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SUBJECT: Removal of Tritium from the Molten Salt Breeder Reactor Fuel

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ABSTRACT

Molten Salt Breeder Reactors will produce large quantities of tritium which can permeate most metals at elevated temperatures and thereby contaminate the environment. In this project it was assumed that the tritium can be removed from the salt stream by a hydrogen-helium purge and that the helium can be separated for recycle with a palladium membrane. Several systems for concentrating and storing the tritium were conceptualized, designed, and economically evaluated. Cryogenic distillation of liquid hydrogen appears to be the most economical system. A cryogenic system with a capacity of 4630 gmoles of hydrogen per hour at a 1000-fold tritium enrichment has an estimated capital cost of $328,000 and an estimated annual operating cost of $81,000 (excluding depreciation).

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Contents

Page

1. Summary 4
2. Introduction 4
3. Design and Evaluation of Alternate Separation Systems 6
   3.1 Approach 6
   3.2 Feed Pretreatment 6
   3.3 Storage of Tritiated Water 7
   3.4 Water Distillation 7
   3.5 Thermal Diffusion 9
   3.6 Cryogenic Distillation 9
4. Discussion of Separation Systems 16
5. Conclusions and Recommendations 16
6. Acknowledgement 17
7. Appendix 18
   7.1 Basis for Water Distillation Costs 18
   7.2 Thermal Diffusion System 21
   7.3 Cryogenic Distillation System 22
   7.4 Computer Codes 26
   7.5 Nomenclature 29
   7.6 Literature References 30

1. SUMMARY

One characteristic of Molten Salt Breeder Reactors (MSBR) is the relatively large quantity of tritium which would be produced in the salt fuel stream. Tritium, like hydrogen, can permeate most metals at elevated temperatures, and thereby contaminate the environment. An efficient means of removing and concentrating tritium from the fuel stream is essential to the development of MSBR.

In this project it was assumed that the tritium can be removed from the fuel stream by a hydrogen-helium purge and that the helium can be separated from the hydrogen for recycle via a palladium membrane. Four systems were conceptualized, designed, and economically evaluated to concentrate or store the hydrogen and tritium: storage of unconcentrated tritiated water, water distillation, gaseous thermal diffusion and cryogenic distillation of liquid hydrogen. On the basis of this evaluation the most economical system, cryogenic distillation, would provide a 1000-fold tritium enrichment at an estimated capital cost of $328,000 and an annual operating cost of $81,000.

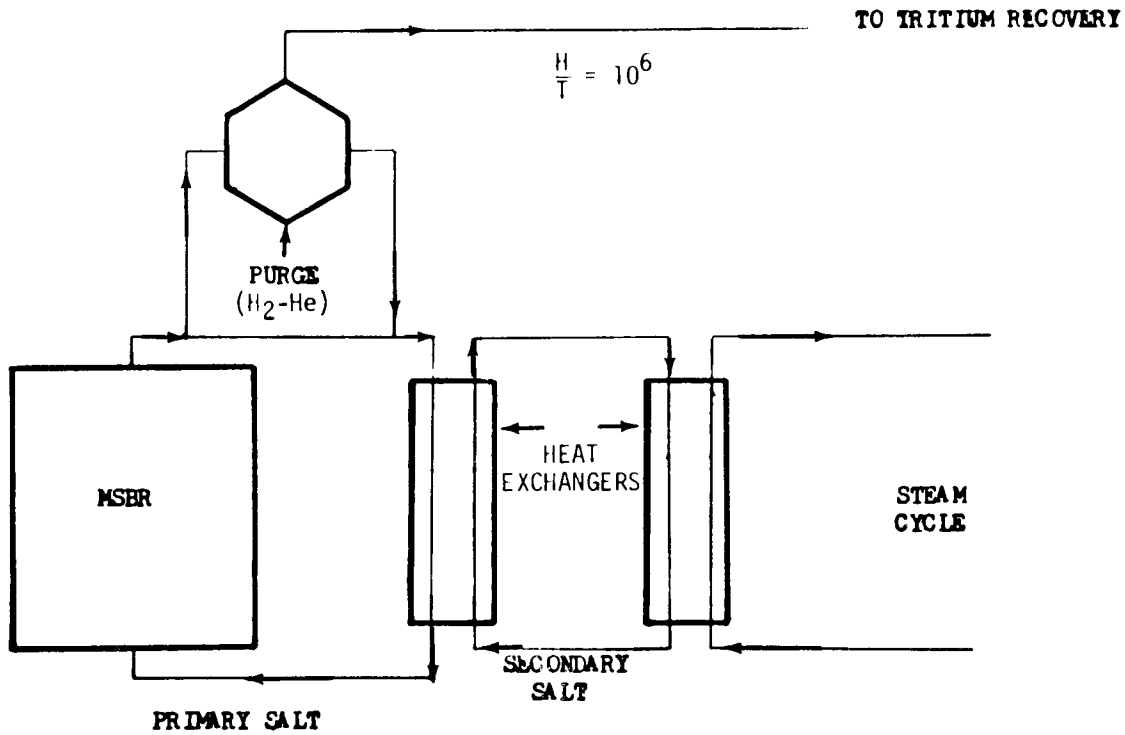
2. INTRODUCTION

There is presently interest at ORNL in the development of Molten Salt Breeder Reactors (MSBR). A characteristic of these reactors, however, is the generation of large quantities of tritium (half life 12.36 yr). Tritium, like hydrogen, has a very high permeability through most metals at temperature and concentration levels of the molten salt; therefore if it is not removed, it will escape from the reactor and contaminate the environment.

Tritium is a weak beta emitter (18.6 kev), but it exchanges readily with hydrogen and as tritiated water can enter the body by penetrating the skin. The effect of radiation in a very localized area and the transmutation of tritium to helium within the body may be of biological significance (1).

One proposed method of removing the tritium from the MSBR fuel stream is by means of a helium-hydrogen purge (2). The hydrogen stream would then be separated from the helium and the tritium would be concentrated and stored as tritiated water (HTO). Since tritium is an isotope, its concentration will depend mainly on physical separation processes.

In the MSBR concept the primary salt stream is comprised of molten salts of uranium, lithium, beryllium, and thorium. The primary salt circulates through the reactor where a critical mass is achieved and fission occurs. The sensible heat generated by fission is transferred to a steam cycle by means of a secondary salt stream. The flow plan is illustrated in Fig. 1.



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MSBR FLOW PLAN

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Tritium is produced in the primary salt stream by neutron absorption. The reactions producing tritium and the estimated production for a 1000 Mw(e) reactor are listed in Table 1.

Table 1. Tritium Production in a 1000 Mw(e) MSBR (3)

Ternary Fission	31 curies/day
$^{6}Li(n, \alpha)$ T	1210
$^{7}Li(n, \alpha n)$ T	1170
$^{19}F(n, {}^{17}O)$ T	9
	2420 curies/day
	$\simeq$ 0.25 gm tritium/day

3. DESIGN AND EVALUATION OF ALTERNATE SEPARATION SYSTEMS

3.1 Approach

In this study it was assumed that the tritium could be removed from the fuel stream by a mixed helium and hydrogen purge. The hydrogen and tritium would then be removed from the purge stream and concentrated. The selection of the most feasible system for effecting the desired concentration was based on a preliminary design and cost estimate for each system. The systems studied were storage of the unconcentrated tritium as tritiated water, water distillation, thermal diffusion, and cryogenic distillation of liquid hydrogen.

The design for all the systems was based on 111,000 gmoles of hydrogen per day at an $H/T = 10^6$. A 100- to 1000-fold enrichment was desired (i.e., $H/T = 10^3$ to 10^4 in the product stream) with a 99 to 99.9% recovery of the tritium. In all cases the product tritium is to be stored as water on the MSBR site (2). For all processes the separation equipment will be enclosed in a separate building to isolate any possible tritium leak.

