CAPILLARY MEMBRANE PRODUCTION DEVELOPMENT

Final Report to the

Water Research Commission

by

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List of Abbreviations

ID	internal diameter
IPS	Institute of Polymer Science
Lmh	membrane product flux (litres per square metre per hour)
MC	methyl cellusolve
NMP	N, methyl, 2-pyrrolidone
OD	outside diameter
PEG	poly(ethylene glycol)
PES	poly(ether sulphone)
PSf	polysulphone
UF	ultrafiltration

EXECUTIVE SUMMARY

OBJECTIVES

The main aim of the present programme is to further the production technology for capillary membranes and to extend it to materials other than poly(ether sulphone), particularly polysulphone. This was to be approached by investigating new membrane formulations and upgrading the research production facility developed during the earlier programme into a commercial production unit. This should decrease membrane handling and production costs and eventually favourably influence the economic acceptability of membrane filtration in the treatment of water intended for potable and other uses.

Many ultrafiltration capillary membranes are available on the commercial market. It is therefore important that in the development of a new membrane, existing technology should not be duplicated, but that those membrane and process technologies which are already commercially available should rather be improved. This is the only manner by which public funding for such endeavours can be justified. Obviously the transfer of membrane production technology and the development and the commercial exploitation of new process technology should be the prime motives for the research.

BACKGROUND

The Water Research Commission (WRC) research project entitled *The Development of Capillary Membrane Production* follows on from an earlier research programme (WRC K5/387) entitled: *The development and production of membrane systems,* which was supported by the WRC for the period 1991 to 1993 (WRC project K5/387). During that period the development of a membrane-production technology for a medium-molecular-mass cut-off ultrafiltration poly(ether sulphone) capillary membrane, including a 50mm cartridge module to house the membranes, was concluded and the technology made available for commercial application.

The research in the present programme was therefore conducted in association with other WRC-funded projects in order that it would complement the development of membrane-process technology. The programme areas concerned were in the fields of

biotechnology (membrane bioreactors and new membranes for use in membrane bioreactors), and in the production of potable water from the highly coloured water in the Southern Cape (membranes and module configurations, and process development). A list of these projects is given below.

Biotechnology

Project K5/553	Investigation into the application of capillary membranes in the biotechnological treatment of industrial effluents (Rhodes University)
Project K5/687	Membrane-based biotechnological systems for the treatment of organic pollutants (Rhodes University)

Potable water production

Project KV/97/95	Research on rural and peri-urban water supply (Stellenbosch University)
Project K5/764	Research into water supply to rural and peri-urban communities using membrane technologies (Stellenbosch University and ML Sultan Technikon)
Project K5/618	The development of specialized cross- and transverse-flow capillary membrane modules (Stellenbosch University)

The collaborative research effort proved both valuable and productive and culminated in the granting of two RSA patents and applications for European and USA patents, publications and oral and poster presentations of research results (see Appendix A).

There were two directives for the development of the skinless membrane described in the report. One was to design a membrane-fabrication protocol that would result in the production of a low-pressure medium-molecular-mass cut-off (MMCO) ultrafiltration membrane producing potable water. The other, more advanced requirement, was to generate a membrane(-system) that would allow the life-cycle of a fungus to be manipulated in a membrane bioreactor to stimulate the continuous production of secondary metabolites (enzymes) useful in the bioremediation of objectionable non-biodegradable organic species in water.

In the latter case it was argued that a suitable membrane for this application should be one that was internally skinned, with a substructure containing closely-packed narrow-bore microvoids that extend all the way from just below the skin layer to the membrane periphery.

The fungus were to be grown within the confines of these microvoids. Furthermore, in order to inoculate the microvoids with spores, the microvoids had to be accessible from the outside. This would be possible only if the membrane had no skin layer on the outside. Since it was regarded as impracticable to develop a mechanical technique to skim the outer layer of a membrane to expose the microvoids in the membrane sublayer, the only alternative was to develop a production procedure that would render the membrane skinless on the outside.

The development of a low-pressure medium-molecular-mass cut-off ultrafiltration membrane is a less demanding task. The pressure-drop across an ultrafiltration membrane depends on the resistance of the membrane skin layer, its supporting sublayer(s) and the membrane substructure. If any of these resistances, which act in series, could be reduced, the overall resistance to transport would also be reduced and, it would be possible to operate the membrane at lower transmembrane pressures. Since all of these requirements could be met by the development of the membrane described above, it was decided to concentrate on the development of the bioreactor membrane and to test the resulting membrane for its usefulness in water filtration applications.

PROGRESS

The development of an outer skinless ultrafiltration membrane is described in the report. Integrally skinned membranes are formed by a procedure known as phase inversion. In essence, the process requires that a membrane forming solution (a polymer dissolved in a solvent(s) with certain modifiers) be contacted with a non-solvent for the polymer. By a process of solvent/non-solvent exchange the polymer coagulates and precipitates, leading to the formation of an asymmetric membrane film. By careful manipulation of both the membrane formulation and the coagulation conditions, membranes with different skin and substructure morphologies can be produced.

In the process that was developed to produce the skinless membrane, the lumen side of the capillary membrane was formed by contacting it with pure non-solvent (water in this case) to form a skin layer on the lumen side of the membrane. The membrane formulation was, however, designed to favour the nucleation and growth of polymer-poor regions away from the skin layer which would result in the formation of microvoids in the sub-regions of the membrane. In order to prevent the formation of a skin layer on the outside of the membrane,

an aqueous solution of the solvent for the polymer was used as external coagulant. The solvent content of this solution was so high that it did not enforce liquid-liquid phase separation, and therefore did not interfere with the membrane-forming process which was controlled from the lumen side of the membrane. However, when the membrane was drawn from the precoagulation tank the membrane exterior was still soft and gel-like. The structure was set by drawing the membrane through a humidifier column, before the membrane was rinsed in a water bath.

The final membrane had a unique structure. A striking feature of the membrane was the regularity of the microvoids present in the substructure and the complete absence of an external skin layer which allowed the microvoids to be inoculated with fungal spores by reverse filtration. It was estimated that there were ~$9{,}6 \times 10^6$ of these narrow bore microvoids in a 1m-length of the membrane. The presence of these microvoids did not seem to impair the mechanical integrity of the membranes. The membranes, which have an instantaneous burst-pressure of >1 800kPa have been operated for more than 12 000h in the field at differential pressures of up to 150kPa without apparent problems (WRC project KV/97/95).

It was very difficult to reproduce the unskinned membranes, and slight variations in the composition of the external coagulant, and changes in temperature and tension shifted the external coagulation conditions into a region in which skin formation was again favoured, resulting in the formation of a membrane with an outer skin. However, the skin which would form under these conditions would be of low definition, due to the high solvent content of the external coagulant, and such a skin would therefore not offer much resistance to fluid transport. Although such skinned membranes would not be adequate for use in the bioreactor application described earlier, the membranes would still be useful as low-pressure membrane filters.

The report also describes some of the equipment that was developed during the course of the project and also discusses some of the problems that were encountered during the development of the membrane and how some of the difficulties were overcome.

