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CASCADES FOR NATURAL WATER ENRICHMENT IN DEUTERIUM AND OXYGEN-18 USING MEMBRANE PERMEATION

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ABSTRACT

Heavy isotope enrichment of water using a hydrophobic membrane permeation process is described. Simple and ordinary countercurrent cascades will not be of practical interest because of high energy demand. A better solution is to employ a double countercurrent cascade, reutilizing part of the heat of condensation.

INTRODUCTION

Water enriched in its naturally occurring less common isotopes plays an important role in research and technology. D_2O (natural abundance of deuterium is $\sim 0.015\%$) is used in nuclear technology and research, and its role will become even more important should nuclear fusion ever be used for energy production.

Water enriched in ^{18}O ($\sim 0.204\%$) is used in research and medicine, primarily in tracer experiments, as is water enriched in ^{17}O ($\sim 0.037\%$). In contrast to ^{16}O and ^{18}O, ^{17}O has a nuclear magnetic moment which permits NMR detection and makes

it particularly valuable. There appears to be a significant market demand for increased production of heavy oxygen. The simplest method for isotope enrichment of water is distillation, but due to the very low values of the separation factor coupled with low feed concentrations, that method requires an inconveniently large number of theoretical plates and inordinately long column equilibration times (1).

For deuterium production, chemical exchange or low-temperature hydrogen distillation technologies are economically useful, even though these technologies are extremely complicated, employ dangerous and/or toxic materials, and are hostile to the environment. For oxygen enrichment, however, chemical exchange rates are too slow for convenience; and in recent years, distillation of water or NO appears to be the only method used for production. NO distillation exhibits a markedly larger liquid/vapor separation factor for oxygen than does water (2). This affords a great advantage, which is offset, at least in part, by the fact that the distillation needs to be carried out at an inconvenient temperature on feedstock, which is expensive and relatively difficult to handle or to obtain in large quantity. It is no doubt for those reasons that the NO distillation plant at Los Alamos has recently been shut down (3).

We have recently developed a new method for enrichment of water in its heavy elements based on a liquid/vapor permeation process through a hydrophobic membrane (4-6). It is convenient to discuss the process in terms of a parameter, R, which is the ratio of the logarithmic enrichment relative to the logarithmic vapor pressure ratio:

$$R = [\ln\{(x'/x)_{downstream}/(x'/x)_{upstream}\}/\{\ln(P^{o'}/P^{o})\}] \; . \qquad (1)$$

The x's are mole fractions, the prime refers to the more lightly substituted molecule, and P^{o} and $P^{o'}$ are vapor pressures. For sufficiently good approximation, $\ln(P^{o'}/P^{o}) = \ln \alpha_{l/v}$, where $\alpha_{l/v}$ is the liquid/vapor separation factor. In contrast to pervaporation through hydrophilic membranes where $R<1$ (5), permeation across hydrophobic membranes shows $R>1$ (6) (see Figure 1). Although $R_{HHO/HDO}$ is modest ($\cong 1.5$–2), the effect is pronounced for oxygen enrichment $R_{16/18} \leftrightarrows 6$ as throughput drops to zero. A qualitative mechanism rationalizing the difference between $R_{16/18}$ and $R_{HHO/HDO}$ has been suggested (6).

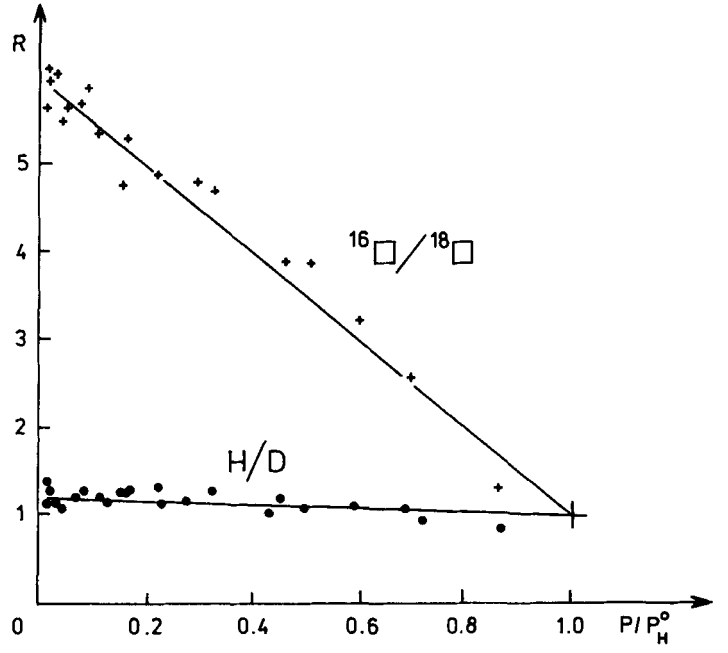

FIGURE 1. $^{16}O^{18}O$ and H/D enrichments on permeation of water through a hydrophobic PTFE Tarflen-6 membrane. $R=[\ln(\alpha)/\ln(\alpha_\cdot)]$ plotted against the relative downstream water pressure $P/P°_{HOH}$. The upper curve is for $^{16}O/^{18}O$, at various temperatures, 323 to 363 K. The lower curve is for H/D.