3.2 Feed Pretreatment

The purge stream will contain helium, hydrogen, and tritium as well as gaseous fission products such as krypton, xenon, iodine, and hydrogen fluoride. It is proposed to pass the purge stream through a charcoal bed to adsorb some of the gaseous fission products. To separate the helium for

recycle from the hydrogen and tritium, a palladium "kidney" would be employed. A palladium membrane which passes 15 scfh of H_2 costs approximately $5000 (4). When the six-tenths power formula is applied to scale to the capacity required for the MSBR, an estimated purchase cost of $136,000 is realized.

It is estimated that the installed cost of the palladium kidney is four times the purchase cost of the kidney, or approximately $544,000. The same cost will be associated with each of the four alternate systems. A second item which is common to the four processes is the oxidation equipment and its installed cost is estimated to be $136,000.

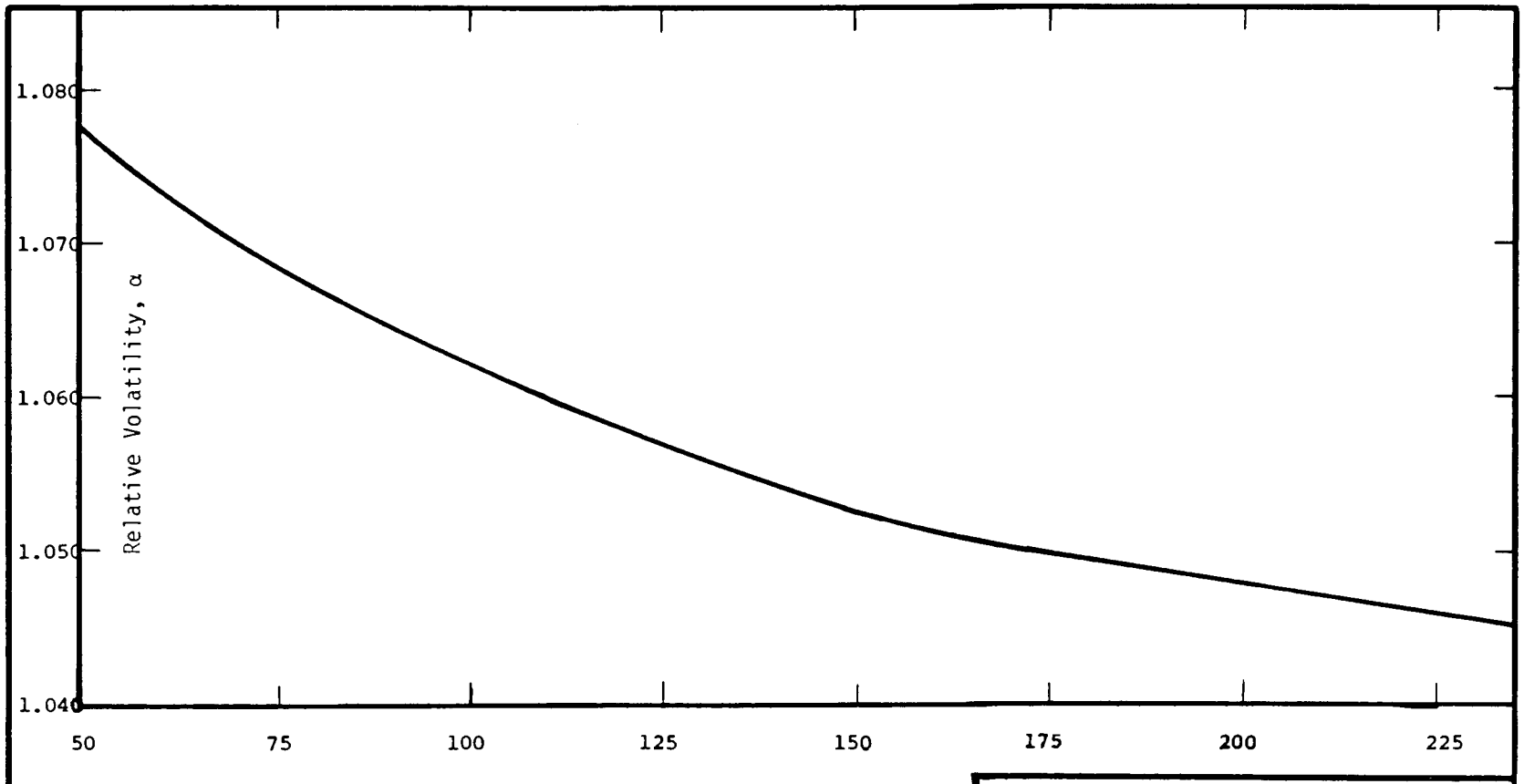
3.3 Storage of Tritiated Water

The hydrogen and tritium would be oxidized after passing through the palladium kidney and the resulting tritiated water condensed and sent to a storage tank. Storage of tritiated water will require steel tanks encased in a concrete tank. Should a leak develop, the liquid would be contained, but an additional tank would be required to effect a transfer before final repairs could be made (5). The tanks were sized to hold 30 years production of tritium, the expected lifetime of the reactor. The liquid will have to be stored until the activity has decreased to less than 1% (approximately 110 yr). At a production rate of 2000 liters/day, a tank capacity of approximately 5.8 million gallons is required. With an estimated capital cost of $1/gal (5), the two-tank system would have a capital cost of $11.6 million. Annual operating cost for this sytem would be the cost of the hydrogen and oxygen burned to form the water ($143,000) and the maintenance cost [2% of the capital cost (13)], $232,000. (See Appendix 7.1 for details.)

3.4 Water Distillation

During World War II the United States built and successfully operated several water distillation plants to produce heavy water. The low value of the relative volatility (α), however, required the use of high reflux ratios and a large number of plates in the distillation column.

Distillation to separate tritiated water (HTO) is not as difficult as that for heavy water, since the value for α is several percent higher. A plot of relative volatility versus pressure indicates that such a system should be operated under vacuum to take advantage of the higher value of α (see Fig. 2). A computer program was written to size the distillation column. The design of the column is based on the use of a high efficiency packing such as Sulzer CY (designed for use in heavy water systems). This packing was found to have 21 theoretical plates/meter and a pressure drop of 0.19 torr/theoretical plate (6) for heavy water separations at a liquid loading of 2000 kg/M^2-hr and a column head pressure of 120 mm Hg. More favorable conditions might be achieved with the tritium system by lowering the head pressure of the column.



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RELATIVE VOLATILITY ($\alpha \cdot \frac{H_2O}{HT}$) (1)

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As shown in Fig. 3 the number of theoretical plates is a sharp function of the reflux ratio. Figure 4 is a schematic diagram of the proposed water distillation design. The optimum systems and operating conditions were determined by varying the reflux ratio for different enrichment and recovery factors (see Tables 4 and 5 in Appendix 7.1). Table 2 shows the major design specifications and the cost estimates for the optimized systems. Capital costs for 99% recovery are \$422,700 at H/T = 10^4 and \$362,600 at H/T = 10^3. For 99.9% recovery, capital costs are \$536,600 at H/T = 10^4 and \$484,600 at H/T = 10^3. Although the column packing and building costs are higher for H/T = 10^3, the overall cost is less than for H/T = 10^4 because of the associated storage costs. The cost of recovering 99.9% of the tritium for H/T = 10^3 is 33% higher than the cost for 99% recovery. Operating costs in all four cases are essentially the same, \$220,000 annually. The cost of H_2 is the major operating expense, \$128,000 annually. A breakdown of the column costs for other reflux ratios is in Appendix 7.1.

