# A new generation of track etched membranes for microfiltration and ultrafiltration. Part I. Preparation and characterisation

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## Abstract

A new experimental apparatus for porous track etched membrane production has been designed, tested and installed near the core of the IEA-R1 nuclear reactor at IPEN-Sao Paulo. The thermal neutron flux close to the centre of the reactor core has been used to produce fission fragments from uranium sample which was deposited on a rod located at the centre of an evacuated aluminium chamber.

These nuclear fragments impinge on a polycarbonate film mounted on the inner cylindrical wall of the irradiation chamber. Under conditions of uniform neutron flux large areas of track etched membranes, with high level of pore uniformity, have been produced in the micro and ultrafiltration range. Membranes with pore diameters ranging from 15 to 100 nm. have been prepared reproducibly, based upon a calibration curve of track diameter versus etching time.

*Keywords:* Track etch; Porous membrane; Ultrafiltration; Microfiltration; Polycarbonate; Fission fragments

## 1. Introduction

The main goal of the present project is to develop a method to produce and characterize high quality track etched membranes (TEM), with a range of pore diameters and pore densities, for industrial and biotechnology applications, by a simple irradiation procedure using the thermal neutron flux close to the core of a nuclear reactor.

In the basic technique, a thin polycarbonate plastic is exposed to a collimated beam of fragments produced by thermal neutron fission of U-235 nuclei. These fission fragments, by ionization and excitation

processes, produce tracks across the entire thickness of the plastic foil. These tracks may be selectively etched by an appropriate chemical solution and a pore is formed in the bombarded material. The pore diameter is controlled by the etching time, and the pore density is determined by the irradiation time [1,2].

The main objectives of the present work were:

1. To design, construct, install and test a new irradiation device, near the IEA-R1 reactor core, for controlled production of porous membranes with high level of pore uniformity.

2. To study the axial profile of the thermal neutron flux at the irradiation position of the U-235 fissile sample.

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3. To obtain a calibration curve track diameter versus etching time in the ultrafiltration region.

4. To produce large areas of etched track membranes with pore sizes ranging from 10 000 nm down to 15 nm and pore density in the interval from $1.0 \times 10^5$ to $1.5 \times 10^9$ cm$^{-2}$, respectively.

## 2. Experimental

The new irradiation device for porous membranes production is shown in Fig. 1. It consists of an evacuated cylindrical aluminium chamber, in which an aluminium rod (4 mm diameter and 140 mm length) containing the uranium sample was fixed
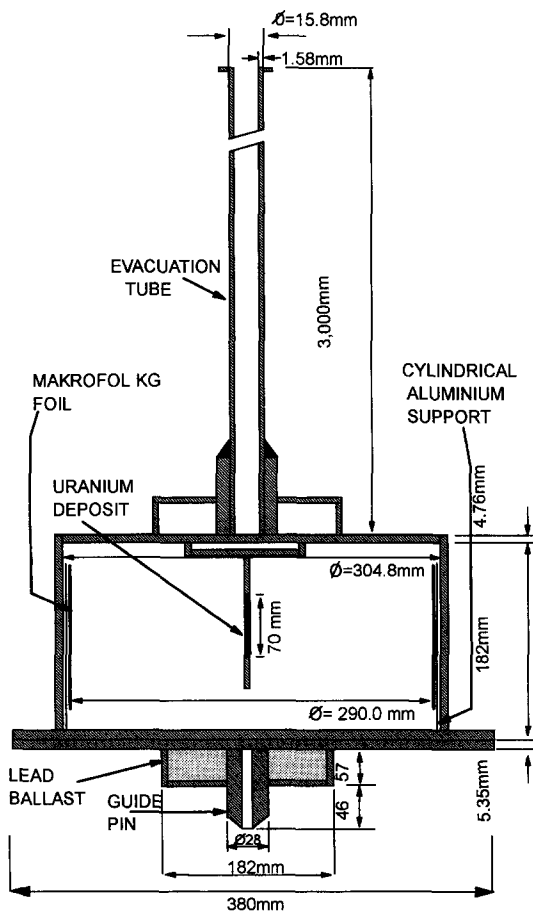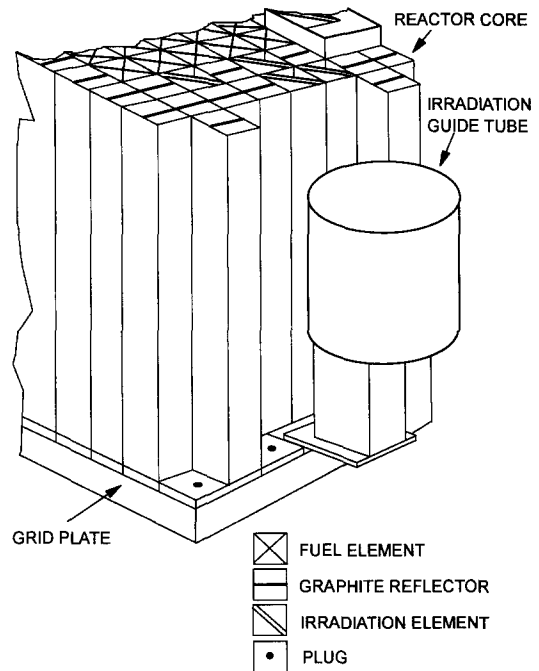
Fig. 2. Schematic view of the irradiation guide tube, holder for the Irradiation chamber, installed near the IEA-R1 reactor core.