Although major advances have been made to improve ultrafiltration capillary membrane production and process technology, some of the priorities listed in the original research contract could unfortunately not receive attention. This was mainly as a result of time

constraints caused by the concerted and time-consuming effort required to develop the low-pressure polysulphone membrane.

For these reasons, no attention was given to the development of poly(ether imide) microfiltration membranes and cellulose ester microfiltration and ultrafiltration membranes. The development of ceramic membranes was not attempted either, although support was provided for research conducted at master's level to generate zeolite-type membranes on unskinned polysulphone membrane templates (J Smith, MSc (1996) Institute of Polymer Science, University of Stellenbosch). The development of poly(vinylidene fluoride) membranes received attention, but the work has been reported on in another WRC project K5/619 entitled: *Tolerant membranes*. The work on the formation of thermally precipitated polypropylene membranes was concluded and was reported on in WRC project K5/387 entitled: *The development and production of membrane systems.*

CONCLUSIONS

The following conclusions were drawn:

- It has been shown that an internally skinned membrane with narrow-bore microvoids extending the full width of the membrane and with no external skin layer can be produced from polysulphone and poly(ether sulphone).
- There is a very narrow region within the experimental factor space over which the skinless membranes can be made successfully.
- The membranes have good mechanical strength and exceptional morphological properties, which make them useful low-pressure ultrafiltration membranes for use in filtration for potable water production and in biotechnological applications.
- The membranes were successfully incorporated into both axial-flow tube-in-shell-type and transverse-flow modules.
- The membranes and modules were extensively and successfully tested in field trials as part of other research programmes where the use of these filters was investigated for water treatment for potable use.
- The membranes proved useful for the immobilisation of whole cells (fungi) and enzymes, and are extensively being tested in novel biotechnological approaches in wastewater remediation.

TECHNOLOGY TRANSFER

The skinless polysulphone membrane that has been developed has been used in a number of filtration and biotechnological applications. These are summarised below:

- Production of potable water from low-turbidity irrigation water in a one-step operation without the addition of any chemicals. It was demonstrated over a period of >12 000h that the membranes were capable of reducing the levels of turbidity, microbes and iron in the feed water to the standards set for potable water. The water-recovery ratio achieved was >95%. The membranes were housed in axial-flow tube-in-shell modules (WRC project K5/618).
  Status: process development, pilot and demonstration scale.

- The membranes have also been tested for producing potable water from the highly coloured surface water in the South Cape region . The ultrafiltration process described above was combined with a limestone contact process and a plant was constructed inside a 6m container. It was demonstrated over a 6-month period at Suurbraak that the membranes were also capable of reducing the colour content of surface water from levels as high as 600 Hazen units to below 10. Recovery ratios greater than 85% have been achieved. The limestone process worked exceptionally well and the pH of the water was raised from ~6,5 to >8, and the carbonate alkalinity from zero to >22mg/l.
  Status: process development, demonstration scale.

- Umgeni Water has shown an interest in the above processes and have entered into discussions with the Water Research Commission regarding the possible commercialisation of the process.
  Status: a demonstration plant has been constructed.

It was also demonstrated that the membranes have potential for use in a membrane bioreactor.

- It was demonstrated during extensive laboratory trials conducted at the Dept. of Biochemistry and Microbiology of Rhodes University that the skinless membranes are ideal support matrices for the sustained cultivation of various fungi, notably *Phanerochaete chrysosporium* (white rot fungus) (WRC project K5/553). It was also demonstrated that the enzymes which are produced by the fungi as secondary metabolites, and which are useful for bioremediating non-biodegradable and obnoxious organic species in water, could be produced continuously for up to 60 days in special transverse-flow modules (WRC project K5/618).
  Status: laboratory scale process development.

- The skinless membranes have also been tested at the Dept. of Biochemistry and Microbiology of Rhodes University as a support matrix for the immobilisation of enzymes (WRC project K5/553). It was demonstrated that the enzyme, polyphenol oxidase, when immobilised on a membrane, is useful in the biotransformation of phenol into useful products.
  Status: laboratory scale process development.

RECOMMENDATIONS

Water filtration

Much ground has been covered to illustrate the use of the skinless capillary membrane in a one-step process for the production of potable water from surface water. However, the question remains as to whether polysulphone is the ideal material for the fabrication for a membrane for this purpose. Literature describes the usefulness of capillary membranes in potable-water production and the role which high-frequency pulsed flow and regular back-flushing plays to enhance membrane flux performance. This raises the question of the mechanical integrity of the membrane, when it is subjected to more severe operating conditions. The membranes have not yet been tested for their usefulness in treating industrial effluents. It is therefore recommended that attention should be given to the following:

- The development of a membrane from materials with lower fouling properties than those of polysulphone. This can be achieved by incorporating new hydrophilizing agents into the membrane spinning solution, or by changing the membrane material. Candidate membrane materials would be cellulose esters or polyacrylates.
- The determination of the performance and mechanical integrity of the membrane operating at high amplitude and high frequency pulsed feed and product flow conditions. Establish limits for the membrane with regards to differential pressures and operating temperatures.
- The evaluation of the membrane and module systems for their usefulness in the treatment of industrial effluents and as a pretreatment option prior to sea water desalination by reverse osmosis.
- An investigation into the possibility of commercialising the present technology, while continuing research to improve the membrane and module technology, with the aim of reducing membrane and module cost and process energy requirements.

Membranes in biotechnological applications

It has been demonstrated that membranes have notable potential in biotechnological applications and much research is being conducted internationally in this area. However, it is safe to say that this technology is still underexploited, as seen in the light of the new contributions that have been made to this advancing science by the collaborative research effort of the Universities of Rhodes and Stellenbosch in the short span of four years.

Although the unskinned membrane which resulted from interactive research has found inventive applications in biotechnology, it is premature to claim that the present membrane product is in its final form and ideal for all applications in biotechnology. Although the development of a membrane and/or membrane system for application in biotechnology is *needs driven,* some of these needs can be pre-empted. It is therefore suggested that attention should be given to the following:

- The development of a membrane filter (ultrafiltration and/or microfiltration) which has greater tolerance to organic solvents than polysulphone has.
- The development of an inexpensive approach to generation of ligands on a membrane surface for the covalent binding or immobilisation of enzymes onto the membrane.
- The development of an inexpensive transverse-flow module which can be autoclaved or steam-sterilized without the integrity of the membranes or the module, or the performance of the membranes being affected.

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1.0 INTRODUCTION

Ultrafiltration is a pressure-driven membrane filtration operation that allows the removal of species of submicron-size from water. Low-molecular-mass cut-off ultrafiltration membranes provide not only the means to reduce microbial counts in water, but readily remove components that contribute colour and turbidity to such waters. It is a filtration technology that can be applied to the production of potable water from contaminated surface and subsurface water resources, and can also be applied to wastewater remediation and the pretreatment of sea water and other water, for desalination by reverse osmosis.