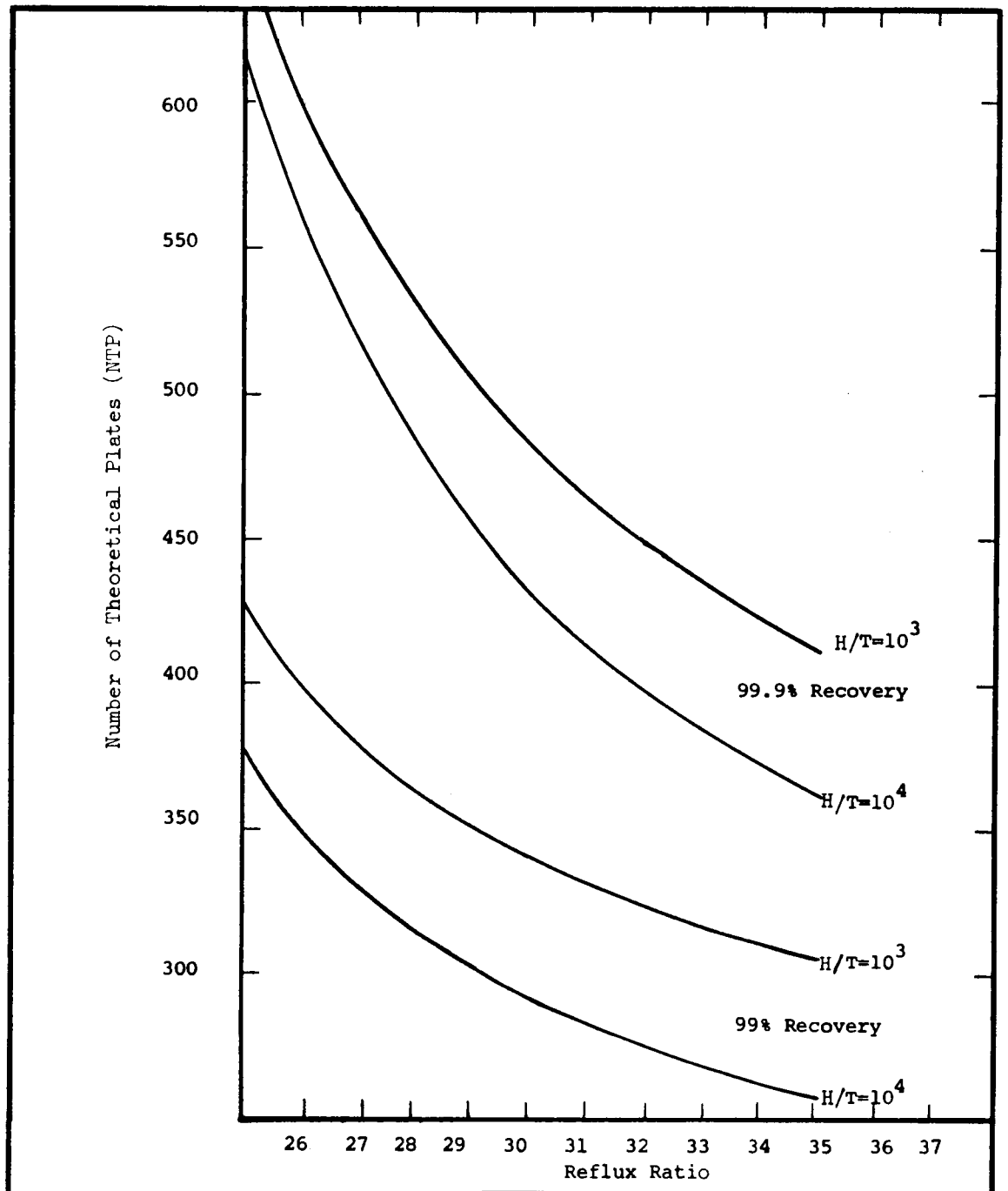
3.5 Thermal Diffusion

Thermal diffusion is based on a temperature gradient in a mixture of gases which gives rise to a concentration gradient, thereby effecting a partial separation. Jones and Furry (9) have presented a detailed discussion on the theory and design of thermal diffusion systems for binary separations. The thermal diffusion constant between two species with masses m_1 and m_2 is equal to $(m_2 - m_1)/(m_2 + m_1)$, and for a hydrogen-tritium system this ratio is 1/3 which is considered high.

In a thermal diffusion column the separation rate is fixed by the temperature and pressure of the system. Theory requires that the rate of production of each column be small compared with the rate of thermal diffusion. The production rate of tritium in an MSBR is so large that 10^3 to 10^4 thermal diffusion columns operated in parallel would be necessary. Based on the theory of Jones and Furry, Verhagen and Sellschop (11) designed and operated a thermal diffusion system for tritium enrichment. A scaleup of their apparatus would require 5150 parallel systems for a 1000-fold enrichment with a power load of 100,000 kwh. The power consumption at \$0.004/kwh would cost \$2.9 million per year. (See Appendix 7.2 for apparatus details and operating conditions.)

3.6 Cryogenic Distillation

Due to recent advances in cryogenic engineering, several plants have been constructed which separate deuterium from hydrogen by cryogenic distillation of the liquid hydrogen feed. The relative volatility of H_2 to HT is not available, but it is believed to be equal to, if not greater, than the relative volatility for the H_2-HD system ($\alpha \cong 1.6$ at 1.5 atm). This is considerably higher than the relative volatility for the water-tritiated water system ($\alpha \cong 1.05$). A second advantage is the lower consumption of H_2 and O_2. For the separation of tritium by water distillation, all the H_2 from the purge stream is oxidized to water, but in the cryogenic system



