Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Chmielewski, Andrzej G. , Zakrzewska-Trznadel, Grazyna , Miljevi°C, N. R. and Van Hook, W. Alexander(1997) 'Multistage Process of Deuterium and Heavy Oxygen Enrichment by Membrane Distillation', Separation Science and Technology, 32: 1, 527 — 539
To link to this Article: DOI: 10.1080/01496399708003213
URL: http://dx.doi.org/10.1080/01496399708003213

SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 527-539, 1997

MULTISTAGE PROCESS OF DEUTERIUM AND HEAVY OXYGEN ENRICHMENT BY MEMBRANE DISTILLATION

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ABSTRACT

Deuterium and oxygen-18 isotope enrichment in water by membrane distillation were studied in a 4-stage cascade. Two configurations of membrane distillation (MD) employing PTFE flat-sheet membranes were investigated, including direct contact MD and air gap MD. The first, direct contact MD is more efficient. It is characterized by high distillate flow rate. The temperature polarization coefficients were higher for direct contact MD. H/D and $^{16}O/^{18}O$ separation factors were determined in the 4-stage cascade.

INTRODUCTION

Membrane processes have been employed in nuclear technology for many years. The application of membrane permeation for natural isotope enrichment was discussed previously [1,2]. It was shown that permeation coupled with phase transition is characterized

by high H/D and $^{16}O/^{18}O$ separation factors [3,4]. An economic analysis of the process for separation of hydrogen and oxygen isotopes in a system of two countercurrent cascades combined in series showed many advantages and suggested that it could compete with other methods of isotope enrichment [5]. One stage experiments demonstrated many advantages of membrane distillation, which can be driven with waste heat. Therefore energy demand can be significantly reduced.

A new experimental setup for investigation of a multistage process of membrane distillation was constructed. Four permeation cells connected in series simulate a 4-stage countercurrent cascade. The warm stream from each stage is fed into the stage next above. The warm stream from stage n is mixed with part of the stream from stage n+2 and the mixture is fed into the stage n+1. The cold stream flows in counter-current fashion. The vapor pressure difference across the membrane which results from the temperature difference causes the evaporation of water and its diffusion from the warm to the cold side. The distillate condensing on the cold side is depleted in heavy isotopes of hydrogen and oxygen and the warm stream is enriched. The system can work in two variants schematically shown in Figure 1.:

A. Direct contact membrane distillation (DCMD). The membrane directly contacts warm and cold solutions. Permeate condenses in the cold stream. The counterflow principle can be applied for both streams and high heat transfer coefficients accompany the heat transport through the membrane. It is easy to recover a part of the heat in this configuration by employing additional heat exchangers.

B. Air-gap membrane distillation (AGMD). An additional air gap is involved. Permeate condenses on a separate surface cooled by the cold stream flowing counter-current to the warm stream. The heat lost in this configuration is lower than in arrangement (A), but heat recovery is more difficult.

EXPERIMENTAL

Membranes

Commercial, Millipore FGLP, polytetrafluoroethylene membranes, supported on polyethylene net are used. The nominal pore size is 0.2μm, thickness 130 μm.

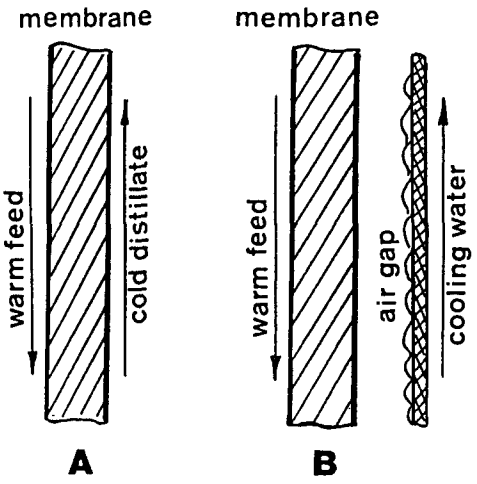

FIGURE 1. Two arrangements for membrane distillation .