Capillary membranes, by definition, are narrow-bore tubular-type membranes, typically with outside diameters that range from 0,7mm to 3mm, and inside diameters that range from 0,4 to 2,4mm. Unlike the larger-bore tubular membrane types that are cast onto a supporting non-woven fabric, capillary membranes, because of their small diameters, are self-supporting. High packing densities in module designs (i.e. filtration area per membrane volume), can be achieved due to the compactness of the membranes.

The capillary UF membranes described in this report fall in the category of integrally skinned asymmetric membranes. *Integrally skinned* refers to the skin layer of the membrane being an integrated part of the membrane substructure. *Asymmetric refers* to the graded porosity of the membrane substructure which is most dense just below the skin layer, but increasingly porous with distance away from the skin layer. The substructure may be entirely sponge-like, or it may contain finger-like macrovoids. The membranes may furthermore be externally or internally skinned, and these membranes, as well as membranes that have skin layers on both sides are commercially available.

Capillary-membrane devices are ideal for filtration at the small and intermediate scale of operation; large-scale filtration plants for potable water production are also in operation. The membranes have, apart from high packing densities, the hydrodynamic advantages of the tubular configuration (i.e. well-defined flow passages). However, although current ultrafiltration technology is advanced, there remain areas where the membrane can be adapted to provide permeates at lower filtration pressures. Low operating pressure is important where the availability of energy is of concern and is therefore a prerequisite for the technology to be commercially attractive for applications in rural communities and sea water pretreatment operations in front of reverse osmosis.

In this report some of the more important experimental findings of the research effort into the production of a low-pressure ultrafiltration membrane are described. The main achievement of the membrane production development research team was to define a narrow experimental region within which an externally skinless capillary polysulphone membrane can be fabricated. It was demonstrated that it is also possible to produce poly(ether sulphone) capillary membranes with no external skin-layer. However, the real challenge remains to extend this capability to the fabrication of polyacrylonitrile copolymer and terpolymer membranes for use as filters, either as surface-active membranes in bioreactors (enzyme immobilisation), or as precursor membranes in the fabrication of carbon membranes for use in membrane bioreactors.

The reasoning which eventually led to the development of the new polysulphone membrane is set forth below.

2.0 EXTERNALLY SKINLESS MEMBRANE

There were two directives for the development of the this membrane. The one was to design a membrane-fabrication protocol that would result in the production of a low-pressure medium-molecular-mass cut-off (MMCO) ultrafiltration membrane for use in potable-water production. The other was to generate a membrane(-system) that would allow the life-cycle of a fungus to be manipulated in a membrane bioreactor to stimulate the continuous production of secondary metabolites (enzymes).

2.1 RATIONALE

2.1.1 Potable water production

The Hagen-Poiseuille model is often used to describe liquid flow through the pores of a membrane:

$$J = \frac{\varepsilon d_p^2 \Delta P}{32 \Delta x \eta}$$

- ε number of pores
- ΔP applied hydrodynamic pressure
- Δx membrane thickness
- η solvent viscosity

d_p pore diameter

This relationship shows clearly that membrane flux is directly proportional to the number of pores in the membrane skin-layer, the pore dimensions and the applied pressure. It also shows that flux is inversely proportional to the membrane thickness. It is evident from the equation that the flux of a membrane with a certain fixed pore size can be increased by reducing the thickness of the membrane skin (i.e. by reducing the membrane resistance), or by increasing the number of pores in the membrane skin-layer.

If the membrane resistance were to be reduced, the driving force required to produce a unit volume of product would likewise be lower, and the possibility of effecting ultrafiltration with 3 to 5m of water head, which has definite advantages, becomes a possibility.

One of the large-area modules of the type that are presently under development in the WRC research programme *(K5/618: The development of specialized cross and transverse flow capillary membrane modules)* is of the axial-flow type. The module design requires the membranes to be skinned on the inside. These membranes are therefore operated from the inside to the outside. It is primarily the morphological properties of the skin layer on the inside of the membrane that effect separation; any skin on the outside of the membrane will contribute to the pressure drop across the membrane and not to the separation efficiency of the membrane. The overall membrane resistance can therefore be lowered if:

- ☐ the thickness of the internal skin layer is reduced;
- ☐ the porosity of the spongy sub-layers increased; and
- ☐ the definition of the external skin layer reduced.

The morphological structures of membranes to be either sponge-like (i.e. the cross-section of the asymmetric membrane has a lacy appearance) or the substructure may consist essentially of micro- and macrovoids, or a mixture of both. If the walls of the microvoids in the wall of the membrane are skinned, which is often the case, or if they are dense, they can contribute substantially to the pressure-drop across the membrane wall. It is therefore important for the wall of the microvoids or cells to be open-porous, particularly if the membrane has no external skin-layer; and if the micropores extend all the way from the membrane periphery to the internal skin layer, membrane resistance will essentially be a function of the properties of the skin layer.

2.1.2 Enzyme production in a membrane bioreactor

Membranes with unique morphologies can be produced by manipulating and adjusting the various factors that control the wet-phase inversion manufacturing process by which most asymmetric membranes are formed [1, 2]. In this way it is possible to produce low-molecular-mass cut-off ultrafiltration or microfiltration membranes from the same polymer by changing only the polymer concentration and spinning-solution solvent system used. Although the final membrane morphology is determined by the spinning solution formulation, the fabrication protocol plays an equally important role in controlling the properties and performance of the final membrane structure.

An important aspect of this study was that adjustment of the membrane-spinning solution formulation and fabrication protocol could result in the development of capillary ultrafiltration membranes with the required properties and morphology for use in a membrane bioreactor. However, it would be a time-consuming and tedious task to develop and design fabrication protocol for another new membrane. It would therefore be convenient if one membrane could be developed that would serve both purposes.

For the biotechnological application, the envisaged membranes had to provide a unique substructure matrix within which a filamentous fungi could be immobilised for biocatalysis [3]. The fungus used in the experiments was *Phanerochaete crysosporium*, the so-called white rot fungus found to decay wood. Initial experiments soon indicated that the fungus was shear sensitive, and that fungal biomass would easily detatch and slough off from membranes with relatively smooth exterior surfaces. In order to cultivate the fungus in a membrane bioreactor [4] it was reasoned that the membrane support matrix had to provide some protection for the fungus. From a careful study of electron micrographs of capillary membrane cross-sections that were tested in this application, it was thought that the fungus should be grown in the wall of the membrane and that the ideal membrane should have the following properties:

- ❑ the membrane should be internally skinned;
- ❑ with an annular wall consisting entirely of narrow-bore, closely packed fingerlike cavities, radiating outwards from just below the skin layer; and

- the internal skin and its integrated support layer should be thin, to reduce membrane resistance.

It was furthermore deduced from the micrographs that an external skin layer of even small definition would hinder free/convective transport of spores into the fingerlike cavities of the macrovoids, leading to non-uniform inoculation of the membrane. To avoid this problem and to improve the loading capacity of the bioreactor, it would be preferable if the membrane had no external skin layer. This would simplify the inoculation procedure as spores could enter into the microvoids by convective transport, induced by reversing the direction of flow across the membrane wall. Under the right conditions the spores would germinate within the microvoids, and the fungus would establish itself within the wall of the membrane, thus creating a thick fungal growth, with certain beneficial results, within the confines of the microvoid [4].