In this paper, we report preliminary engineering calculations based on the cascade theory which are designed to establish operating conditions for membrane-based water isotopomer separations within very broad ranges. We do not address considerations of stage design, heat transfer, pumping costs, membrane areas, etc., important matters all, but ones which deserve detailed study only after the points addressed in this paper are brought forward.

MEMBRANE CASCADES FOR WATER ENRICHMENT

The principle of the membrane separation process is shown in Figure 2. Liquid water is placed on one side of the membrane and evaporates through the

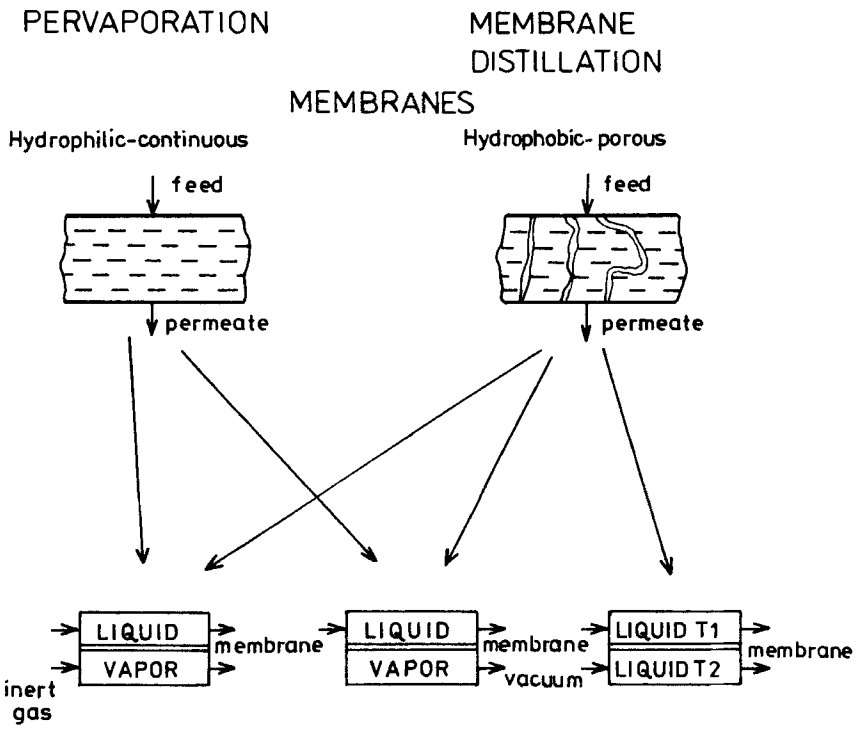

FIGURE 2. The principle of heavy isotope enrichment in water using vapor, carrier gas, or liquid on the permeate side of the membrane.

barrier to vacuum, liquid at another temperature, or to an inert carrier gas. Evaluation of such a (multistage) process involves (1) consideration of materials balance throughout the separation cascade; (2) design of the cascade, including the number of stages and their configuration; (3) evaluation of cascade operating parameters (separative power and value functions) and optimal conditions for operation, using Cohen cascade theory (1,7); and (4) technical and economic evaluation of permeation as compared to other enrichment methods.

Enrichment of Water in Simple No-Mixing and Countercurrent Cascades

Caculations following Cohen (1,7) for simple no-mixing and single countercurrent cascades demonstrated these processes to be economically much less