Apparatus

A single permeation cell is shown in Figure 2. The cell made of polytetrafluoroethylene consists of three sections, 1, 2, 3, which are sealed by rubber gaskets, 5,7. The flat-sheet membrane, 6, with an effective area of 8.04×10^{-4} m^2, separates the warm stream (feed) and distillate chambers, 4. The distillate chamber and the cold stream are separated by a thin stainless steel plate, 8, which enables efficient heat exchange. The inlet and outlet for the warm stream (S) are located on the top of the cell, and the cold stream (W) inlet and outlet are located on the bottom. The outlet for the distillate (D) is placed in the middle section of the cell.

The cell described above is in the configuration employed in air-gap MD. When the process of direct contact membrane distillation is carried out, the middle section of the cell shown in Figure 2 is removed. In this variant the distillate is collected directly in the cooling water, which performs the role of carrier liquid.

The flow rate of warm and cold streams is adjusted by delivery pumps, and measured by rotameters. Permeate flow rate is measured in one of two ways:

- in the direct contact configuration, when distillate passing the membrane condenses directly in

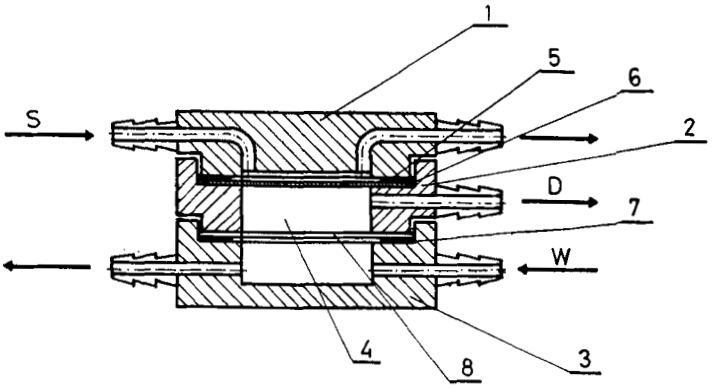

FIGURE 2. Permeation cell. 1,2,3-three sections of the cell, 4- distillate chamber, 5,7- rubber gasket, 6- membrane, 8- stainless steel plate.

the cold stream, the permeate flow rate is measured by means of a float system located in the cold reservoir,

- in the air-gap configuration the permeate is collected in four separate collectors, which are continuously weighed.

Temperature is measured using thermocouples inside the permeation cell located close to the membrane surfaces. The experimental setup is equipped with a data acquisition system composed of a 486/256KB computer CPU (486DX/66MHz) and PCL 813, 32-channel A/D converter card. All temperatures and increments of permeate weight are recorded and controlled by computer. The measuring signals are collected by a system of 13 thermocouples, 12 resistance thermometers, and 4 electronic balances.

Process operation

A diagram of the experimental setup showing the points of measurement is shown in Figure 3. Distilled water of natural abundance is placed in the hot and cold liquid reservoirs. Temperatures of the hot stream, T, and cold streams, $t<T$, are adjusted and held stable for the time of the experiment. Flow rates of the warm, cold, and recycle streams are kept constant. All temperatures

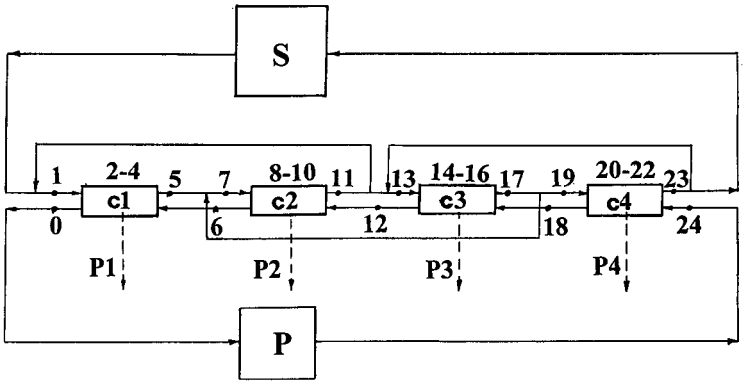

FIGURE 3. Measurement points lay-out. S- warm water reservoir, P- cold water reservoir, P1-P_4-permeate, C_1-C_4- permeation cells, 1-24-measurement points.

along the cascade and the temperature distribution inside the permeation cell are controlled and recorded by computer. Permeate increments are measured by the float system or weighed by electronic balances, with an accuracy of 0.1g. Every few hours samples of water are collected along the cascade, as are samples of permeate. The samples were analyzed by a SIRA 12 V6 mass spectrometer (Vinca Institute of Nuclear Sciences), and the concentration of deuterium and oxygen-18 determined.