No membranes that met the latter prerequisite are commercially available, neither was any reference to the fabrication of such membranes found in the literature. However, if such a membrane could be developed, depending on the mechanical integrity of the resulting membrane, the membrane could also be of use in low-pressure ultrafiltration of water for potable use.

2.2 MEMBRANE FORMATION

Isotropic and anisotropic membranes are generally produced by phase inversion. During this process a homogeneous polymer solution is transformed into two liquid phases, the one a polymer-rich phase and the other a polymer-poor phase.

The polymer-rich phase coagulates to form the membrane matrix, whereas the polymer-poor phase forms the interconnected porous mass that eventually opens into the skin layer of the membrane as pores in the nanometer size range.

Wet-phase inversion membranes may be made from any polymer mixture which forms a homogeneous solution under certain conditions of composition and temperature, but which separates into two phases at a different composition and temperature. In the wet-phase inversion process, water is the most commonly used medium to bring about the change in phase. From a costing and safety point of view, it is also the preferred medium in our studies.

Capillary ultrafiltration membranes are made by spinning a polymer solution from a spinneret into a non-solvent bath. The bore-side is kept open by co-extrusion of a bore-side coagulant. By changing the membrane formulation and composition of the coagulant, and by introducing a vapour-treatment step, membranes with distinctly different structures may be produced, as will be shown later in the text. Figure 1 is a schematic view of a simple spinning line, illustrating a side and bottom view of the extrusion die, the coagulation and rinse bath and the wind-up device on which the continuously produced membrane is accumulated.

It is well described in the literature [5] that delayed precipitation of a membrane casting solution leads to the formation of Type I asymmetric membranes which nearly always exhibit sponge-like structures with dense skin-layers; this structure is typical of high-pressure reverse osmosis membranes. Conversely, instantaneous or rapid precipitation leads to the formation of Type II membranes which are thin-skinned, often with finger-like microvoids in the sublayers. It seemed logical that development of the membrane should be continued in the latter direction. The following generalizations [6] apply to the formulation of spinning solutions for the formation of the Type II membrane discussed here:

- ❑ strong non-solvents (e.g. water) increase the miscibility gap in the ternary phase diagram and favour composition profiles that support rapid phase separation;
- ❑ low initial polymer concentration will favour the formation of membranes with thin open-porous skin layers and microvoids;
- ❑ small additions of non-solvent additive(s) to the casting solution will favour the formation of thin-skinned membranes with microvoids; and
- ❑ addition of high solvent concentrations to the coagulation medium will favour the formation of low-density and thinner skin layers, with sponge-like sublayers.

For reasons of simplicity, the membranes under discussion were to be fabricated by the well-known wet-phase inversion technique. However, the literature offered no clear information regarding the formulation of a spinning solution which would give rise to a membrane with narrow-bore, densely packed macrovoids nor of the fabrication protocol necessary to produce such a membrane without an external skin layer. The following three important considerations were taken into account in the development of the spinning formulation and fabrication protocol for an internally skinned capillary membrane with a void-like substructure.

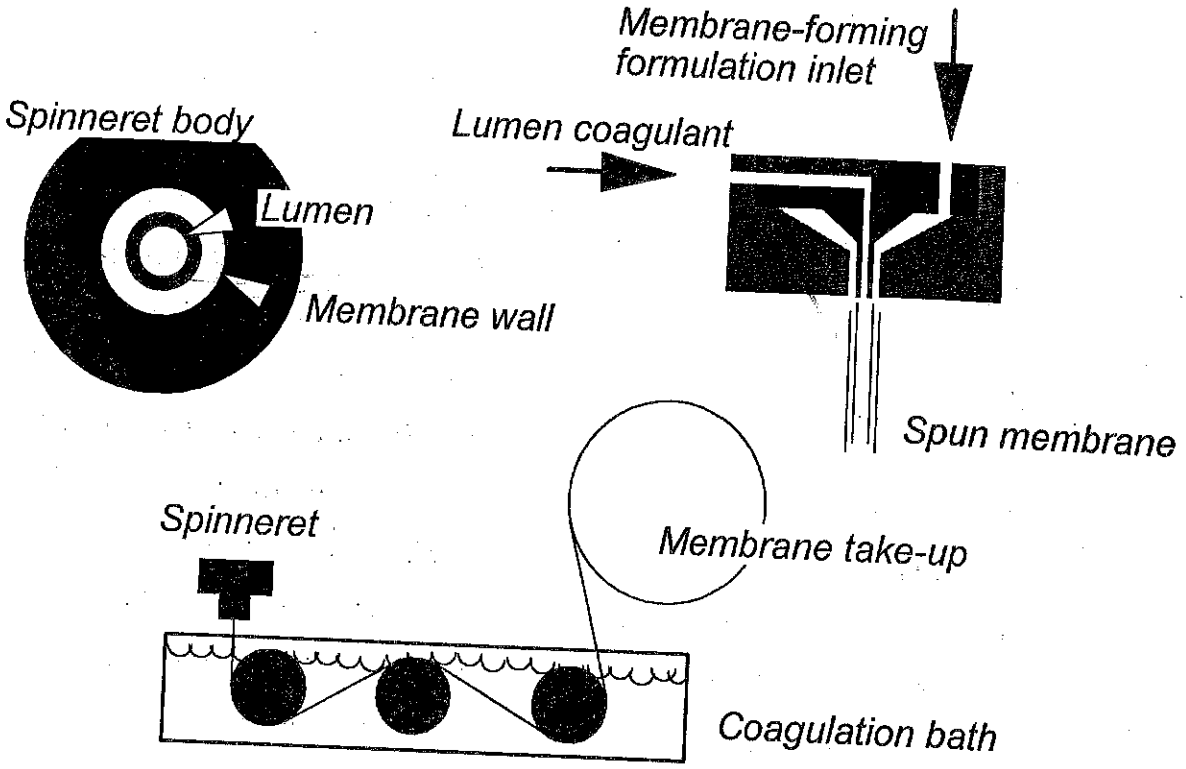


Figure 1: Schematic view of a simple capillary membrane extrusion line

- Skin-formation on the lumen side generally results from contact with a strong non-solvent; the classical gelation step is well-described in the literature [5]. Pure water with no solvent or other additives was therefore used as the internal coagulant to generate a thin-skinned membrane.
- The formation of microvoids follows from the nucleation and rapid growth of polymer-poor nuclei [7]. Much work has been reported in the literature on the mechanism of microvoid formation, and on the approaches best followed to suppress their formation [8, 9]; for our investigation, these had to be reversed as the formation of solvent-rich nuclei had to be stimulated and the solvent composition of the casting solution and internal coagulant chosen to sustain growth of the microvoid from just below the skin layer all the way up to the membrane periphery.
- To form an open-porous skin on the membrane, gelation on contact with the external precipitation bath had to be suppressed. It is known that gelation (skin-formation) can be suppressed and liquid-liquid phase separation thermodynamically favoured if the contact bath contains low concentrations of non-solvent for the membrane-forming polymer [8]. It was argued in this study that if the composition of the external coagulation tank mirrored that of the advancing polymer-poor phase front as it neared the membrane exterior, there should be no driving force for diffusion or heat of mixing (no concentration gradient), and that the phase-inversion process would cease. It was therefore decided, as a first approach, to use an external coagulation bath at a solvent/non-solvent ratio near to the cloud-point of the casting solution. N, methyl, 2-pyrrolidone (NMP) was used as solvent, and a 20% aqueous solution of NMP was chosen as a starting point.