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NUMBER OF THEORETICAL PLATES
VERSUS REFLUX RATIO

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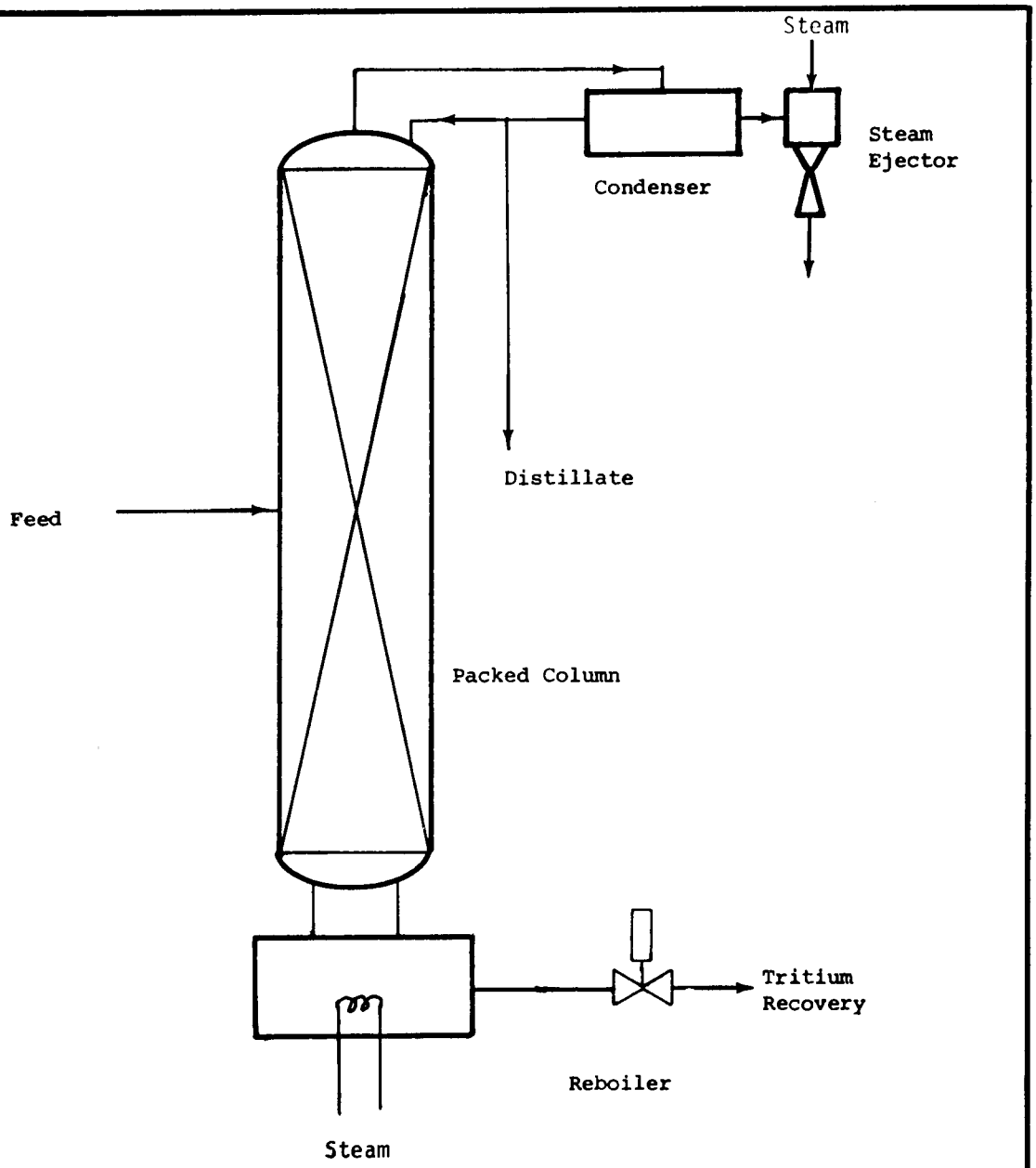

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WATER DISTILLATION SYSTEM

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Table 2. Cost Estimate of Optimum Water Distillation Systems
(See Appendix 7.1 for Details)

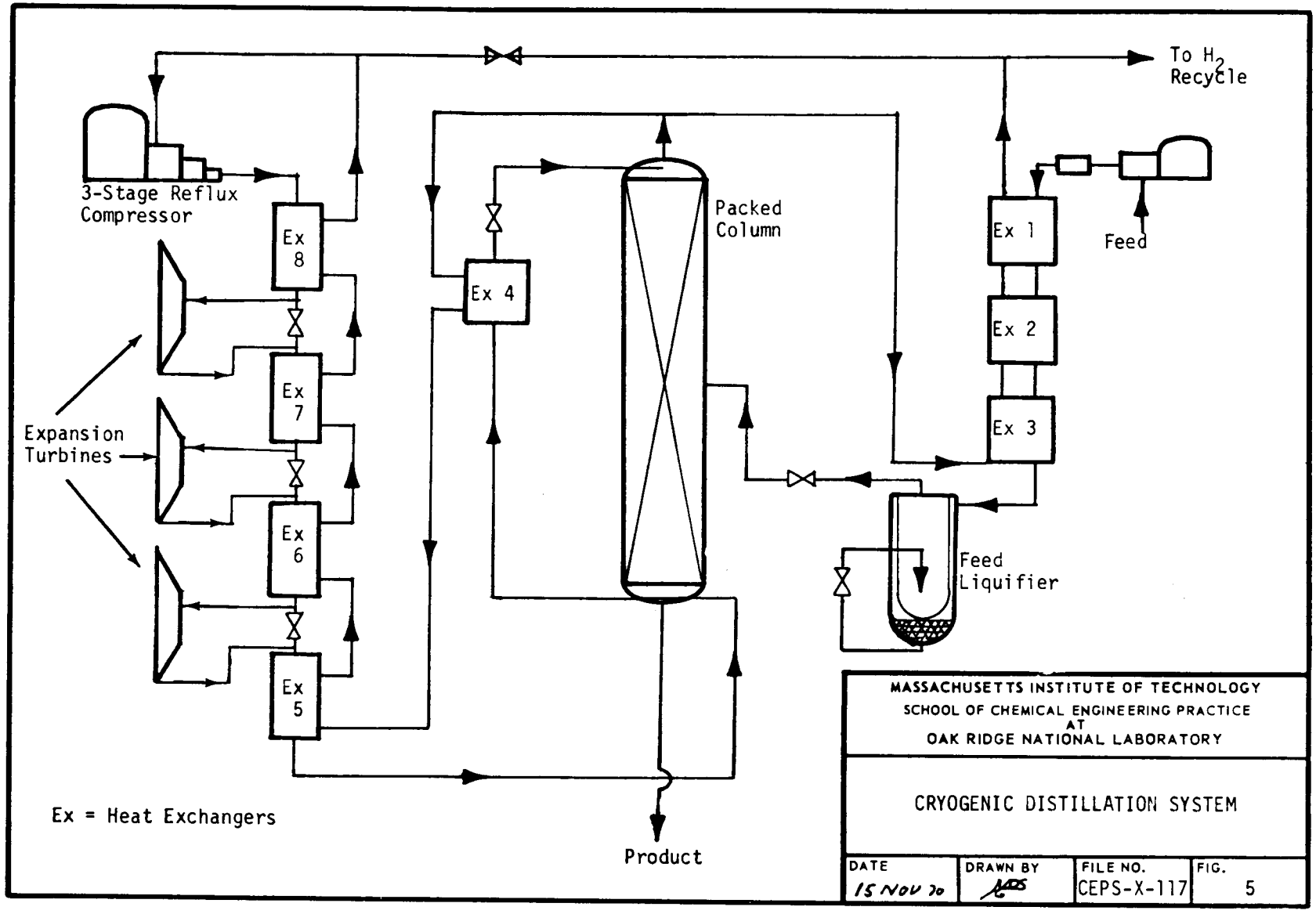
Recovery	99%	99%	99.9%	99.9%
Product H/T	10^4	10^3	10^4	10^3
Column Diameter	1.32 M	1.32 M	1.32 M	1.32 M
Number Theoretical Plates	275	323	362	412
Designed No. Plates = 1.1 (NTP)	303	355	398	453
Column Height	14.4 M	16.9 M	19.0 M	21.6 M
Reflux Ratio	32	32	35	35
Installation Column Cost	$90,600	$106,200	$138,000	$157,200
Flow Distributors	1,500	1,200	1,200	1,200
Packing	139,000	163,000	200,000	228,000
Building	19,600	23,000	25,900	29,500
Covering	3,000	3,400	4,100	4,100
Ejector (installed)	2,000	2,000	2,000	2,000
Site Preparation	1,000	1,000	1,000	1,000
Instruments	50,000	50,000	50,000	50,000
Total	306,700	349,800	422,200	473,000
Storage Tanks	116,000	11,600	116,000	11,600
Total	$422,700	$361,400	$538,200	$484,600
Operating Costs, $/yr (Depreciation Not Included)				
Steam	$10,570	$10,570	$11,530	$11,530
H_2 Usage	128,160	128,160	128,160	128,160
O_2 Usage	14,685	14,685	14,685	14,685
Labor	45,000	45,000	45,000	45,000
Maintenance @ 5% Investment	21,135	18,070	26,910	24,230
Total	$219,550	$216,485	$226,285	$223,605

only the final product is burned, and the remainder, more than 99% of the H_2 can be recycled.