RESULTS AND DISCUSSION

Determination of the operational conditions for the cascade

The economic evaluation of the permeation process was carried out using separation cascade theory [5]. The parameters of a cascade enriching heavy isotopes of hydrogen and oxygen were determined. However theoretical calculations need experimental verification. An attempt to establish the operational conditions of the multistage apparatus for isotope separation by membrane was made. The estimation of the parameters of the present system will help in further process development.

The present experiments were run for 15-50 hours with temperatures kept roughly constant: warmside inlet temperatures in the range 35-60°C, and coldside, 15-30°C. The flow rate of both streams was $10x10^{-3}$ m^3/h and the recycle stream flow was $4x10^{-3}$ m^3/h. Experiments were carried in two configurations; membrane distillation with air gap, and direct contact membrane distillation.

Air-gap membrane distillation: The experiments were conducted using the permeation cell shown in Figure 2. The warm stream inlet temperature was 35.6-47°C and the cold stream inlet temperature - 16-18.3 °C. Temperature of both streams along the cascade varied. (Figure 4). The distillate flow rate equaled 0.66-0.72 dcm^3/m^2h.

Direct contact membrane distillation: The middle section of the permeation cell was removed. The process was conducted with warm liquid inlet temperature 50.3°C and cold liquid inlet temperature 19.7° C. The distillate flow rate was higher than for air-gap arrangement and equaled 6.23 dcm^3/m^2h.

Knowledge of interfacial temperatures in the direct neighborhood of the membrane is very important for heat transfer calculations. These temperatures may vary significantly from the inlet temperatures of both streams due to temperature polarization. In the experiments described in the paper, attempts to measure the temperatures as close to the membrane as possible were made. The measured temperature difference across the membrane permits the calculation of the temperature polarization coefficient, TPC_m,

$$TPC_m = \frac{T_1 - T_o}{T - t}$$

where:

T_1 and T_o are the temperatures measured in the vicinity of the membrane,

T - warm stream bulk temperature,

t - cold stream bulk temperature.

TPC_m values from two configurations of membrane distillation are shown in Figures 5 and 6. Due to the variation of temperature along the cascade and temperature dependence of temperature polarization coefficient, the TPC_m values are different for each permeation cell.