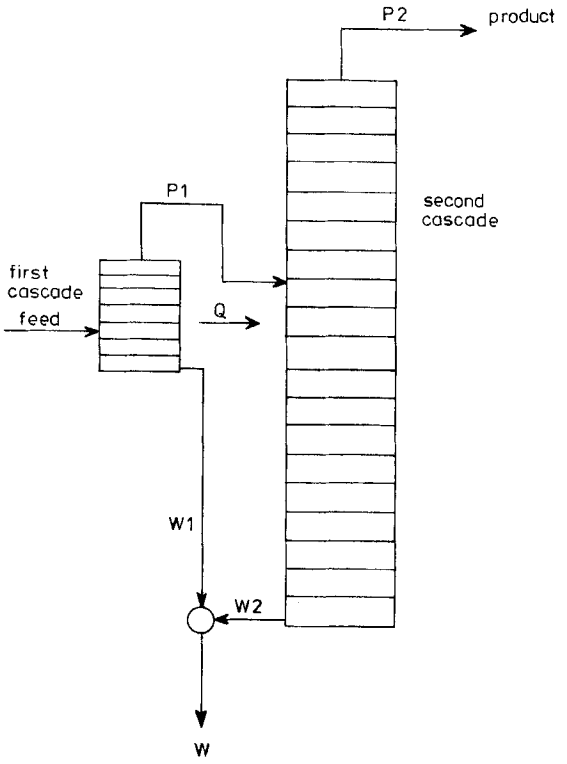

FIGURE 3. The scheme for a double countercurrent cascade.

favorable than simple distillation for enrichment of the heavier isotopes in water. The results have been reported (8).

Isotope Enrichment in Two Connected Countercurrent Cascades

In a single countercurrent cascade for liquid-vapor membrane permeation, the waste from each stage is obtained as vapor. It must be condensed and reheated to the temperature of the process, and this introduces a high-energy consumption hundreds of Gj per kg product. A better solution is to employ a set of two countercurrent cascades connected in series and working at different pressures and

TABLE 1. COMPARISON OF COUNTERCURRENT MEMBRANE-ENHANCED DEUTERIUM ENRICHMENT AND DISTILLATION

	Membrane Permeation	Distillation
Mass of feed, tons/kg 99.5% D_2O	353	200 - 250
Material efficiency, % D in feed recovered	1.8	2.5 - 3.0
Number of stages, 10^{-6} x total flow/kg	296 - 699	1100 - 1200
Product, kg	7 - 36	77
Separative power, kg/10^3 kg feed	18	25 - 100
Energy consumption per kg product, 10^9 j	189 - 5351	70 - 100

temperatures, as shown in Figure 3. Feedwater enters cascade-I, where primary enrichment takes place. Product from cascade-I forms the feed for cascade-II, where the final product is obtained. Condensate waste liquid from cascade-I, which works under higher pressure and temperature than cascade-II, is used to supply process heat for cascade-II. The only use of external thermal energy is to heat feed for cascade-I. The high specific heat of water permits a relatively small size for cascade-I. The thermal energy consumption for a double cascade is significantly less than for a single one operating between the same end points.

The parameters characterizing the system were calculated on the basis of the isotope separation theory (1,7). The theory yields for the number of stages in the i'th ideal cascade, $n_i = n_1$ or n_2, is

$$n_i = (2/\{\alpha_i - 1\})\ln[X(P_i)(1-X(W_i))/X(W_i(1-X(P_i))] \quad (2)$$

and for the separation powers:

$$U_1 = W_1 (2X(W_1)-1)\ln\{X(W_1)/(1-X(W_1))\} + P_1 (2X(P_1)-1)\ln\{X(P_1)/(1-X(P_1))\} - S(2X(S)-1)\ln\{X(S)/(1-X(S))\} \quad (3a)$$

TABLE 2a. PARAMETERS OF DOUBLE-CASCADE SYSTEM FOR MEMBRANE-ENHANCED DEUTERIUM ENRICHMENT FROM NATURAL ABUNDANCE TO 0.995 FRACTION: FIRST CASCADE

Membrane		Temp. (°C)	Pressure (torr)	α	Efficiency (%)	Sep. Power ($kg/10^3$ kg feed)	Stages	Total Flow (10^3 kg/kg)
1	T-6	40	40	1.0661	91.0	8.5	12	15
2	T-6	65	160	1.0456	90.6	6.8	16	26
3	T-6	65	160	1.0456	92.4	7.4	18	28
4	T-6	65	160	1.0383	90.6	5.0	16	27
5	T-6	65	160	1.0383	90.6	5.0	16	27
6	T-5	40	40	1.0661	91.5	11.4	14	21
7	T-5	65	160	1.0456	93.8	9.4	22	36
8	T-6	65	160	1.0383	93.8	6.7	22	36
9	T-6	70	160	1.0447	93.1	5.0	16	20
10	T-6	70	160	1.0447	93.1	5.0	16	20
11	T-6	65	160	1.0383	93.8	8.8	25	47
12	T-6	65	160	1.0383	91.5	9.0	22	49
13	T-6	65	160	1.0383	91.5	9.4	23	51
14	T-6	70	160	1.0447	89.7	6.5	15	26
15	T-6	65	160	1.0383	92.4	11.5	26	62
16	T-6	65	160	1.0383	92.1	11.9	27	65

$$U_2 = W_2\,(2X(W_2)-1)\ln\{X(W_2)/(1-X(W_2))\} + P_2\,(2X(P_2)-1)\ln\{X(P_2)/(1-X(P_2))\} - P_1\,(2X(P_1)-1)\ln\{X(P_1)/(1-X(P_1))\} \quad (3b)$$

and total flow:

$$i(S) = 8\,\Delta U_i/(\alpha_i - 2)^2 \quad \text{with} \quad i(S) + i(S_1) + i(S_2)\,. \quad (4)$$