The liquid hydrogen distillation system is based on a plant built by Gebrüder Sulzer for heavy water production in DOMAT/EMS, Switzerland (18, 19). A schematic for this plant is shown in Fig. 5. The hydrogen feed is initially compressed to 3.7 atm, cooled in a series of three heat exchangers (Nos. 1, 2, and 3), then liquified and re-evaporated in the feed liquifier before it enters the column. The vapor from the top of the column is split into two streams. One stream passes through exchangers 3, 2, and 1 to cool the feed, and then is recycled to the hydrogen purge stream. The remainder passes through exchangers 4 through 8, exchanging against the returning reflux stream. It exits exchanger 8 at ambient temperatures, and enters the reflux compressor. Because of interstage compressor cooling, the H_2 gas leaves the compressor at 14 atm and 300°K. The stream re-enters exchanger 8 and the expansion turbines, and finally exits exchanger 5 as saturated vapor at 4.5 atm. The saturated vapor then passes through the bottom of the column where it is condensed by boiling the liquid in the reboiler. The stream passes through exchanger 4, flashes to 1.5 atm, and enters the column as saturated liquid.

The computer code used in Sect. 3.4 was modified for use with this system. Calculations showed that a column with 100 theoretical stages operating at a reflux ratio of two would yield a separation of $H/T = 10^3$ at a recovery of 99.9%. Although calculations showed that a reflux ratio of two was sufficient for the desired separation, the design was based on a reflux ratio of five to allow for variation of the operating conditions and to ensure a conservative cost estimate. With a packing material similar to Sulzer CY, the column would be only 13 ft high at a liquid loading of 1500 kg/m^2-hr (6). As seen in Table 3 the column cost represents a small fraction of the total cost; therefore, the less difficult separations were neglected in the analysis.

Capital cost is estimated at $328,100 and operating costs at $80,600 annually. The building for this system must not only isolate the system, but also insulate the apparatus for the low temperatures involved. The distillation column and the low temperature heat exchangers and expansion turbines are enclosed in steel vacuum bottles to maintain cryogenic temperatures. No cost information was obtainable on the new high efficiency insulation currently being used on some cryogenic equipment. However, it is believed that the cost estimate presented is conservative. The cost of the expansion turbines was estimated from cost information for a 200 ton/day oxygen plant. This unit has 100 times the capacity required for the hydrogen liquification unit. Further details on the cryogenic distillation system, including an explanation of the cost estimate, are given in Appendix 7.3.


To H_2 Recycle
3-Stage Reflux Compressor
Ex 8
Ex 7
Ex 6
Ex 5
Ex 4
Expansion Turbines
Packed Column
Ex 1
Ex 2
Ex 3
Feed
Feed Liquifier
Product
Ex = Heat Exchangers
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CRYOGENIC DISTILLATION SYSTEM
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FIG.
5

Table 3. Cost Evaluation of Cryogenic Distillation System

Recovery	99.9%
H/T in Product	10^3
Designed Number of Stages	100
Reflux Ratio	5
Column Diameter	8 in.
Column Height	13 ft

	Purchase Cost	Factor	Installed Cost
Capital Cost			
Column	$ 1,000		
Packing	925		
	1,925	5	$ 9,600
Feed Compressor	8,700		
Reflux Compressor	31,000		
	39,700	2	79,400
Heat Exchangers	46,000	2	92,000
Expansion Turbines			25,000
Instrumentation			50,000
Insulated Building			24,500
Vacuum System	9,000	4	36,000
Storage Tank			11,600
Total Capital Cost			$ 328,100
Annual Operating Costs (Depreciation not Included)			
Electricity			
a) Compressors			1,300
b) Vacuum System			200
H_2 and O_2			1,300
Labor			45,000
Maintenance at 10% Capital Cost			32,800
Total Operating Cost			$ 80,600

4. DISCUSSION OF SEPARATION SYSTEMS

Storage of tritiated water without any form of concentration requires a capital cost twenty times greater than for water distillation and thirty-five times that of cryogenic distillation. Thermal diffusion also represents an unsatisfactory solution to the problem of tritium concentration. Monitoring over 5000 two-stage thermal diffusion columns and maintaining control of the feed to each column appears horrendous; and the annual power cost of $2.9 million certainly makes this system unfeasible.

Water distillation is a technically sound alternative. However, its capital and operating costs are not competitive with those of cryogenic distillation. The packing represents the major capital expense, and since all of the hydrogen is oxidized to water, the major operating expense is the cost of hydrogen. However, if the hydrogen concentration in the purge stream is sufficiently high, it might be feasible to oxidize the hydrogen directly without the use of a palladium kidney and separate it from the purge stream as water. This would not be sufficient to make water distillation competitive with the cryogenic system based on operating costs.

Cryogenic distillation has the lowest capital cost estimate as well as the lowest operating costs. Part of the economic advantage is realized by recycling 99.9% of the hydrogen to the purge stream. It should be noted that the cryogenic distillation was designed for a reflux ratio of five, although for 99.9% recovery at $H/T = 10^3$, a reflux ratio of two is sufficient. Thus the system is capable of recoveries in excess of 99.9% at concentrations lower than $H/T = 10^3$.

5. CONCLUSIONS AND RECOMMENDATIONS

1. Cryogenic distillation of liquid hydrogen is the most economical of the alternatives studied. A cryogenic distillation system which will enrich 4630 gmole/hr of hydrogen from $H/T = 10^6$ to $H/T = 10^3$ at 99.9% recovery has an estimated capital cost of $328,100 and an estimated annual operating cost of $80,600 (excluding depreciation). There is also the associated capital cost of $680,000 for the palladium pretreatment and oxidizing systems.

2. Water distillation or storage of unconcentrated tritiated water represents too great a capital expenditure and annual operating cost.

3. Thermal diffusion is unattractive for concentrating tritium from a 1000 Mw(e) MSBR.

6. ACKNOWLEDGEMENT

The authors would like to express their gratitude to R.B. Korsmeyer for the assistance and insight he provided during this project. His enthusiasm was a constant source of encouragement. The assistance of J.T. Corea is also gratefully acknowledged.

7. APPENDIX

7.1 Basis for Water Distillation Costs

1. Column Shell thickness 0.5 in., type 304 stainless steel

   $1.25/lb fabricated (12)

2. Flow Distributors: 1 approximately every 5 meters

   $300 each (installed) (13)

3. Packing

   $200/ft^3 (14)

4. Building Cost

   $2.70/ft^3 (25)

5. Building Insulation

   $1/ft^2 wall (15)

6. Steam Ejector

   $2000 installed (13, 16)

7. Storage Tanks

   $1/gal (5)

8. Steam

   $0.25/10^6 Btu (Use of waste steam from the MSBR)

9. Raw Materials

   H_2 = $0.0048/scf

   O_2 liquid = $25/ton (17)

10. Labor

    1 man/shift at $15,000 yr = $45,000

11. Maintenance at 5% of investment (13)

12. 7000 hr of Operation Per Year

Tables 4 and 5 reflect the costs of the various H_2O distillation systems.