Fig. 1. Irradiation chamber for production of track etched membranes (TEMs).

axially. The uranium (with 93.15% enrichment in U-235 isotope) was deposited electrolytically over a length of 70 mm on the central part of the aluminium rod and was in the form of $U_3O_8$. The membrane film used was Makrofol KG foil, thickness 10 000 nm, manufactured by Bayer Chemicals, Germany. This polycarbonate film was mounted on a cylindrical aluminium support diameter, 290.0 mm and height 160 mm as shown in Fig. 1 and held in place using silicon rubber adhesive. The membrane was at a radial distance of 145 mm from the fissile material coated on the central aluminium rod. This arrangement allowed irradiation of Makrofol foil areas as large as around 1000 cm$^2$, in a well collimated beam of fission fragments.

The irradiation chamber was placed inside an irradiation guide tube (Fig. 2) installed near the core of the IEA-R1 reactor, a 2 MW pool-type research reactor, at a position where the thermal neutron flux is about $2.7 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$. The chamber was evacuated down to a pressure around $10^{-3}$ torr, through a long aluminium tube, 15.8 mm diameter and 10 m length, (see Figs. 1 and 3). The radioactive
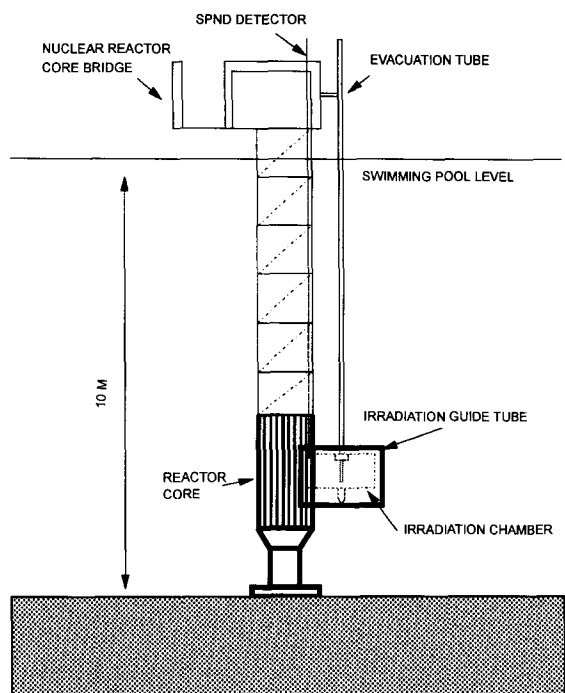
Fig. 3. Overall view of the experimental apparatus used for irradiations near the reactor core.

gases released by the fission reactions, were captured by a very low temperature glass trap, placed at the output of the evacuation tube. This glass trap was kept at liquid nitrogen temperature during the irradiation period.

During reactor operation the neutron flux usually varies and in order to control the neutron dose received by the fissile material, a silver wire self powered neutron detector (SPND) fixed outside the irradiation tube guide and in front of the reactor core (see Fig. 3), was used. This neutron detector utilises the $\beta$-decay of the radioactive isotopes ($^{108}$Ag and $^{110}$Ag) to produce a current which is proportional to the neutron flux. The current was measured by a digital current integrator and counted on a scaler. In this way, the irradiation time was defined. The SPND detector has to be periodically calibrated against gold foil monitors irradiated simultaneously. This activation technique [3] with gold foil is a routine method usually employed for measurements of thermal neutron fluxes.