The heat transferred from cascade-I to cascade-II is:

$$i(S_1)\,L(P_1) = i(S_2)\,C_p\,(t_{pr2} - t_{s2})\,, \quad (5)$$

TABLE 2b. PARAMETERS OF DOUBLE-CASCADE SYSTEM FOR MEMBRANE-ENHANCED DEUTERIUM ENRICHMENT FROM NATURAL ABUNDANCE TO 0.995 FRACTION: SECOND CASCADE

Membrane		Temp. (°C)	Pressure (torr)	α	Efficiency (%)	Sep. Power ($kg/10^3$ kg feed)	Total Flow (10^6 kg/kg)
1	T-6	30	15	1.0851	52.8	655	724
2	T-6	30	15	1.0851	71.1	1080	1186
3	T-6	40	40	1.0572	72.7	1155	2808
4	T-6	30	15	1.0851	72.1	1120	1230
5	T-6	40	40	1.0572	71.4	1098	2668
6	T-6	20	4	1.0906	47.1	555	539
7	T-6	20	4	1.0906	64.6	940	910
8	T-6	20	4	1.0906	65.0	955	920
9	T-6	30	15	1.0851	60.1	832	912
10	T-6	40	40	1.0572	59.3	815	1977
11	T-6	40	15	1.0703	55.9	740	1192
12	T-6	30	4	1.0812	55.2	703	850
13	T-6	50	40	1.0555	55.4	706	1827
14	T-6	20	4	1.0906	54.1	672	652
15	T-6	51	15	1.0678	50.0	612	1060
16	T-6	40	4	1.0731	47.7	577	861

and the energy consumption is:

$$Q = (1/2)i(S_1)\, C_p\, (t_{pr1} - t_{s1})\,. \tag{6}$$

Materials balance yields:

$$S = P + W = P_1 + W_1;\ P = P_2;\ W = W_1 + W_2;\ P_1 = P_2 + W_2;$$

$$S\,XS = P\,X(P) + W\,X(W) = P_1\,X(P_1) + W_1\,X(W_1);\ X(P) = X(P_2);$$

$$X(W) = [W_1X(W_1) + W_2X(W_2)]/W;\ \text{and}\ P_1\,X(P_1) = P_2\,X(P_2) + W_2\,X(W_2)\,.$$

TABLE 2c. PARAMETERS OF DOUBLE-CASCADE SYSTEM FOR DEUTERIUM ENRICHMENT: OVERALL PERFORMANCE

Production (10^3 kg feed/kg prod)		Material Efficiency (%)	Separative Power (kg/10^3 kg feed)	Stages	Flow (10^6 kg/kg)	Energy Use (10^9 j/kg)
1	13.4	48.1	656	381	9.9	3.56
2	10.0	64.4	1033	396	12.1	3.87
3	9.6	67.1	1113	586	27.2	3.88
4	9.9	65.3	1061	398	12.4	3.88
5	10.0	64.7	1043	583	26.8	3.91
6	14.9	43.1	565	358	8.4	4.90
7	10.6	60.6	934	375	10.0	4.90
8	10.6	61.0	943	375	10.1	4.90
9	11.5	55.9	821	389	10.7	6.57
10	11.7	55.3	806	570	23.3	6.64
11	12.3	52.4	744	474	15.2	6.75
12	12.8	50.5	704	410	11.5	7.12
13	12.7	50.7	707	590	23.9	7.34
14	13.3	48.6	666	362	9.0	8.93
15	13.9	46.2	621	487	15.6	9.21
16	14.5	44.4	588	454	13.4	9.86

In the previous equations, n_1 is the number of stages, U_1 is the separation power, and $i(S_1)$ is the total flow, all in cascade-I. Also, i(S) is the total flow in the double system, Q is the thermal energy input, P is the final product and W the waste flow from the double system, and P_1 and W_1 the product and waste flows in the separate cascades, respectively. Continuing, S is the feed flow; X(P), X(W), and X(S) are mass fractions of heavy isotope in product, waste, and feed for the double system, respectively; and $X(P_1)$ and $X(W_1)$ mass fractions of heavy isotope in the product and