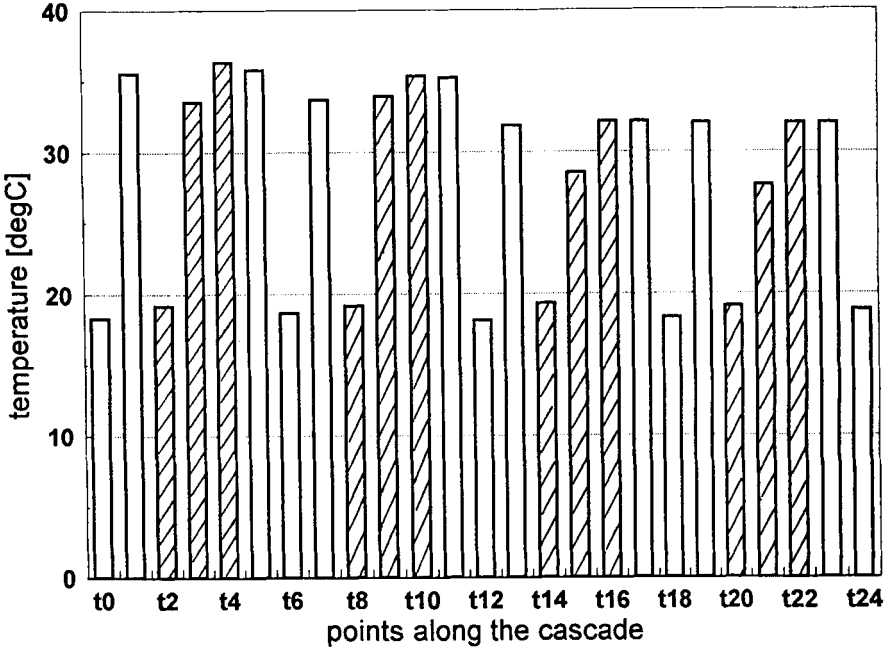

FIGURE 4. Temperatures along the cascade - air-gap membrane distillation. t_o, t_6, t_{12}, t_{18}, t_{24} - cold stream temperatures, t_1, t_5, t_7, t_{11}, t_{13}, t_{17}, t_{19},t_{23}- warm stream temperatures, t_2-t_4 - temperatures in the I cell, t_8-t_{10} - in the II cell, t_{14}-t_{16} - in the III cell, t_{20}-t_{22} - in the IV cell.

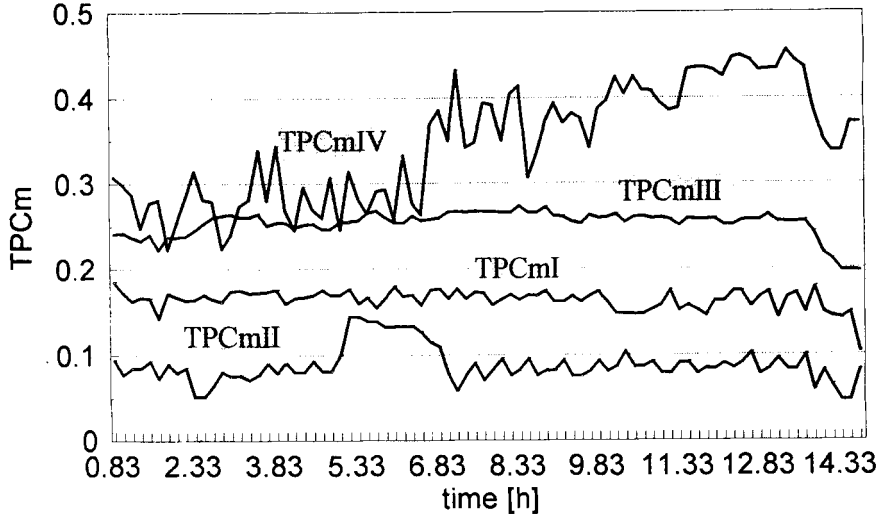

FIGURE 5. Variation of TPC_m in time - air-gap membrane distillation.

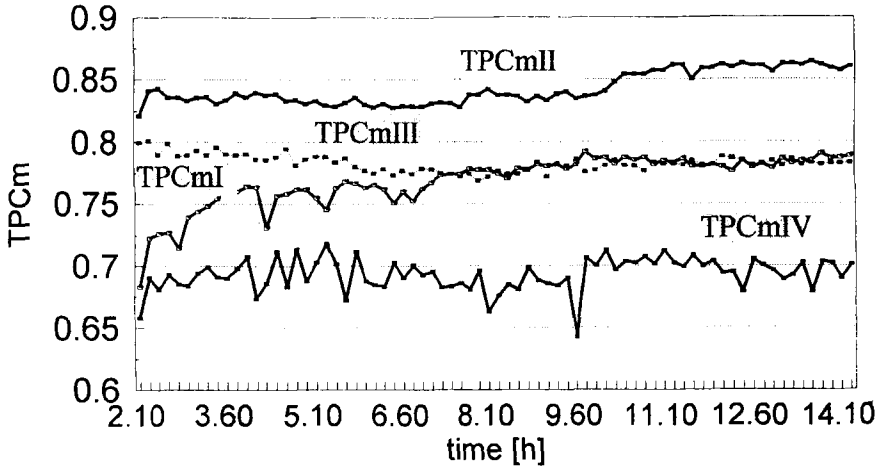

FIGURE 6. Variation of TPC_m in time - direct contact membrane distillation.