## 3. Results and discussion

The results obtained in the calibration measurements indicated a counting rate of $261.4 \pm 0.2$ s$^{-1}$ for the SPND detector, for an average thermal neutron flux (see next section) of $\phi = 2.70 \pm 0.05 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$ at the fissile sample position.

In order to verify the reproducibility of irradiation procedures three independent membrane preparations were performed by using a natural uranium deposit. Employing irradiation times of approximately 120 s and appropriate chemical etching conditions (35% KOH solution at 60°C during 30 min) [4], filters in the microfiltration region were produced with density around $10^6$ pores/cm$^2$ and pore size of 3000 nm, suitable for inspection by a simple light microscope. Pores were counted on several different areas ($4.76 \times 10^{-4}$ cm$^2$) of the filter samples and an average pore density determined for each of the three irradiations. These averaged data, divided by the SPND (neutron flux) counting obtained in the corresponding irradiation, represent equivalent quantities. The error of the weighted average determined the reproducibility of the irradiation process [5] and in these measurements a reproducibility of 2.6% was achieved. The $\chi^2$ was lower than 1 showing a consistency between the scatter of the average values, normalised with relation to the SPND counting, and the assigned errors.

To obtain the desired uniformity of pore density in the plastic film, the neutron flux and the fissile sample thickness, must be as homogeneous as possible over the entire uranium deposit.

The uniformity of the thickness of the deposit was verified previously [1,4], by analysis of the pore distribution on the plastic film, produced by irradiations with a collimated and homogeneous flux of thermal neutrons. The results indicated uniformity variations around 10% which is in good agreement with the value presented by commercially available membranes [6]. The data presented previously [1,4] were obtained with prototypes: less sophisticated versions of the present irradiation device.

The thermal neutron flux profile was measured by the activation technique with gold foils. In this experiment, gold foil monitors (diameter 5 mm and approximate mass 20 mg) wrapped in thin aluminium sheets, were positioned at regular distances

on the surface of another aluminium rod, which was placed in the same position as the previous rod containing the uranium deposition. One of these gold foils was irradiated under a cadmium sheet cover (1 mm thickness), in order to verify the contribution of epithermal neutrons [7]. The foil activities, induced by $^{197}$Au $(n,\gamma)$ $^{198}$Au reactions, were determined by counting the emitted gamma-rays (411.8 KeV), in a high purity germanium detector (HPGe). All irradiated gold foils were counted in a well defined geometry (172 mm from the detector). The gamma-ray efficiency curve for the HPGe detector was determined by a method described previously [5]. It was determined in the energy interval from 244 to 1408 KeV, employing four standard sources: $^{60}$Co, $^{133}$Ba, $^{137}$Cs and $^{152}$Eu, supplied by the International Atomic Energy Agency. The experimental efficiency values were curve-fitted, as a function of the gamma-ray energy, using least square methods and covariance matrix analysis. The best curve obtained was a second degree polynomial on a log–log scale. Corrections for "pile-up" effects, self absorption, dead time, geometry and decay were applied in the activity calculations. The thermal neutron fluxes $(\Phi)$ based on a Maxwellian energy distribution spectrum are described by the following relationship:

$$\Phi = \frac{(A - ACd)}{\epsilon N\sigma}$$

where $ACd$ and $A$, are the activities (Bq/g) for the gold foils irradiated with and without cadmium cover respectively. $N$ is the number of $^{197}$Au nuclei/gram and $\sigma$ is the thermal neutron cross section (from Ref. [8]) corrected for a neutron temperature of 32°C in the reactor moderator (light water), $\epsilon$ is the gamma-ray detector efficiency at 411.8 KeV. The measured neutron flux profile is shown in Fig. 4, in which position 0 corresponds to the upper end of the aluminium rod, Fig. 1, when the irradiation device is in its operational position close to the reactor core.