TABLE 3. DOUBLE-CASCADE MEMBRANE-ENHANCED DEUTERIUM ENRICHMENT COMPARED WITH DISTILLATION

	Membrane Permeation	Distillation
Mass of feed, tons/kg 99.5% D_2O	9 - 19	200 - 250
Material efficiency, % D in feed recovered	33 - 70	2.5 - 3.0
Number of stages, 10^{-6} x total flow/kg	360 - 600	1100 - 1200
Product, kg	8 - 27	77
Separative power, kg/10^3 kg feed	475 - 1200	25 - 35

waste streams in the separate cascades, respectively. Finally, t_{pr-1} is the process temperature of the i'th cascade, t_{s-1} the liquid/vapor saturation point in the i'th cascade, $L(P_1)$ the heat of vaporization in the i'th cascade, and C_p the specific heat of water.

Calculations directed to minimizing energy consumption were carried out using Eqs. (2-6). Tables 2a and 2b report deuterium enrichment for conditions with energy consumption less than 10 Gj/kg using Tarflen-6 membranes in cascade-II with (usually) Tarflen-6 in cascade-I. Similar data are available for other membrane configurations (8). The parameters characterizing the overall double cascade are in Table 2c and compared with distillation in Table 3. The data show (see Figure 4) that to obtain minimal energy consumption, the process must be carried out with relatively high material efficiency. The best results can be obtained by optimizing operating conditions in cascade-II, then selecting parameters for cascade-I accordingly. The saturation temperature in cascade-I should be higher than the process temperature in cascade-II, and the difference (t_{pr-1} - t_{s-1}) minimized. Figure 5 illustrates how the

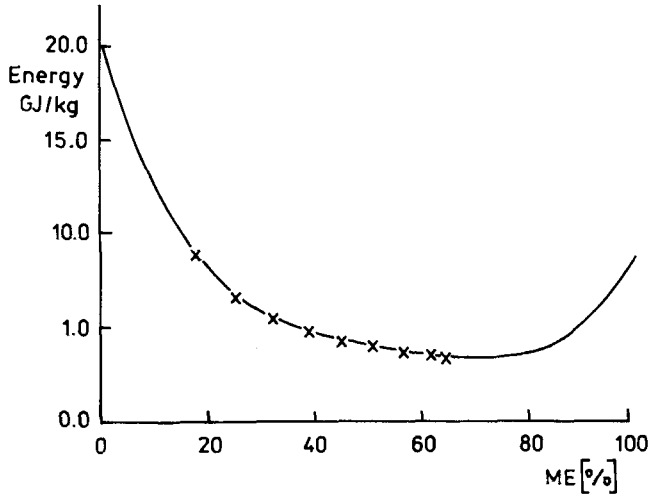

FIGURE 4. Energy consumption versus material efficiency for a double-cascade system for membrane-enhanced deuterium enrichment.

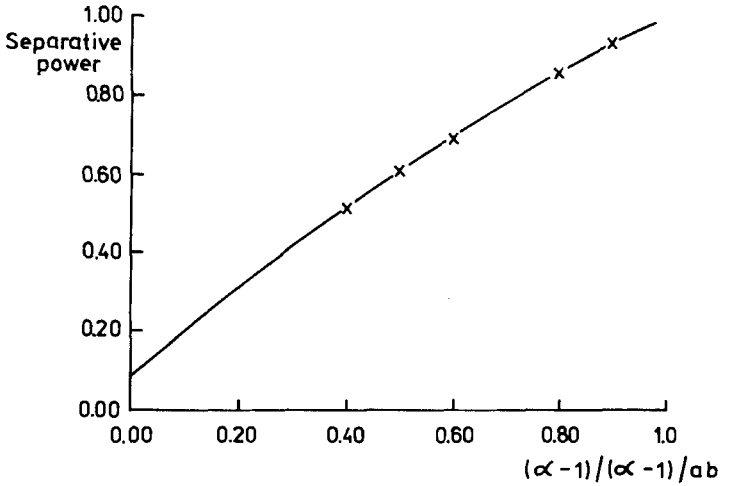

FIGURE 5. The influence of the single-stage separation factor in cascade-II on separative power for a system of two countercurrent cascades for membrane-enhanced deuterium enrichment. The variation of alpha and separation power with reference to the values measured in laboratory.