Table 4. Cost of Various Water Distillation Systems

	For 99% Recovery with H/T = 10^4						For 99% Recovery with H/T = 10^3					
Reflux	25	27	30	32	35	40	25	27	30	32	35	40
Column Diam (M)	1.17	1.22	1.28	1.32	1.38	1.47	1.17	1.22	1.28	1.32	1.38	1.47
NTP	377	330	291	275	258	239	425	379	340	323	306	287
ANP = NTP x 1.1	415	363	320	303	284	263	471	417	374	355	337	316
Column Height (M)	19.8	17.3	15.2	14.4	13.5	12.5	22.4	19.9	17.8	16.9	16.05	15.0
Column Cost	$18,300	$16,700	$15,400	$15,100	$14,800	$14,600	$20,800	$19,200	$18,000	$17,700	$17,500	$17,500
Installation (5x)	91,500	83,500	77,000	75,500	74,000	73,000	104,000	96,000	90,000	88,500	87,500	87,500
Flow Distributors	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,500	1,200	1,200	1,200
Packing	150,000	143,000	138,000	139,000	143,000	150,000	170,000	164,000	162,000	163,000	169,000	180,000
Building	27,000	23,600	20,700	19,600	18,400	17,000	30,500	27,000	24,200	23,000	21,800	20,400
Covering	3,800	3,400	3,100	3,000	2,800	2,700	4,200	3,900	3,500	3,400	3,200	3,100
Ejector (installed)	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000
Site Preparation	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Instrumentation	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000
Subtotal	345,100	324,700	308,700	306,700	307,500	311,800	384,000	364,600	352,200	349,800	353,200	362,700
Storage Tanks	116,000	116,000	116,000	116,000	116,000	116,000	11,600	11,600	11,600	11,600	11,600	11,600
Total Capital Cost	$461,100	$440,700	$424,700	$422,700	$423,500	$427,800	$395,600	$376,200	$363,800	$361,400	$364,800	$374,300
Steam Cost/yr	8,330	8,980	9,940	10,570	11,530	13,130	8,330	8,980	9,940	10,570	11,530	13,130

Table 5. Cost of Various Water Distillation Systems

	For 99.9% Recovery with H/T = 10^4						For 99.9% Recovery with H/T = 10^3					
Reflux	25	27	30	32	35	40	25	27	30	32	35	40
Column Diam (M)	1.17	1.22	1.28	1.32	1.38	1.47	1.17	1.22	1.28	1.32	1.38	1.47
NTP	614	518	431	397	362	329	660	561	482	448	412	378
ANP = NTP x 1.1	675	570	474	437	398	362	726	617	530	494	453	416
Column Height (M)	32.1	27.1	22.6	20.8	19.0	17.2	34.6	29.4	25.2	23.5	21.6	19.8
Column Cost	$35,900	$29,000	$25,400	$24,100	$23,000	$22,200	$36,900	$31,500	$28,300	$27,300	$26,200	$25,500
Installation (5x)	180,000	145,000	127,000	121,000	115,000	111,000	185,000	158,000	142,000	137,000	131,000	128,000
Flow Distributors	2,100	1,800	1,500	1,200	1,200	1,200	2,100	1,800	1,500	1,500	1,200	1,200
Packing	265,000	224,000	205,000	200,000	200,000	206,000	272,000	243,000	229,000	227,000	228,000	237,000
Building	43,800	37,000	30,800	28,400	25,900	23,400	47,200	40,000	34,400	32,000	29,500	27,000
Covering	6,200	5,000	4,300	4,400	4,100	3,800	6,400	5,300	4,700	4,400	4,100	3,800
Ejector (installed)	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000
Site Preparation	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Instrumentation	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000	50,000
Subtotal	596,000	494,800	447,000	432,100	422,200	420,600	602,600	532,600	492,900	482,200	473,000	475,500
Storage Tanks	116,000	116,000	116,000	116,000	116,000	116,000	11,600	11,600	11,600	11,600	11,600	11,600
Total Capital Cost	$712,000	$610,800	$563,000	$548,100	$538,200	$536,600	$614,200	$544,200	$504,500	$493,800	$484,600	$487,100
Steam Cost/yr	8,330	8,980	9,940	10,570	11,530	13,130	8,330	8,980	9,940	10,570	11,530	13,130

7.2 Thermal Diffusion System

The theory of Jones and Furry (9) states that the temperature and pressure fix the operating parameters of a thermal diffusion system. The calculations are presented to illustrate that thermal diffusion systems of the scale required by an MSBR are uneconomical. From Equations 70-72 of Jones and Furry, we obtain for concentric columns:

$$H = \frac{(2w)^3 \rho^2 \alpha g B}{6!\ \eta} (\Delta T/T)^2$$

$$K_c = \frac{(2w)^7 \rho^3 g^2 B}{9!\ \eta D} (\Delta T/T)^2$$

$$K_d = 2w \rho D B$$

These equations are used subject to the constraint that $5 < K_c/K_d < 25$. For an efficient operation $K_c/K_d = 10$. The ratio of $B/2w = 20$ corresponds to the value of Jones and Flurry and Verhagen (11).

Inserting the appropriate values for hydrogen, we find that:

$P = 1$ atm	$P = 5$ atm
$T_1 = 300°K$; $T_2 = 600°K$	$T_1 = 300°K$; $T_2 = 600°K$
$\eta = 1.18 \times 10^{-4}$ poise	$\eta = 1.18 \times 10^{-4}$ poise
$\rho = 0.54 \times 10^{-4}$ g/cc	$\rho = 2.71 \times 10^{-4}$ g/cc
$D = 2.99$ cm^2/sec	$D = 0.5225$ cm^2/sec
$\alpha = 0.174$	$\alpha = 0.149$
$2w = 1.253$ cm	$2w = 0.574$ cm
$B = 15.9$ cm	$B = 11.48$ cm
$H = 0.774 \times 10^{-4}$ g/sec	$H = 8.17 \times 10^{-4}$ g/sec
$K_c = 5.06 \times 10^{-2}$ g-cm/sec	$K_c = 2.66 \times 10^{-3}$ g-cm/sec
$K_d = 5.07 \times 10^{-3}$ g-cm/sec	$K_d = 2.66 \times 10^{-4}$

σ = rate of mass transport of the desired species, i.e., the production rate in g/sec.

McInteer (10) has reported that σ/H must be much less than one; and from Jones and Furry (9) we see that σ/H should be on the order of 10^{-4} to 10^{-6} for each stage. MSBR requirements are such that the total flow rate is 9.55×10^{-4} g/sec. To satisfy theory 10^4 to 10^6 columns in parallel will be required. Based on the theory of Jones and Furry, Verhagen and Sellschop (11) designed and operated a thermal diffusion system for tritium enrichment. Their apparatus is schematically shown in Fig. 6. The specifications are given in Table 6.

Table 6. Thermal Diffusion System of Verhagen and Sellschop (11)