As can be seen in Fig. 4, the flux is approximately constant $(\Phi = 2.70 \pm 0.05 \times 10^{11}$ cm$^{-2}$ s$^{-1})$ within the interval from 0 to 11.25 cm and that it drops rather slowly beyond this, reaching about 80% of the plateau value at 18 cm. The uranium deposit on the aluminium rod, was within the plateau interval (shown in Fig. 4) and so all the fissile material was irradiated uniformly. The cadmium ratio (de-
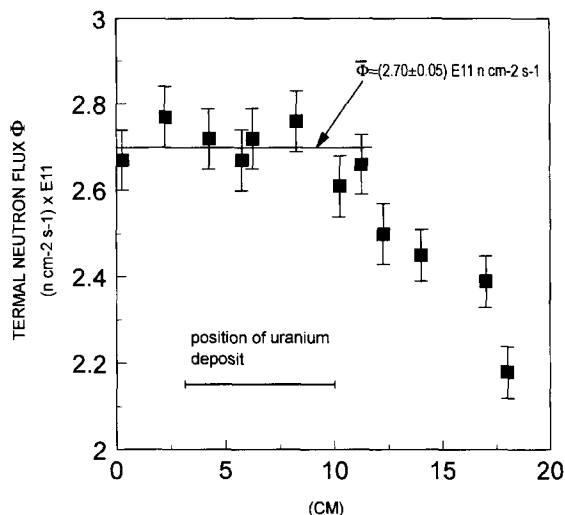


Fig. 4. Axial profile of neutron flux relative to the position of the uranium deposit. Distances are measured relative to the upper end of the axial rod (shown in Fig. 1).

fined as the ratio of the count/gram obtained without and with cadmium cover) measured at the 8.25 cm position was $12.3 \pm 0.4$ which is consistent with the result reported [9] for another irradiation position, near the reactor core.

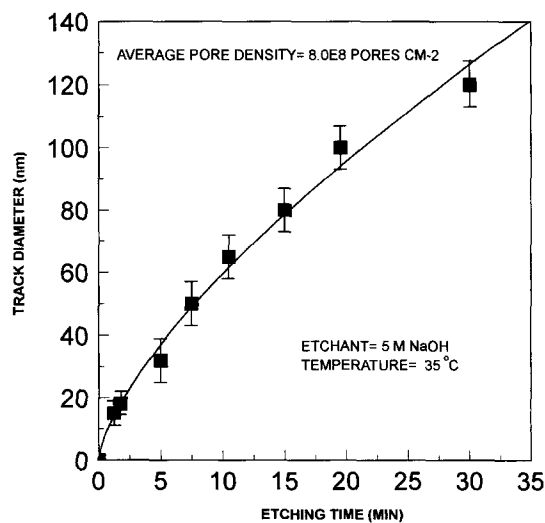Irradiation times from 3 to 6 minutes were ade-



Fig. 5. Experimental correlation of TEM pore diameter (nm) as a function of etching time (min) using 5 M NaOH at 35°C.
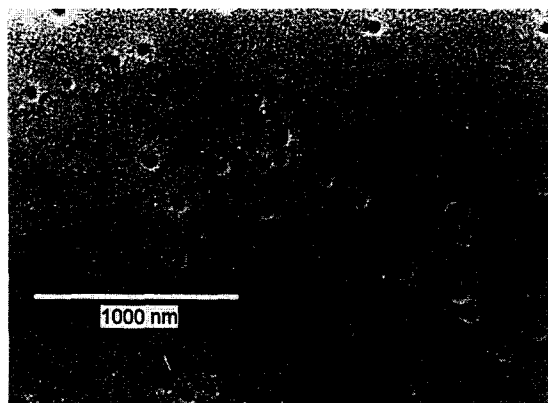
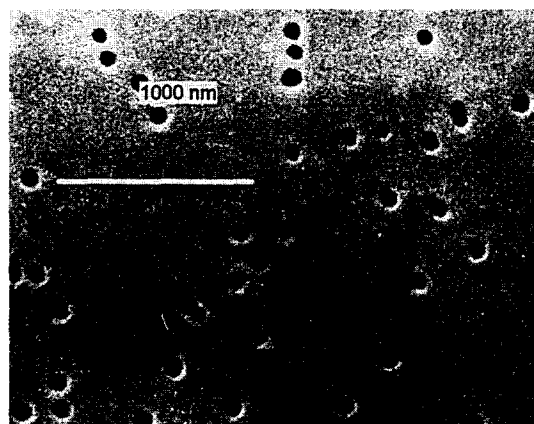Fig. 6. Surface of a TEM with average pore size 50 nm and pore density $8.0 \times 10^8$ pores/cm$^2$.



Fig. 7. Surface of a TEM with average pore size 80 nm and pore density $8.0 \times 10^8$ pores/cm$^2$.

quate to obtain membranes of $8.0 \times 10^8$ to $1.5 \times 10^9$ pores/cm$^2$, using the new equipment.