TABLE 4a. PARAMETERS OF DOUBLE-CASCADE SYSTEM FOR MEMBRANE-ENHANCED OXYGEN-18 ENRICHMENT FROM NATURAL ABUNDANCE TO 0.995 FRACTION: FIRST CASCADE

Membrane		Temp. (°C)	Pressure (torr)	α	Efficiency (%)	Stages
1	T-5	46	76	1.0073	60	3.6
2	T-5	44	68	1.0075	60	3.1
3	T-6	80	355	1.0050	50	5.9
4	T-6	64	179	1.0059	60	4.1
5	T-5	65	188	1.0058	60	4.1
6	T-6	70	234	1.0054	60	4.5
7	T-6	69	219	1.0055	60	4.0
8	T-6	72	255	1.0053	60	3.1
9	T-6	73	266	1.0053	60	5.2
10	T-6	73	266	1.0053	60	5.0
11	T-6	80	355	1.0050	50	3.4
12	T-6	80	355	1.0050	20	4.2

separative power of the two cascade systems depends on the single-stage enrichment factor in cascade-II.

Heavy Oxygen Enrichment in the Double-Cascade System

We have performed cascade calculations for ^{18}O enrichment in the system described above. Even though the hydrophobic membrane enhancement $R(^{18}O/^{16}O)$ is a good deal larger than R(D/H), $\ln(P_{16}°/P_{18}°)$ lies below 0.01 at temperatures of interest to us so that the separation factor remains small. In fact, under our conditions it lies well below the HHO/HDO vapor pressure ratio, which, coupled with

TABLE 4b. PARAMETERS OF DOUBLE-CASCADE SYSTEM FOR MEMBRANE-ENHANCED OXYGEN-18 ENRICHMENT FROM NATURAL ABUNDANCE TO 0.995 FRACTION: SECOND CASCADE

Membrane		Temp. (°C)	Pressure (torr)	α	Efficiency (%)	Stages
1	T-5	40	10	1.0367	1.7	677
2	T-5	30	10	1.0340	1.7	730
3	T-6	65	40	1.0284	3.0	875
4	T-6	55	60	1.0223	1.7	1113
5	T-5	50	40	1.0242	1.7	1028
6	T-5	50	10	1.0342	1.7	726
7	T-6	55	60	1.0223	1.7	1113
8	T-5	30	10	1.0340	1.7	730
9	T-6	70	60	1.0255	1.7	976
10	T-6	70	200	1.0093	1.7	2675
11	T-6	65	40	1.0284	1.0	874
12	T-6	65	40	1.0284	2.5	875

the low natural abundance of ^{18}O and ^{17}O, underscores the difficulty of this isotope separation. For these reasons, the membrane permeation process requires many stages configurated to minimize energy demand.

The parameters for the double-cascade system for enriching ^{18}O using Tarflen-6 are presented in Table 4. Figure 6 reports the calculated dependence of thermal energy consumption on materials cycling efficiency for the two-cascade system. A broad minimum is apparent. Figure 7 demonstrates a linear dependence of total flow on the process temperature in cascade-I. The dependence of total flow on the process temperature in cascade-II is not linear and is described by a fifth-order function with a minimum around 40°C. The same minimum is apparent when the number of stages required to effect a given separation (Figure 8) are graphed versus

TABLE 4c. PARAMETERS OF DOUBLE-CASCADE SYSTEM FOR OXYGEN-18 ENRICHMENT: OVERALL PERFORMANCE

Material Efficiency (%)		Stages	Total Flow (10^6 kg/kg)	Energy Use (10^9 j/kg)
1	1.0	680	3.13	5.66
2	1.0	733	3.13	5.70
3	1.5	881	5.27	8.75
4	1.0	1117	8.25	9.87
5	1.0	1032	7.07	9.85
6	1.0	731	3.66	10.64
7	1.0	1117	8.25	10.79
8	1.0	733	3.59	11.04
9	1.0	981	6.50	11.54
10	1.0	2680	46.80	15.27
11	0.9	877	5.24	23.18
12	0.5	879	5.26	25.18

the process temperature of cascade-II. At 40°C, the double-cascade system has its minimum energy consumption and minimum number of stages. The influence of pressure on total flow and stage number is also significant. It is profitable to maintain pressure in the first cascade close to saturation, but in cascade-II the pressure should be as low as possible.