The temperature polarization factor may be estimated theoretically, applying the procedure described by Schofield [6]. Calculated *TPC* values were obtained from the bulk temperatures of warm and cold streams circulated in the system and distillate flow rates measured in the experiment. They are reported in Table 1.

The physical properties within the system were evaluated at the average membrane temperature. Figure 7 shows the temperature dependence of TPC for Millipore PTFE membrane as used in the process for both configurations. The calculated TPC_{calc} values for direct contact MD are 4.3-7.4 times higher than corresponding values for air-gap MD. A comparison of *TPC* values obtained by the two methods is presented in Table 1.

In Figure 8, permeate weight vs. time for the air gap MD experiment is shown. Permeate flow in cells I and II is higher than III and IV even though IV has the highest temperature difference across the membrane. Most likely, permeate flow depends mainly on the average temperature of the membrane interface and cooling surface. The average temperature decreases along the cascade (Figure 4).

The estimation of separation factors

The separation factor values are one of the most important parameters to be taken into account before any decision about the technical application of the separation process is made. The

TABLE 1. COMPARISON OF *TPC* EVALUATED FROM HEAT TRANSFER BALANCE AND MEASURED IN EXPERIMENT.

	I cell	II cell	III cell	IV cell
Air- -gap MD				
TPC_{calc}	0.16	0.13	0.175	0.175
TPC_{m}	0.17	0.09	0.25	0.26
Direct contact MD				
TPC_{calc}	0.67	0.68	0.7	0.71
TPC_{m}	0.78	0.78	0.77	0.69

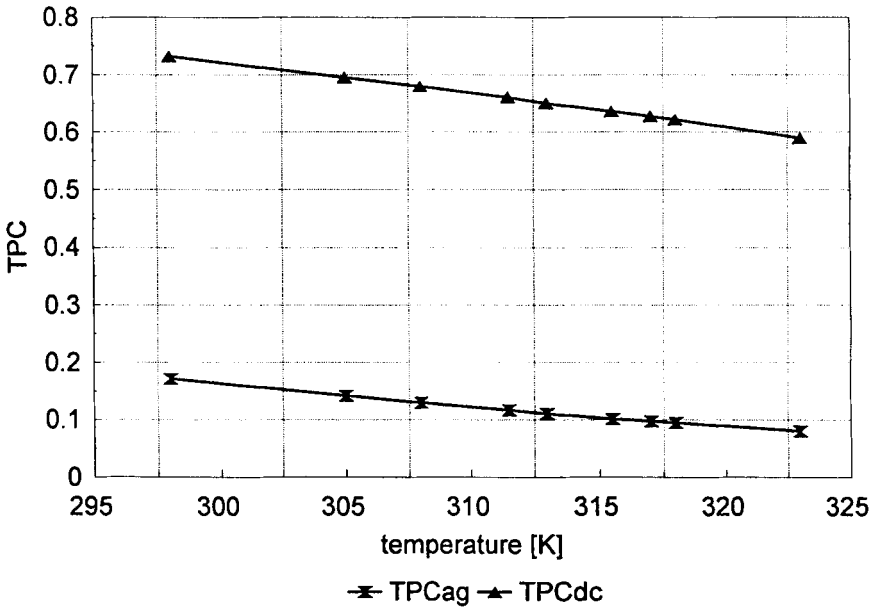

FIGURE 7. Temperature dependence of temperature polarisation coefficient.