Calibration curves track diameter versus etching time for membranes in the microfiltration region (pore diameters from 100 to 10,500 nm) and pore density from $10^8$ to $10^5$ pores/cm$^2$ respectively, have been obtained previously and reported in [1]. Makrofol KG microfilters were also easily produced with large areas and have been successfully applied [10], to separate two different and strongly mixed liquid phases (emulsion).

To produce TEM membranes from the irradiated films of Makrofol in the ultrafiltration range (pore diameters $\angle 100$ nm), the best results were obtained with 5 M NaOH solutions at 35°C. Pore diameters in the etched Makrofol foils were measured using a scanning electron microscope (SEM). The calibration curve of pore diameter versus etching time, for track diameter ranging from 15 to 120 nm and average pore density of $8.0 \times 10^8$ pores/cm$^2$, is shown in Fig. 5. The curve is not linear, as observed previously for larger pores in the microfiltration range, and this result is in good agreement with those of other authors [11,12].
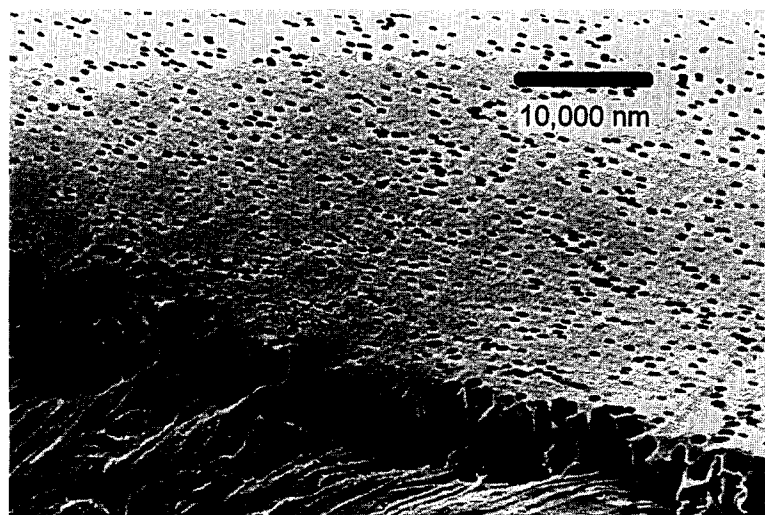


Fig. 8. Lateral view of a TEM with average pore size 800 nm and pore density $2 \times 10^7$ pores/cm$^2$.

For illustration SEM micrographs of two samples of Makrofol membranes, with average pore size around 50 and 80 nm respectively, pore density about $8.0 \times 10^8$ pores/cm$^2$ and magnification of 40000 are shown in Figs. 6 and 7. Fig. 8 gives a lateral view of another sample of Makrofol KG TEM with an average pore size of 800 nm, pore density about $2 \times 10^7$ pores/cm$^2$ and magnification of 2000.

It is clear from the micrograph that most of the pores are ideally normal to the membrane surface and pores crossing the membrane with low entry angles are few. This is a consequence of the method of preparation. Around the circumference of the radiation chamber, the length of the membrane foil, (the $x$-direction) all radiation tracks (subsequently pores) are at 90° to the surface, corresponding to an effective radial distribution of fission products from the axial uranium deposit. At right angles to this, across the membranes 160 mm width (the $y$-direction) the centrally placed 70 mm length of uranium deposit allows for radiation to penetrate at angles less than 90°, Fig. 9. The maximum and minimum penetration angles are pre-defined by the length of the uranium coated rod and the dimensions of the radiation chamber. With the test configuration, Fig. 1, used in this study, a point on the membrane in the middle of the 160 mm width will have penetration angles in the range 76 to 90°. Directly opposite one or other end of the uranium coated section of the central rod, the range is 64 to 90° and at the mem-
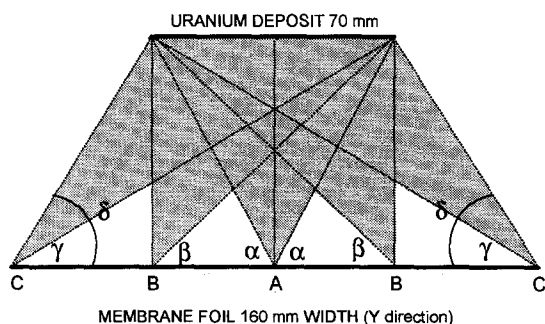


