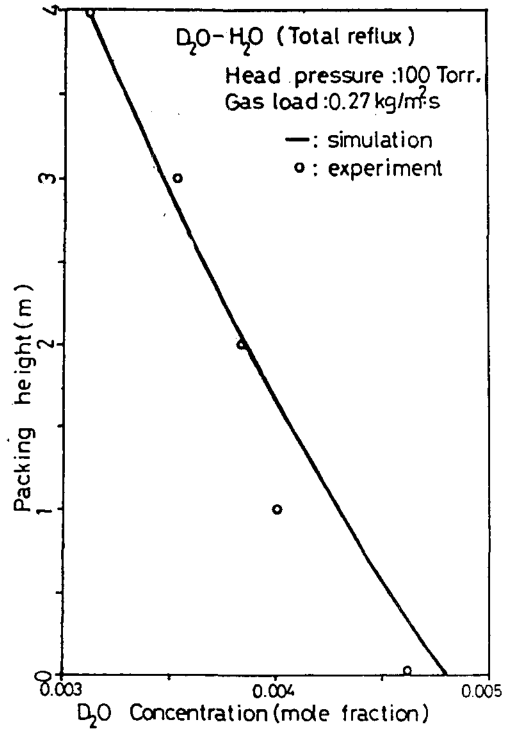

Fig. 10. Concentration Profile at Steady State.

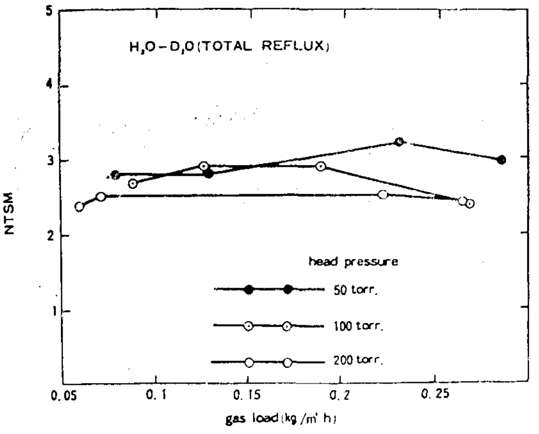

Fig. 11. Number of Theoretical Stages Per Meter for Various Gas Load and Operating Pressure

V. Conclusion

The present study was performed for a pilot scale heavy water distillation column. The column separates H_2O and D_2O at total reflux operation mode. The current experiment and analytical solution provides very useful information to the design and analysis of heavy water distillation column.

Some significant conclusions are recapitulated here.

1) For unsteady state analysis, the dynamic column behavior predicited by modified Cohen's equation based on equilibrium stage was in very close agreement with the experimental observation.

2) For steady state analysis, the column behavior predicted by the computer aided simulation was in good agreement with experimental results.

3) The newly developed wire mesh packing has very desirable characteristics such as

—high NTSM

—low holdup and pressure drop.

References

1. M. Benedict and T.H. Pigford, "Nuclear Chemical Engineering," McGraw-Hill, New York,1957.
2. C.J. King, "Separation Processes," McGraw-Hill, New York, 1971.
3. M.V. Winkle, "Distillation," McGraw-Hill, New York, 1967.
4. W.L. McCabe and J.C. Smith, "Unit Operations of Chemical Engineering," 3rd ed.,McGraw-Hill, New York, 1976.
5. W.P. Bebbington, et al., "Production of Heavy Water Savannah River and Dana Plants," DP-400, 1959.
6. J.A. Ayres, "Production of Heavy Water-Status Report," BNWL-884, 1968.
7. H.K. RAE, "Selecting Heavy Water Processes," AECL-6054, 1978.
8. R. Zmasek, "Sulzer Rectifying Plants for Enriching Heavy Water," Sulzer Technical Review, Nuclex 1972.
9. K. Cohen, "The Theory of Isotope Separation," McGraw-Hill book Co. New York, 1951.
10. K. Cohen, "The Theory of the Steady-State Ope ration of a Packed Column for Isotope Separation," J. Chem. Phys., Vol. 8, p. 588, 1940.
11. M. Shimizu and S. Hibino, "Some analyses on the Operation of Water Rectification Tower," J. JNS, Vol. 4, No. 5, 1972.
12. K. Cohen, J. Chem. Phys., Vol. 8, p. 588, 1940.
13. A.M. Rozen, "Theory of Isotope Separation in Column," Atomizdat, Moscow, 1960.
14. S.I. Babkov and N.M. Zavoronkov, Kernenrgie, Vol. 5, p. 219, 1962.
15. H. London, "Separation of Isotopes," George Newnes Ltd., London, 1961.
16. B.D. Smith, "Design of Equilibrium Stage Process," McGraw-Hill, New York, 1963.
17. C.D. Holland, "Fundamentals and Modeling of Separation Process es," Prentice-Hall, New Jersey, 1975.
18. J.H. Ernest and J.D. seader, "Equilibrium-Stage Separation Operations in Chemical Engineering," John-Wiley & Sons, New York, 1981.
19. J.F. Boston and S.L. Sullivan, Can. J. Chem. Eng., Vol. 50, p. 663, 1972.
20. H.C. Urey, J. Chem. Soc., Vol. 69, p. 562, 1947.
21. I. Kirshenbaum, "Physical Properties and Analysis of Heavy Water," McGraw-Hill, New York, 1951.
22. R.L. Combs and J.M. Googin, J. Chem. Phy., Vol. 58, p. 1000, 1945.
23. W.H. Stevens et al., "Heavy Water Analysis in the 1% to 99% D_2O Range by Infrared Spectrometry," AECL-1391, 1961.
24. R.M. Abernathey et al.,"Determination of Heavy Water Purity by Infrared Absorption," IDO-14576, 1962.
25. R. Billet, J. Macowiak and S. Suder, Ger.Chem. Eng., Vol. 1, p. 226, 1978.
26. R.H. Perry and C.H. Chilton, "Chemical Engineer's Handbook," 5th ed., McGraw-Hill, New York, 1973.
27. AECL Proprietary. "Heavy Water Upgrading Distillation Plant," Wolsung-1 G.S., TS-59-38420-3. 1983.