In this report some of the results of the production of an outer-skinless polysulphone capillary membrane are highlighted. Although some thoughts will be advanced, no quantitative discussion will be offered to elucidate the striking regularity of the microvoids that was obtained, nor to explain the absence of an external skin layer under certain conditions of coagulation. This in itself would have involved a fundamental study of the membrane formation process which was regarded as beyond the scope of the programme.

2.3 SPINNING SOLUTION FORMULATION

The thermodynamic state of a membrane system with more than one component and limiting miscibility may be described in terms of the free energy of mixing. At constant pressure and temperature, three different states exist:

- A positive free energy of mixing; all components are stable and miscible in one phase.

$$\Delta G > 0 \qquad (P, T = const)$$

- An equilibrium state represented by the composition at the phase boundary.

$$\Delta G = 0 \qquad (P, T = const)$$

- Negative free energy of mixing. This state is associated with the miscibility gap in the ternary phase diagram, and refers to the unstable state in which the homogeneous spinning solution spontaneously separates into two phases which are then in equilibrium.

$$\Delta G < 0 \qquad (P, T = const)$$

There are certain restraints in the preparation of a membrane . The two phases that form during the phase inversion process must both be continuous. If the polymer-rich phase is discontinuous the end-result of the inversion process will be a powder, If the polymer-poor phase is discontinuous the structure will be dense and non-porous. Solvents, non-solvents and polymer additives that are used in the formulation of the casting solution must be soluble in the non-solvent used as coagulation medium.

Thin-skinned membranes, whether for ultrafiltration or reverse osmosis, are prepared by casting membranes from solutions that are formulated to allow rapid demixing. Such membranes will develop microvoids in their substructures if the nucleation and growth of the solvent-rich phase predominates. Once nucleation has taken place by depletion of solvent from the adjacent areas, the front end of these droplets will grow spontaneously and rapidly outwards.

The formation of microvoids and their elimination from membranes has been the subject of much discussion over the years. In this case, however, the membrane formulation had to be reverse-engineered to stimulate the formation of microvoids, as their presence is normally regarded as detrimental to the mechanical integrity of the membrane. For example,

high-viscosity solutions reduce diffusion rates and generally suppress the formation of microvoids. For this reason the viscosity of the membrane-forming solution had to be in the low to medium range, and the polymer concentration in the intermediate range. Also, heat of mixing of the polymer solvent and the main coagulant had to be high and the formulation had to contain a low-specific-gravity, low-boiling point non-solvent. The formulation had to have a composition close to the binodal on the ternary phase diagram.

As it happened, the formulation from which the skinless membrane was produced (described later) exhibited interesting behaviour in that microvoid formation did not occur when membranes were cast in flat-sheet form, that is, either on a glass plate or on a non-woven fabric carrier. However, when capillary membranes were produced from this spinning solution, the presence of the microvoids was a very pronounced feature of the membrane morphology. This complicated the development of a suitable spinning formulation, as casting flat-sheet membranes is a much faster and simpler operation.

It is not quite clear why this is so. The membrane is under slight tension when it leaves the spinneret, and is postulated, although difficult to prove, the induced strain generates the formation of solvent-rich nuclei (growth centres for the polymer-poor phase) . Also, the membrane has a high shrinkage rate of >14%. At the point of extrusion, where the bore-side comes into contact with the pure-water non-solvent, further stress is induced by two-dimensional shrinkage of the membrane, which may also lead to the nucleation of solvent-rich sites that could subsequently grow into microvoids.

In the spinning of the membrane, the bore-side is kept open by co-extrusion of a bore-side coagulant. By changing the membrane formulation and the composition of the coagulant, and by introducing a vapour-treatment step, membranes with distinctly different morphologies may be produced. A large number of membranes were spun from different formulations during the initial stages of the programme. Electron micrographs of a selection of some of the earlier membranes produced are shown in Figures 2a to 2f. The membranes were produced under similar spinning conditions and the micrographs clearly depict the different membrane substructure morphologies that arise when small alterations are made to the spinning formulation. The membranes were spun from the formulations given in Table 1. In this instance pure water and an aqueous solvent solution (80% N, methyl, 2-pyrrolidone) were

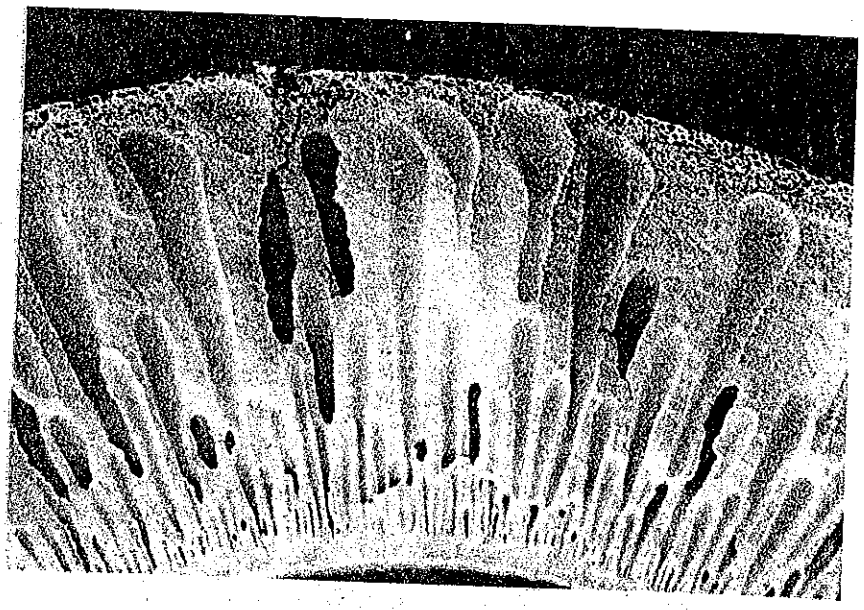


Figure 2a: Electron micrograph of the cross-section of capillary membrane (formula #1, Table 1)