Fig. 9. A schematic representation of maximum and minimum penetration angles across the width (160 mm) of a membrane foil, in the radiation chamber (Fig. 1). The dimensions are those of the experimental chamber used in these studies. Position A, centre. Position B, directly opposite the upper or lower ends of the axial uranium deposit. Position C, at the extreme edges for the membrane. Angles $\alpha = 76°$, $\beta = 64°$, $\gamma = 52°$, $\delta = 73°$.
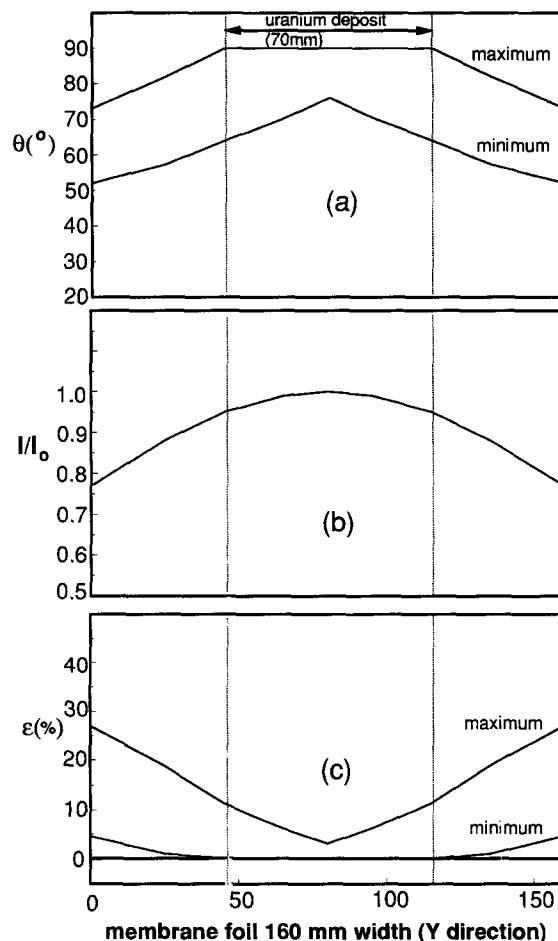


Fig. 10. (a) Maximum and minimum angle of radiation incidence ($\theta$), (b) total relative variation of intensity of radiation which is proportional to pore density, (c) maximum and minimum % pore elongation due to variable incidence of radiation, over the width of the membrane foil in the irradiation chamber relative the centre point of the film.

brane edges the range is 52 to 73°. Fig. 10a shows the maximum and minimum penetration angles ($\theta$) for pores across the width (160 mm) of a membrane foil, Fig. 10b shows the relative variation in the intensity of bombardment of fission fragments which impinge on membrane surface and is directly proportional to pore density distribution and Fig. 10c the corresponding maximum and minimum % pore elongations ($\epsilon$) due to these variations in incidence, where $\epsilon = [(1 - \sin \theta)/\sin \theta] \times 100$.

Thus, despite observed the good pore uniformity for this irradiation geometry (Figs. 6 and 7), the pore length at the membrane edges, can be up to 27% higher than those produced at normal incidence and this obviously can affect the membrane permeability. This effect can be minimized by using only the central part (70 mm width) of the plastic foil or if a better homogeneity is necessary, by decreasing the length of the uranium coated rod and/or increasing the irradiation chamber diameter. It is an intrinsic advantage of the cylindrical conformation of the radiation chamber that without physically collimating the particle emissions using barriers or radiation guides, low angle penetration is prevented, strengthening the membrane and making it more nearly ideal.

## 4. Conclusion

The new irradiation device is described which is well suited for controlled production of microfiltration and ultrafiltration TEMs when irradiated by thermal neutrons in a nuclear reactor. Membranes are obtained with precisely defined pore sizes and pore densities and with pores normal or close to normal to the membrane surface. Large areas ($\approx 1000$ cm$^2$) of track etched membranes with a high level of pore uniformity can be prepared using this new configuration, and periods of irradiations as short as few minutes. The methodology for producing ultrafiltration membranes has been developed down to a pore size of 15 nm employing a pore density around $8.0 \times 10^8$ pores cm$^{-2}$. However, the lower limit for the present technique should be, in principle, the hole size produced by the fission fragment without the chemical etching, which is approximately 8 nm according to [13]. In this way, the upper limit for the pore density should be $4 \times 10^{11}$ pores cm$^{-2}$, assuming a minimum separation of 8 nm between 2 pores.

## Acknowledgements

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