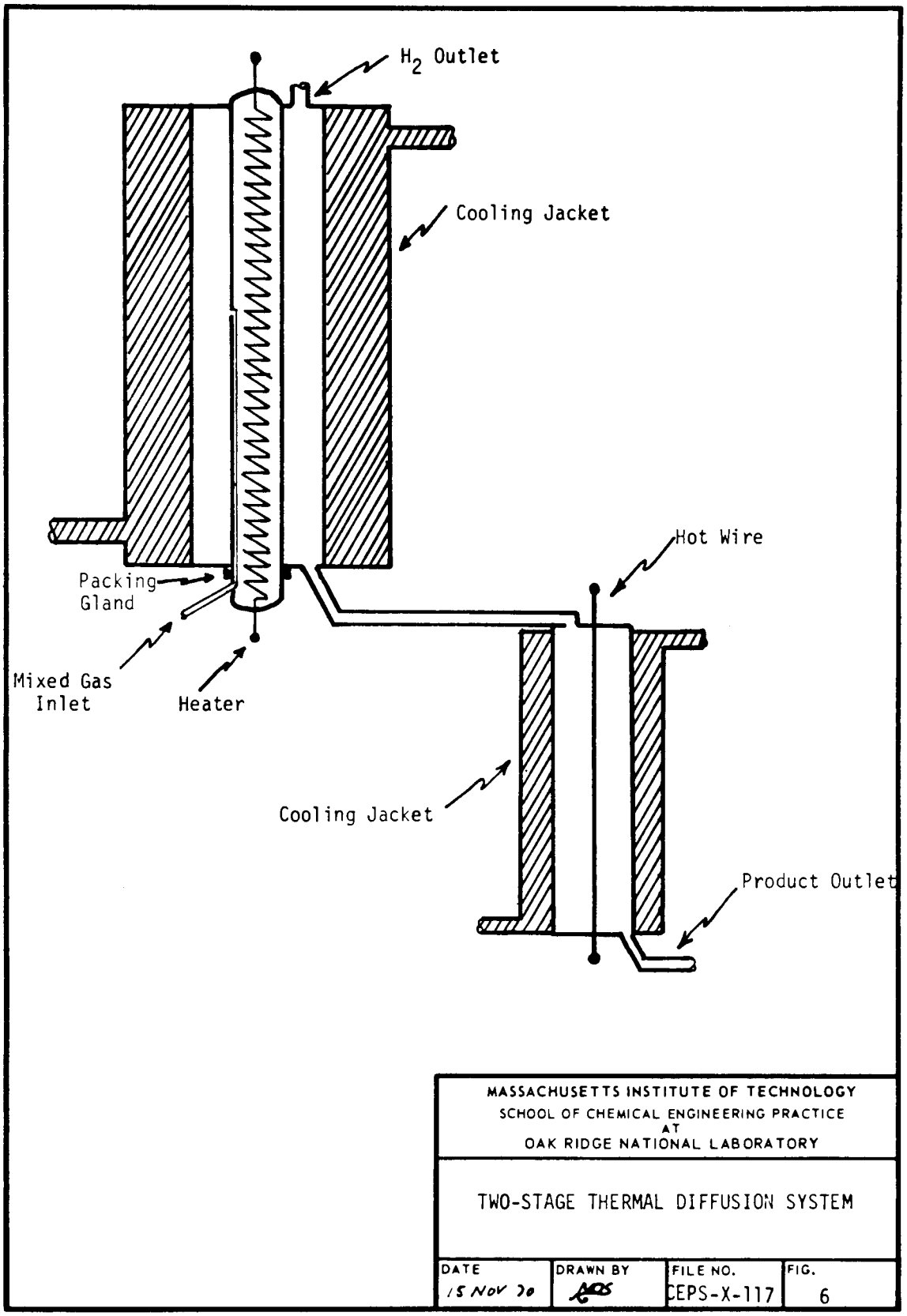
	Stage 1	Stage 2
Type of unit	concentric tube	hot wire
Radius, hot wall	6.30 cm	0.02 cm
Radius, cold wall	8.76 cm	1.50 cm
Length	7.20 m	2.75 m
Temperature, hot wall	600°K	1200°K
Temperature, cold wall	300°K	300°K
Power consumption	18.5 kwh	1.66 kwh
Pressure	1 atm	1 atm

At the required enrichment of 1000-fold, this system has a production capacity of only 0.125 cc(STP)/min of tritium. Based on this design approximately 5150 systems in parallel are necessary to process the 642 cc(STP)/min from the MSBR. Aside from the extreme difficulty in maintaining a uniform feed rate to each column [to which thermal diffusion systems are very sensitive (9)], the power consumption is extremely high. The overall system requires 72.7×10^7 kwh/yr at \$0.004/kwh or a yearly power cost of \$2.9 million.

7.3 Cryogenic Distillation System

7.3.1 Design of Cryogenic Distillation Column

The specifications given in Table 3 were based on an α of 1.6. This value is for a hydrogen-deuterium system; however, it is believed that the α for the tritium system would be at least as great if not greater.


H_2 Outlet
Cooling Jacket
Hot Wire
Packing Gland
Mixed Gas Inlet
Heater
Cooling Jacket
Product Outlet
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
TWO-STAGE THERMAL DIFFUSION SYSTEM
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FILE NO.
CEPS-X-117
FIG.
6

Computer calculations were made for the four different separations at various reflux ratios and for both saturated liquid and saturated vapor feeds. Selected results are presented in Table 7.

Table 7. Variation of NTP with Operating Parameters for H_2 Distillation Column

NTP	53	58	88	93	98	76	49	50
Q'	1	1	1	1	0	0	1	0
Reflux Ratio	2	2	2	2	2	2.2	3	3
% Recovery	99.0	99.0	99.9	99.9	99.9	99.9	99.9	99.9
H/T Product	10^4	10^3	10^4	10^3	10^3	10^3	10^3	10^3

For a liquid feed and R = 2, it is seen that lowering H/T from 10^4 to 10^3 causes an increase of only five stages for either 99.0 or 99.9% recovery. The difference between 99 and 99.9% recovery is 40 plates at R = 2, but NTP is still under 100 for 99.9% recovery. If the feed is a saturated vapor, NTP is slightly higher but the difference is insignificant. NTP drops rapidly at reflux ratios above 2. A 10% increase in reflux from 2 to 2.2 lowers NTP from 98 to 76, and increasing the reflux from 2 to 3 lowers NTP from 93 to 49.

In view of these results it was felt that a column with 100 theoretical stages operating at a reflux ratio of 2 would be adequate for the most difficult separation, i.e., recovery = 99.9% and H/T = 10^3. However, in calculating the cost of the system a reflux ratio of 5 was used to provide operational flexibility, conservative separation capability, and cost estimate.

7.3.2 Basis for H_2 Distillation Costs

1. Column shell thickness 1/4 in., type 304 stainless steel

   \$1.25/lb fabricated (12)

2. Packing

   \$200/ft^3 (14)

3. Heat exchangers

   \$4/ft^2 purchase price for plate-fin type (20)

   area calculated from $Q = UA\Delta T$

where $U = 2$ Btu/hr-ft^2-°F for gas-gas exchange

$\Delta T = 5°K = 9°F$

$$Q = (4630 \text{ mole feed/hr})(6 \text{ mole reflux/mole feed})(7.44 \frac{\text{Btu}}{\text{mole reflux}})$$

$$= 207{,}000 \text{ Btu/hr}$$

7.44 Btu is the ΔH per mole of H_2 from saturated vapor at 1.5 atm to 295°K at 1.5 atm (21)

$$\text{area} = (207{,}000)/(2)(9) = 11{,}500 \text{ ft}^4$$

4. Compressors

purchase cost = \$7740 + (\$99.5)(HP) (20)

For 3-stage reflux compressor,

$$\text{cost} = 3(7740) + 99.5(\text{HP})$$

Calculated compressor size based on

$$W_n \text{ (adiabatic)} = \frac{k\,N\,R\,T_1}{k-1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(k-1)/k}\right] \quad (22)$$

where: $k = C_p/C_v = 1.405$ for normal H_2 (23)

From this equation the work of compressing the feed was calculated: $T_1 = 300°K$, $P_1 = 1$ atm, $P_2 = 3.7$ atm, and $W_n = 0.947$ kcal/mole. For a feed of 4630 mole/hr,

$$W_n = (4385 \text{ kcal/hr})\left(\frac{0.00156 \text{ HP}}{\text{kcal/hr}}\right) = 6.8 \text{ HP}$$

A 20% margin of safety was allowed and an overall efficiency of 85% was assumed, yielding a design of 10 HP.

For the 3-stage reflux compressor with interstage cooling, a T_1 of 245°K was used for all three stages. The initial pressure is 1.5 atm and interstage pressures of 5.5 and 9.5 atm were used in applying the above equation which yields $W_n = 1.51$ kcal/mole. For a reflux ratio of 5 the power requirement is 54 HP, and with a 20% margin of safety and 85% efficiency the design is 77 HP.

5. Expansion Turbines

Lady (24) quotes a capital cost of \$25,000 for an expansion turbine in a 200 ton/day liquid O_2 plant. To be on the conservative side the same

figure is used in this cost estimate for the installed cost of the three expansion turbines.