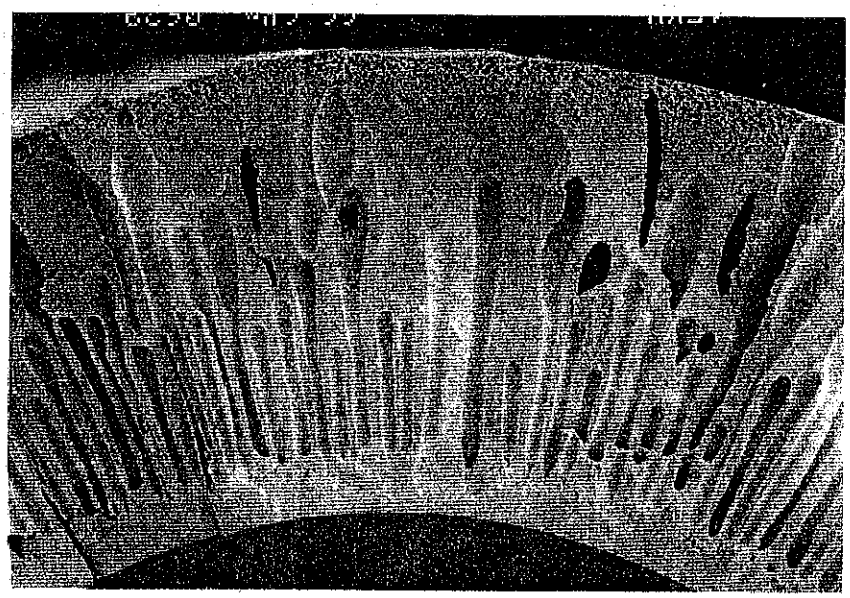


Figure 2b: Electron micrograph of the cross-section of capillary membrane (formula #2, Table 1)

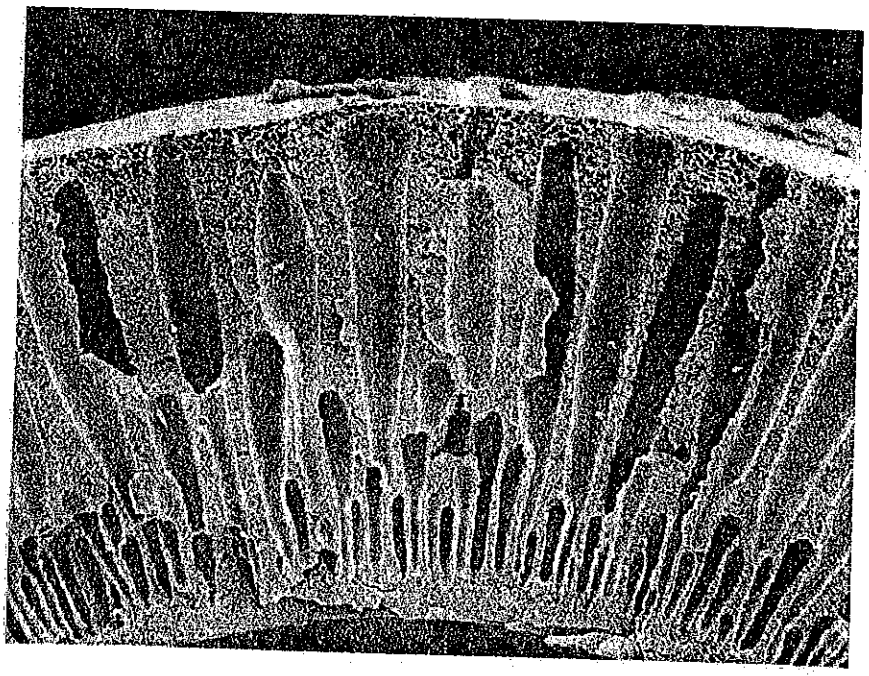


Figure 2c: Electron micrograph of the cross-section of capillary membrane (formula #3, Table 1)

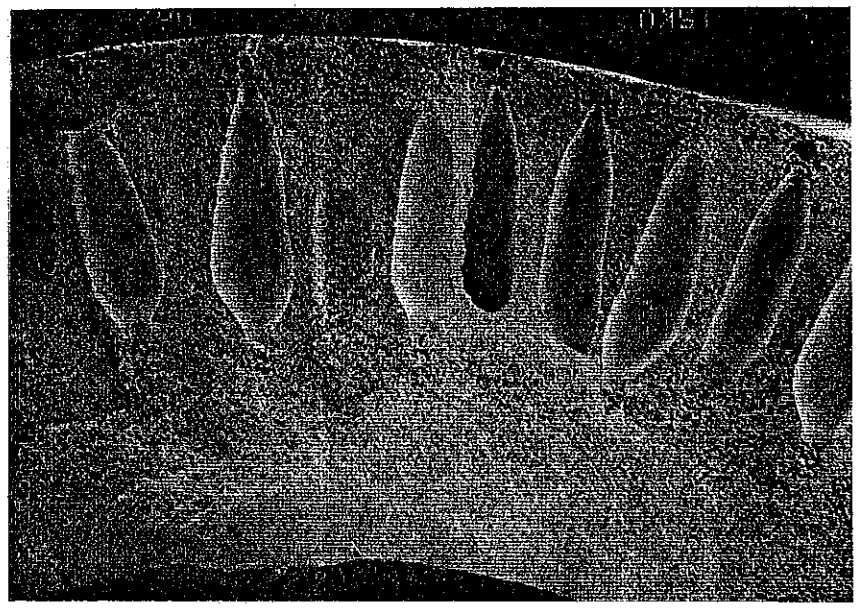


Figure 2d: Electron micrograph of the cross-section of capillary membrane (formula #4, Table 1)

Figure 2e: Electron micrograph of the cross-section of capillary membrane (formula #5, Table 1)

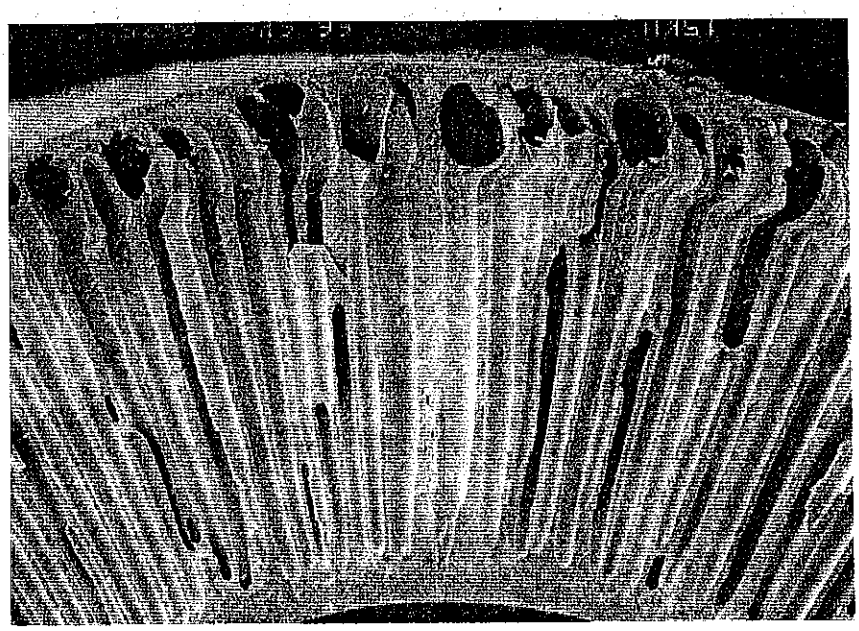


Figure 2f: Electron micrograph of the cross-section of capillary membrane (formula #6, Table 1)

used as internal and external coagulants, respectively. The micrographs also indicate the presence of an outside skin on these membranes.