The dependence of total flow on material efficiency is shown in Figure 9. We have already seen that a change in material efficiency in cascade-I does not affect total flow or energy consumption significantly, rather the size and material efficiency of cascade-II determines the size and efficiency of the entire system. Table 5 compares the double-cascade ^{18}O enrichment process with distillation. The results indicate the possible superiority of the membrane permeation process over distillation

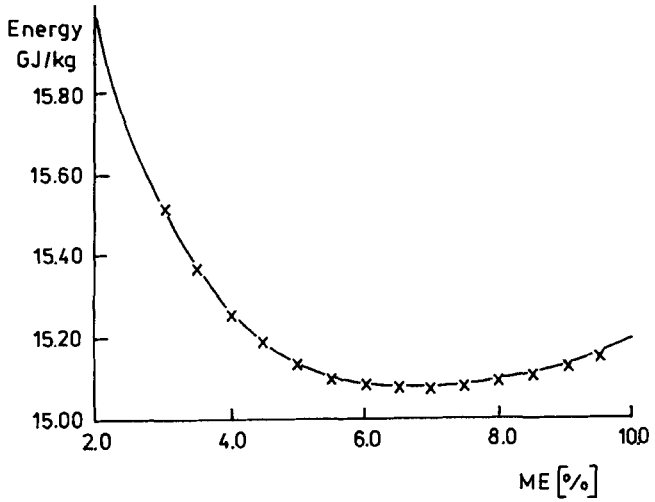

FIGURE 6. The dependence of energy consumption on material efficiency in the double cascade for ^{18}O enrichment [T(cascade-I) = 40°C, T(cascade-II) = 30°C, P(cascade-II) = 30 torr].

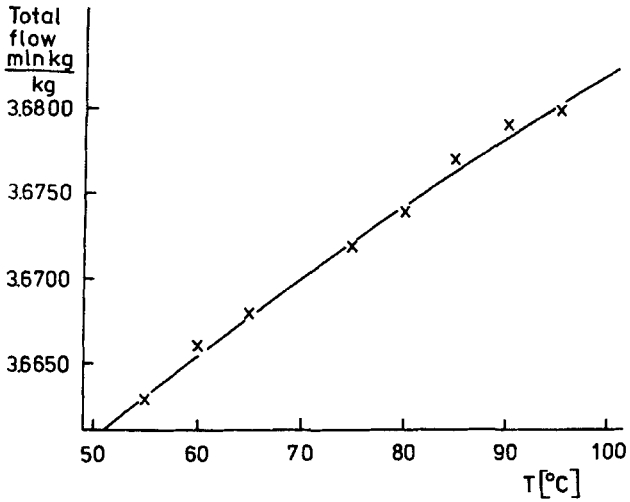

FIGURE 7. The influence of T(cascade-I) on total flow per kg ^{18}O product. [T(cascade-II) = 50°C, P(cascade-II) = 10 torr, material efficiency cascade-I = 60%, material efficiency overall system = 1%].

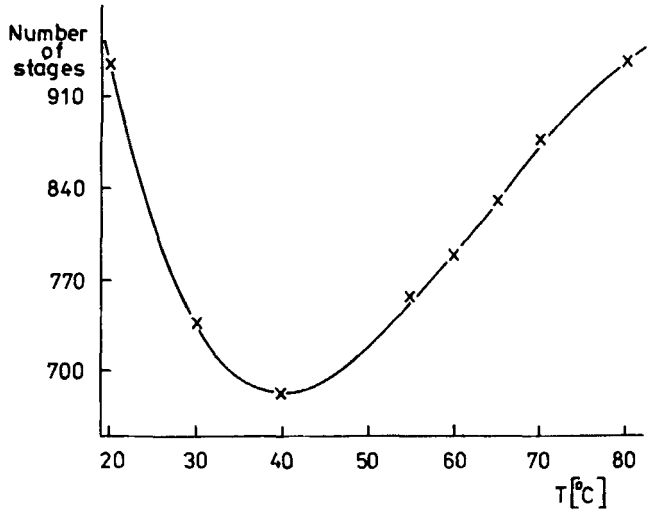

FIGURE 8. The influence of T(cascade-II) on the number of stages for the entire system for ^{18}O enrichment. [T(cascade-I) = 85°C, P(cascade-II) = 10 torr, material efficiency cascade-I = 60%, material efficiency overall system = 1%].