6. Insulated building

   $500/ft^2 floor space (15)

7. Two vacuum tanks, type 304 stainless steel

   0.5-in.-thick x 15-ft-high x 3.5- ft -diam at $1.25/lb

   fabricated = $9000 (12)

Installed cost of vacuum bottles including all vacuum equipment is $36,000.

8. Electricity

   $0.004/kwh (2)

9. Raw materials:

   H_2 = $0.0048/scf (17)

   O_2 = $25/ton (liquid)

10. Labor

    one man/shift = $45,000

11. Maintenance

    10% of investment (13)

12. 7000 hr operation per year

7.4 Computer Codes

A listing of the computer program for the water distlllation column is shown below. The basis of calculation was a feed of 100 mole.

```
XF=.999998
55 ACCEPT $K= $,K; IF(K),57,; ACCEPT KK;IF(KK),58,
ACCEPT $PRT= $,PRT,$NP= $,NP,$DELP= $,DELP
58 ACCEPT $REC= $,REC,$WØT= $,WØT,$R= $,R
BHTØ=REC*0.0002;BWAT=BHTØ*WØT;B=BHTØ+BWAT;XB=BWAT/B;D=100.-B
DWAT=99.9998-BWAT;XD=DWAT/D;RLØV=R/(R+1.);SLØV=(R+100./D)/(R+1.)
DXD=XD/(R+1.);BXB=(B/D)*XB/(R+1.)
60 FØRMAT(15,F15.10,F9.5)
N=1;J=1;JJ=1;Y=XD;PR=PRT;A1=RLØV;A2=DXD
```

```
20 CALL ALPHA(PR,A)
X=Y/(A-(A-1.)*Y);IF(J-JJ*K)24,22,22
24 IF(N),29,;IF(X-XF)30,30,25
29 IF(X-XB)40,,
25 Y=A1*X+A2;J=J+1;IF(J-NP)26,27,27
26 PR=PR+DELP;GØ TØ 20
27 DISPLAY  $STAGES= $,J,$X= $,X;J=1;PR=PRT;JJ=1;GØ TØ 20
22 JJ=JJ+1;WRITE(1,60)J,X,A;GØ TØ 24
30 N=0;A1=SLØV;A2=-BXB;GØ TØ 25
40 WRITE(1,60)J,X;GØ TØ 55
  57 STØP
END
S'E ALPHA(PR,A)
D'N AL(9),P(9)
DATA AL/1.0775,1.0735,1.07,1.067,1.062,1.056,1.0512,1.0478,1.044/
DATA P/50.,60.,70.,80.,100.,130.,160.,200.,250./
DØ 8 J=1,10
IF(P(J)-PR) 8,9,10
8 CØNTINUE
9 A=AL(J); GØ TØ 15
10 A=AL(J-1)+(AL(J)-AL(J-1))*(PR-P(J-1))/(P(J)-P(J-1))
15 RETURN
END
*
```

The following list defines the important variables in the program.

XF — mole fraction of H_2O in the feed

PRT — pressure at the top of the column (torr)

NP — maximum number of plates in a column; if NP is exceeded the program continues with a new column, resetting the top pressure to PRT

DELP — pressure drop per theoretical stage (torr)

REC — fractional recovery of HTO

WØT — ratio of H_2O to HTO in the bottoms

R — reflux ratio = L/D

BHTØ — number of moles of HTO in bottoms based on 100 moles feed

BWAT — number of moles of H_2O in bottoms

B — number of moles in bottoms

D — number of moles in distillate

XB — mole fraction H_2O in bottoms

XD mole fraction H_2O in distillate

DWAT number of moles H_2O in distillate

RLØV L/V above the feed

SLØV L/V below the feed

DXD D · XD/V

BXB B · XB/V

A relative volatility of H_2O to HTO

PR pressure at any point in the column (torr)

X liquid mole fraction of H_2O at any point

Y vapor mole fraction of H_2O at any point

The program assumes constant molal overflow which is certainly justified since the liquid and vapor streams are at least 99.9% H_2O. The variation of relative volatility with pressure is introduced according to the curve in Fig. 2. The feed is assumed to be saturated liquid.

For the cryogenic H_2 distillation the program was modified for the thermal condition of the feed, and the variable alpha subroutine was replaced with a constant alpha. The following printout shows the modified program.

```
XF=.999998; A=1.6
55 ACCEPT $K= $,K; IF(K),57,
 ACCEPT $REC=$,REC,$WØT= $,WØT,$R= $,R,$Q= $,Q
BHTØ=REC*0.0002;BWAT=BHTØ*WØT;B=BHTØ+BWAT;XB=BWAT/B;D=100.-B
DWAT=99.9998-BWAT;XD=DWAT/D;RLØV=R/(R+1.);VL=D*(R+1.)-100.*(1.-Q)
SLØV=(R*D+Q*100.)/VL;BXB=B*XB/VL;DXD=XD/(R+1.)
60 FØRMAT(I5,F15.10)
IF(Q.EQ.1.0) GØ TØ 70;XIN=(XF/(Q-1.)+XD/(R+1.))/(Q/(Q-1.)-R/(R+1.))
DISPLAY $XIN= $,XIN; GØ TØ 69
70 XIN=XF
69 N=1;J=1;JJ=1;Y=XD;A1=RLØV;A2=DXD
20 X=Y/(A-(A-1.)*Y);IF(J-JJ*K)24,22,22
24 IF(N),29,;IF(X-XIN)30,30,25
29 IF(X-XB)40,,
25 Y=A1*X+A2;J=J+1;GØ TØ 20
22 JJ=JJ+1;WRITE(1,60)J,X;GØ TØ 24
30 N=0;A1=SLØV;A2=-BXB;GØ TØ 25
40 WRITE(1,60)J,X;GØ TØ 55
  57 STØP
```

Definitions of the new variables are as follows:

Q $\frac{\text{heat to convert one mole feed to a saturated vapor}}{\text{molar heat of vaporization}}$

For a staurated liquid feed Q = 1; for a saturated vapor feed Q = 0.

VL vapor rate below the feed

XIN liquid mole fraction of H_2O at the intersection of the Q-line with the upper operating line; at this X value the program switches from the upper operating line to the lower operating line

7.5 Nomenclature

A heat transfer area, cm^2

ATP actual number of plates

B mean circumference = $\pi(r_1 - r_2)$, cm

C_p specific heat at constant pressure, cal/g-°C

C_v specific heat at constant volume, cal/g-°C

D coefficient of self diffusion, cm^2/sec

Ex heat exchanger

g acceleration of gravity, cm/sec^2

H transport coefficient of thermal diffusion, g/sec

K ratio of specific heats (C_p/C_v)

K_c transport coefficient of mixing due to convection

K_d transport coefficient of mixing due to diffusion

m atomic mass

N number of gram moles

NTP number of theoretical plates

P system pressure, atm

Q heat transferred per unit time, Btu/hr

Q' ratio of molar enthalpy change in converting feed to saturated vapor to the molar heat of vaporization

R reflux ratio, gas constant

r radius ($r_1 > r_2$), cm

STP standard temperature and pressure

T temperature, °C

ΔT temperature driving force, °C

U overall coefficient of heat transfer

w half the annular distance = $\frac{1}{2}(r_1 - r_2)$, cm

W_n work of adiabatic compression per mole, Hp

α relative volatility, thermal diffusion constant

η viscosity, poise

ρ density, g/cc

σ mass transport rate of desired species, g/sec

Subscripts

1,2 atomic mass of components 1 and 2 respectively, or initial and final conditions of temperature or pressure

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Internal

1. E.S. Bettis
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