The membrane shown in Figure 2f (formula #1, Table 1) had particularly interesting features, namely the well-defined and regularly spaced microvoids present in the substructure and the thin internal skin-section. Although the microvoids extended almost throughout the wall of the membrane, the interior walls of the microvoids were semi-skinned and not microporous. However, the membrane formulation was reserved as a good candidate from which to prepare the outer skinless membrane.

Table 1: Initial capillary membrane spinning formulations

Casting solution component	Membrane formulation number					
	#1	#2	#3	#4	#5	#6
	mass percent					
Polysulphone - *Ultrason S* 3010	24	24	24	24	24	24
N, methyl, 2-pyrrolidone	66		56	46	46	36
N, dimethyl acetamide		66				
Methyl cellusolve			10	10		10
Polyethylene glycol 600				10	20	30
Poly(vinyl pyrrolidone) K40	10	10	10	10	10	

2.4 MEMBRANE FABRICATION

The many factors that affect the performance and morphology of a membrane may be of two types namely, the membrane formulation and the fabrication protocol followed to produce the end-product. These may be subdivided further:

Membrane formulation:

- ☐ Solvents, non-solvent and polymer and inorganic additives in the casting solution;
- ☐ Membrane-forming polymer material;
- ☐ Inorganic and solvent additives in the coagulation bath;
- ☐ Relative concentrations of the various components that constitute the spinning formulation; and
- ☐ Viscosity and temperature of the spinning dope.

Fabrication protocol:

- ❑ The air-gap (distance between the spinneret and coagulation bath);
- ❑ Temperature of the coagulant (external and internal) and the membrane formulation;
- ❑ Velocity of the membrane solution through the annular spinning die;
- ❑ Volume-flow of the lumen coagulant;
- ❑ Draw-off rate;
- ❑ Temperature and composition of the coagulation bath; and
- ❑ Post-treatment operations such as thermal treatment and conditioning for storage.

The aim with the work was to produce a capillary membrane with no external skin-layer, which meant that those conditions which favour gelation must be avoided. If skin formation is to be depressed, there must be little difference between the chemical potential of the coagulant and the membrane formulation to depress diffusional exchange of solvents and non-solvents. In other words, the content of non-solvent in the contacting fluid on the outside of the membrane must be very low. This will favour liquid-liquid phase separation and the growth, respectively, of solvent-poor and solvent-rich phases that will eventually constitute the membrane matrix and pores within the matrix.

Therefore, as the membrane had to have the skin on the inside, pure water was used as the bore-side coagulant. Contact with pure water resulted in instantaneous gelation and membrane skin-formation, as the membrane formulation was designed close to the binodal. Because of shrinkage caused by the gelation step, and the slight tension that is maintained on the extruded fibre, nucleation of the solvent-rich phase is favoured and growth of this phase controls the final finger-like void morphology. If the composition of the outside coagulant is carefully controlled, as will be indicated shortly, a small window exists where skin-formation on the exterior of the membrane does not occur. This is an equilibrium concentration and is very dependent on the temperature and the types of true-solvent, non-solvent, polymer and polymer additives used.

The capillary membranes were formed by extruding a polymer solution through an annular tube-within-tube extrusion die by means of a Barmag stainless steel precision-gear metering pump. In the first experiments the spinning die was positioned above the non-solvent

coagulation tank, and the membrane was spun into the tank at a linear production rate of 4m/min. Pure water was metered into the lumen side so that the more dense thin inner skin layer would be formed. As the external coagulant or contact bath, on the other hand, was high in solvent content (typically 80% solvent), the outside of the nascent membrane was still highly swollen, gel-like and soft when it was withdrawn from the external contact fluid. The membrane had therefore to be exposed to a non-solvent vapour atmosphere, humidified air in this case, to fix the structure once the membrane had been withdrawn from the bath.

This completed the phase-inversion membrane-formation process and the membrane could be transferred to guide rollers in the rinse tanks without damage. The initial experimental membrane-formation equipment is illustrated in Figure 3.

For reasons that will be explained later, the extrusion line was modified and the membranes were extruded in the vertical position. The alternative experimental approach is illustrated in Figure 4.

2.3 Spinning solution preparation

Grade 3010 *Ultrason S* (PSf) and *Ultrason E* (PES) from BASF were used. The NMP solvent and methyl cellusolve (MC) non-solvent were vacuum distilled in an inert atmosphere and stored over 3Å molecular sieve. A chemically pure grade of polyethylene glycol (PEG600, i.e. molecular mass 600 dalton) was used as low-molecular-mass polymer additive; and industrial grade polyvinyl pyrrolidone (PVP) was used as high-molecular-mass polymer additive. (molecular mass 40 000 dalton).

The solutions were prepared in a 2l resin kettle equipped with a high-speed overhead stirrer, placed in a temperature controlled oil bath. The solvation temperature was maintained at 60°C. The shaft of the stirrer passed through a Liebig condenser which prevented loss of low-boiling solvent(s). A minimum period of 48h was required to obtain a homogeneous solution. The solution was then decanted into Schott bottles, rotated slowly for 48h on rollers at ambient temperature, filtered through a 5μm stainless-steel filter and degassed in a desiccator for 24h directly before use.

After fabrication the membranes were rinsed in pure-water for 24h and then conditioned in a 1:1 aqueous glycerine solution before they were dried in a high-humidity chamber at ambient