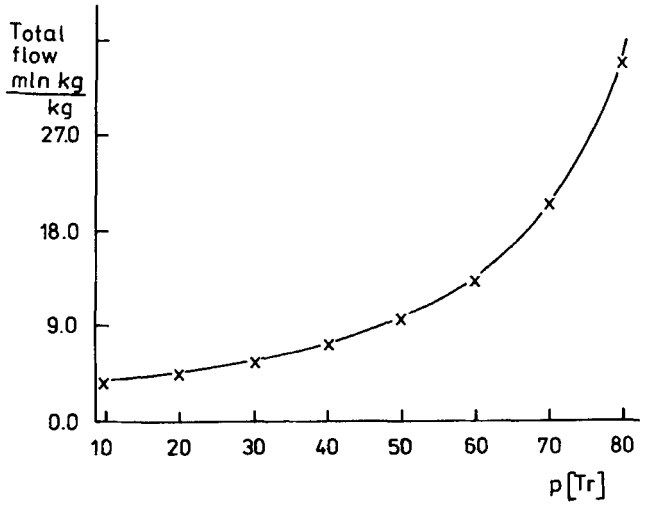

FIGURE 9. The dependence of total flow/kg product on pressure in cascade-II for ^{18}O enrichment, [T(cascade-I) = 60°C, T(cascade-II) = 50°C, material efficiency cascade-I = 60%, material efficiency overall system = 1%].

TABLE 5. DOUBLE-CASCADE MEMBRANE-ENHANCED OXYGEN-18 ENRICHMENT COMPARED WITH DISTILLATION

	Membrane Permeation	Distillation
Mass of feed, tons/kg of 99.5% $H_2{}^{18}O$	5 - 100	12 - 20
Material efficiency, % of ^{18}O in feed recovered	0.5 - 10	2.5 - 4
Number of stages	700 - 2000	6100 - 6200
10^{-6} x total flow per kg prod	3 - 30	250
Separative power, kg/10^3 kg feed	5 - 110	25 - 40
Energy consumption per kg prod, 10^9 j	1 - 12	4 - 8

(leaving unanswered questions about single-stage design, capital cost, and other engineering matters). They indicate that membrane separation is clearly worth further study to test such practical matters.

A Comparison of Membrane Permeation with Other Methods of Isotope Enrichment in Natural Water

Membrane permeation is a process highly analogous to distillation, often used in heavy water enrichment. It is for that reason that we have continually made comparisons with distillation in this paper. Water distillation is a simple and well developed process, of modest capital cost and high environmental safety. Its principal disadvantages for water separations are the low enrichment coefficients and low initial concentrations of the heavier isotopes. This implies a large number of stages, high reflux, and long equilibrium times.

Deuterium enrichment. Because the demand for deuterium is so much larger than for heavy oxygen, we separate further discussion of present enrichment

processes. The most popular and widely applied method of D_2O production is chemical exchange between water and hydrogen sulfide (the GS process, until recently the most common), or other catalyzed exchanges like water-hydrogen, or ammonia-hydrogen (9). Distillation of liquid hydrogen is another useful method (9).

The GS method has a high separation factor (1.3 to 1.4) and a low energy consumption ($\simeq$ 25 Gj/kg D_2O) but employs highly corrosive and dangerous materials. The water-hydrogen and ammonia-hydrogen exchanges have higher enrichment coefficients and lower energy consumption but must be catalyzed, and this leads to difficulties. In any industrial-scale process, it is necessary to keep in mind that large amounts of material need to be handled; therefore, one is limited to very cheap feedstocks or to separation schemes designed to be parasitic to large industrial facilities (such as ammonia synthesis plants).

Membrane permeation is a simpler process than chemical exchange but is characterized by a lower enrichment factor. Even so, as far as energy consumption is concerned, it can be energetically competitive provided one employs multiple countercurrent cascades. However, this alone does not define the economics of a process, and a good deal of further analysis and experiment will be required to determine whether membrane pervaporation can become a practical method of deuterium enrichment.

Permeation and heavy oxygen enrichment. Oxygen-18 was first enriched to 99.5% in 1943 using thermal diffusion. Other enrichment processes that have been considered include electrolysis, chemical exchange, and distillation of NO and water. Thermal diffusion is difficult to scale up and shows high energy demand. Chemical exchange for oxygen enrichment has proved impractical because the single-stage factors are not large enough to overcome disadvantages implied by chemical reflux of large amounts of material. NO distillation enjoys an interestingly large separation factor (2,3) but apparently cannot compete with water distillation.

Water distillation for heavy oxygen enrichment has been carried out in many laboratories. Dostrovsky and Epstein (10) have described an improved method. The resolution of problems connected with the low separation factor and low initial concentration of the desired isotopes demands highly efficient columns of large physical dimension. As a consequence, long equilibrium times to production are required and the columns contain a high inventory of product. Nevertheless, in spite

of its low fractionation factor (0.0032 at 100°C for $^{18}O/^{16}O$), the fractional distillation of water is the only process currently used in the production of heavy oxygen. Because of the much larger fractionation factors and concomitant savings in stage number, reflux ratio, and energy demand, membrane-enhanced permeation for heavy oxygen separation can be considered to be of practical interest and certainly warrants further detailed study.

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