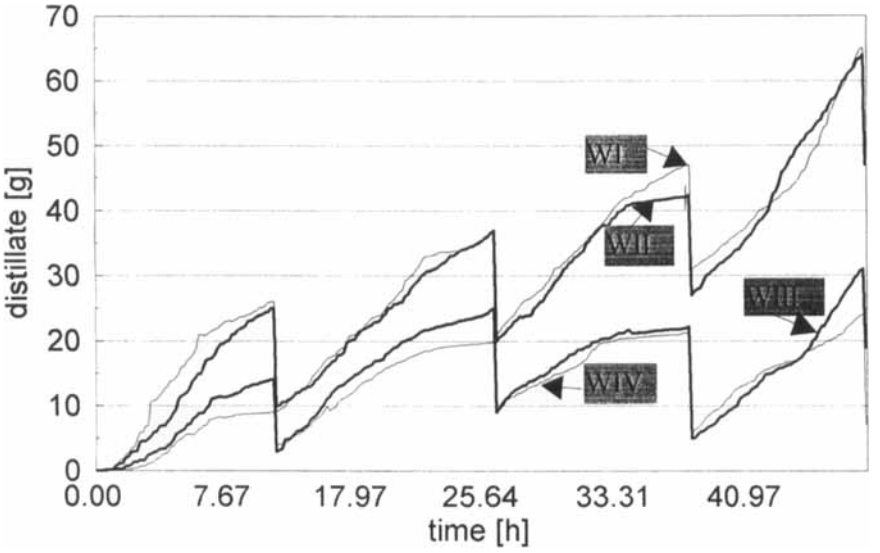

FIGURE 8. Output from electronic balances measuring permeate weight in air-gap MD experiment.

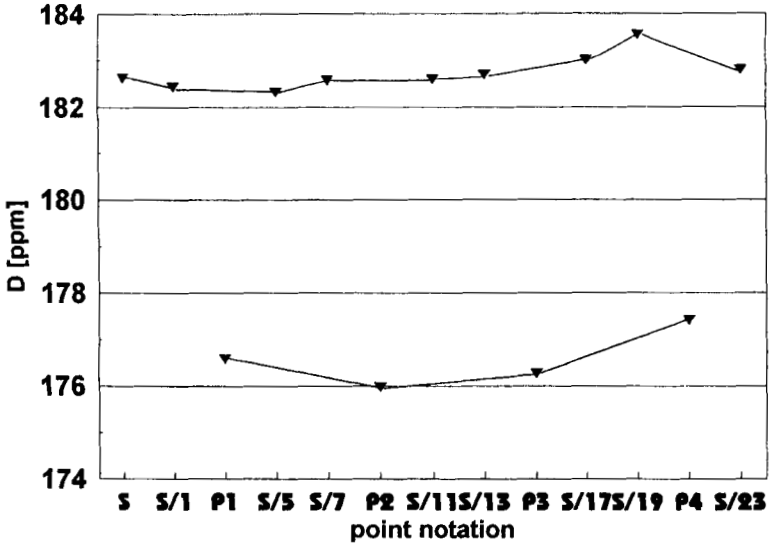

FIGURE 9. The concentration of deuterium along the 4-stage permeation cascade after 13.59h of experiment - air-gap membrane distillation.

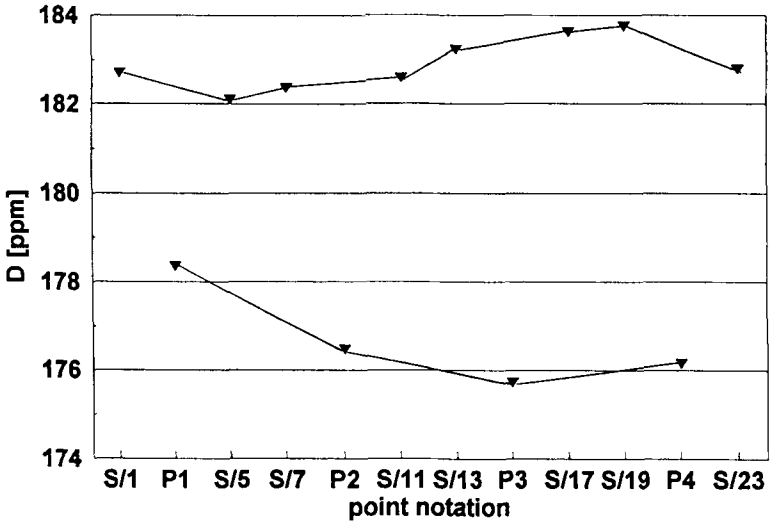

FIGURE 10. The concentration of deuterium along the 4-stage permeation cascade after 64.92h of experiment - air-gap membrane distillation.

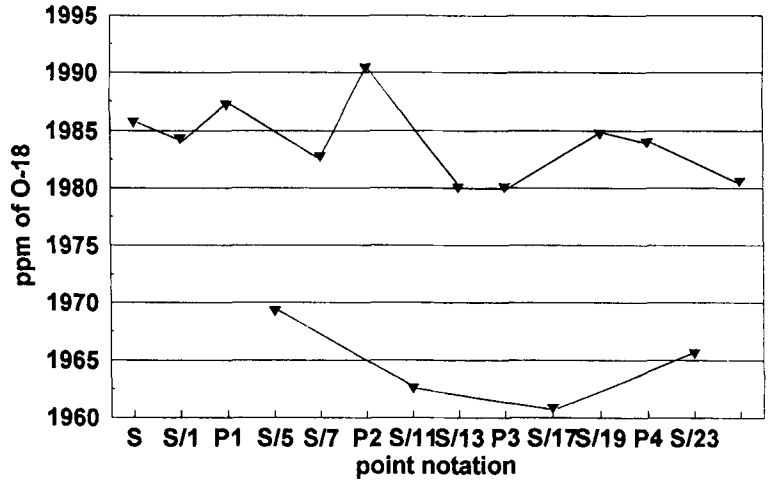

FIGURE 11. The concentration of oxygen-18 along the 4-stage permeation cascade after 11.16h of experiment - air-gap membrane distillation.

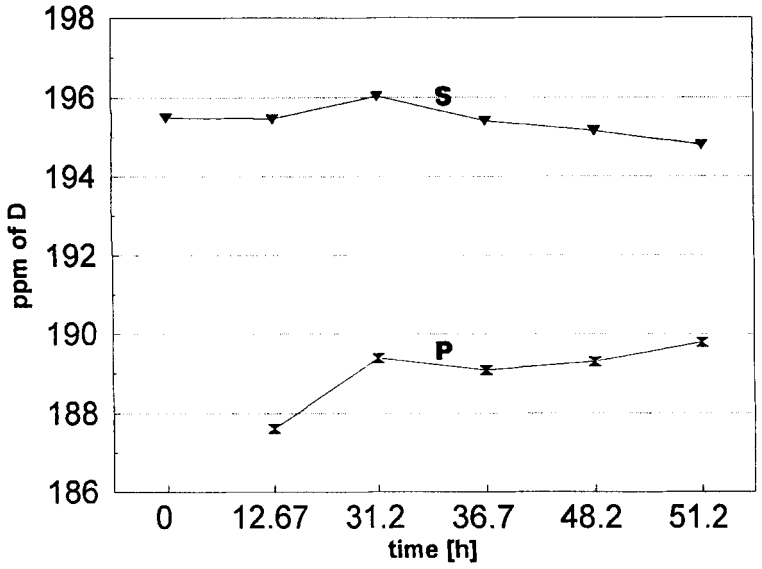

FIGURE 12. The variation of the concentration of deuterium along the 4-stage permeation cascade - direct-contact membrane distillation.

previous experiments showed the process of permeation through PTFE membrane is characterized by high enough separation factors (higher than in fractional distillation) and therefore it may be attractive from a practical point of view. The parameters of the process evaluated from the cascade theory proved this statement. The present experiments were designed to establish the operating parameters for the four unit apparatus. The cascade was not ideally tapered nor were the operating flows adjusted to optimize the overall separation factor for the cascade.

The results of spectrometric analyses of the samples collected in the experiments conducted with the 4-stage permeation unit are shown in Figures 9-12. In Figures 9 and 10 the variation of deuterium concentration in the warm stream along the cascade and in the permeate collected from the four cells of the system for air-gap MD after 13.59 and 64.92 hours of the experiment are presented. The concentration is approximately equal along the cascade. The mean separation factor for H/D enrichment for the cascade is 1.04.

Figure 11 shows the results of oxygen-18 enrichment. The $^{16}O/^{18}O$ separation factor, 1.01, is higher than for fractional distillation. In Figure 12 the variation of deuterium concentration in

warm and cold streams as a function of time for direct contact membrane distillation is presented. The lower curve represents the concentration of D in the cooling water which is mixed with the permeate depleted in heavy isotopes. The higher curve shows the concentration of deuterium in the retentate. Either configuration can be used depending on economic considerations.

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