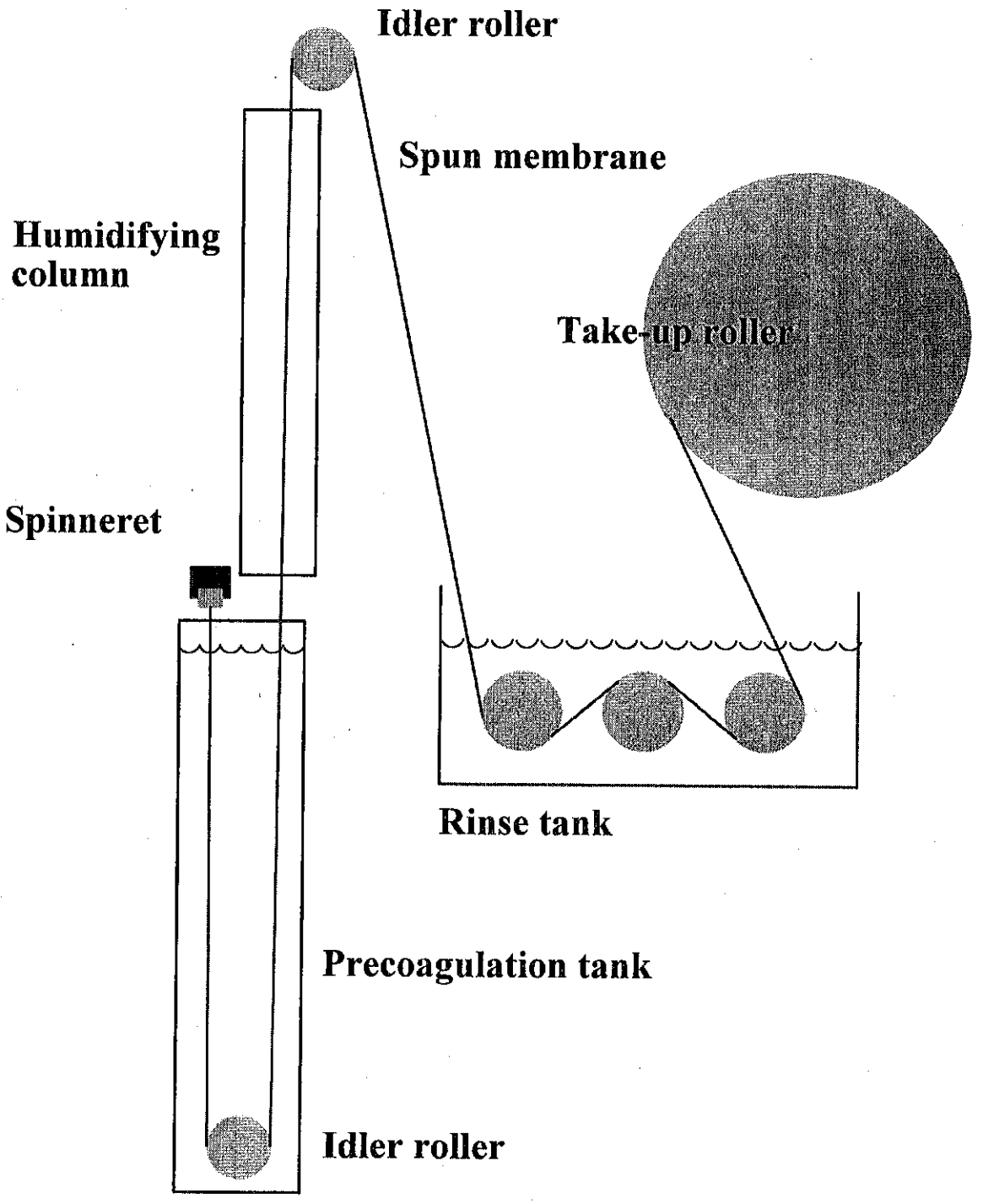


Figure 3: Schematic view of the initial capillary membrane extrusion line - spinning vertically downwards

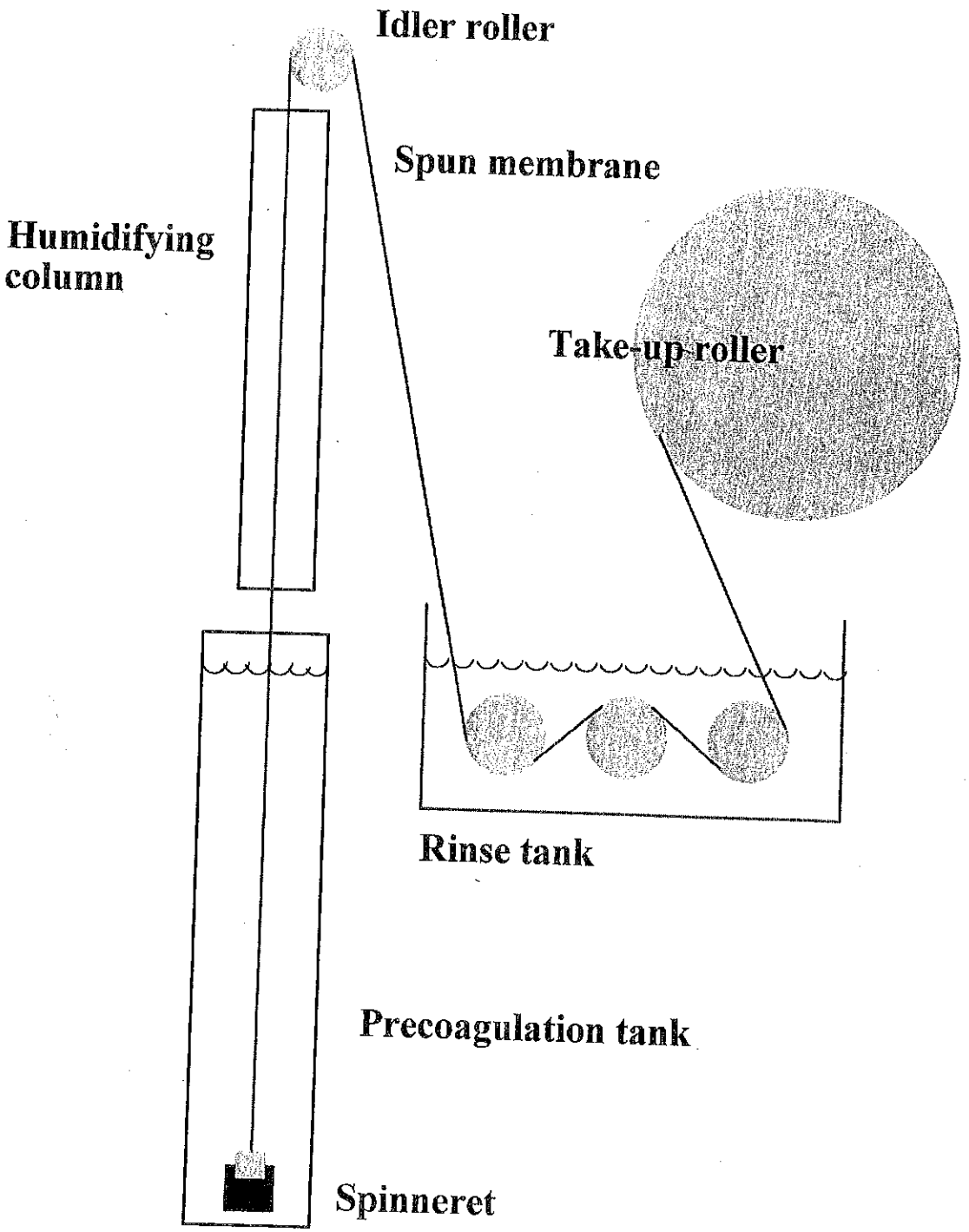


Figure 4: Schematic view of the alternative capillary membrane extrusion line - spinning vertically upwards

temperature for a period of 7 days. The membrane specimens did not undergo thermal or any other form of post-treatment.

2.4.2 Spinneret

A new stainless steel tube-in-tube spinneret was designed. In contrast with previous spinnerets, this spinneret had only two parts. The spinneret was of much simpler design and therefore less troublesome to machine than the previous designs. The core-side fluid passages were kept as short a possible, which allows the spinneret to be machined accurately from more resistant stainless steel which is a necessity if the spinneret must remain in the high-solvent content first-contact coagulation bath. (See Figure 5). The extrusion die is also easy to clean.

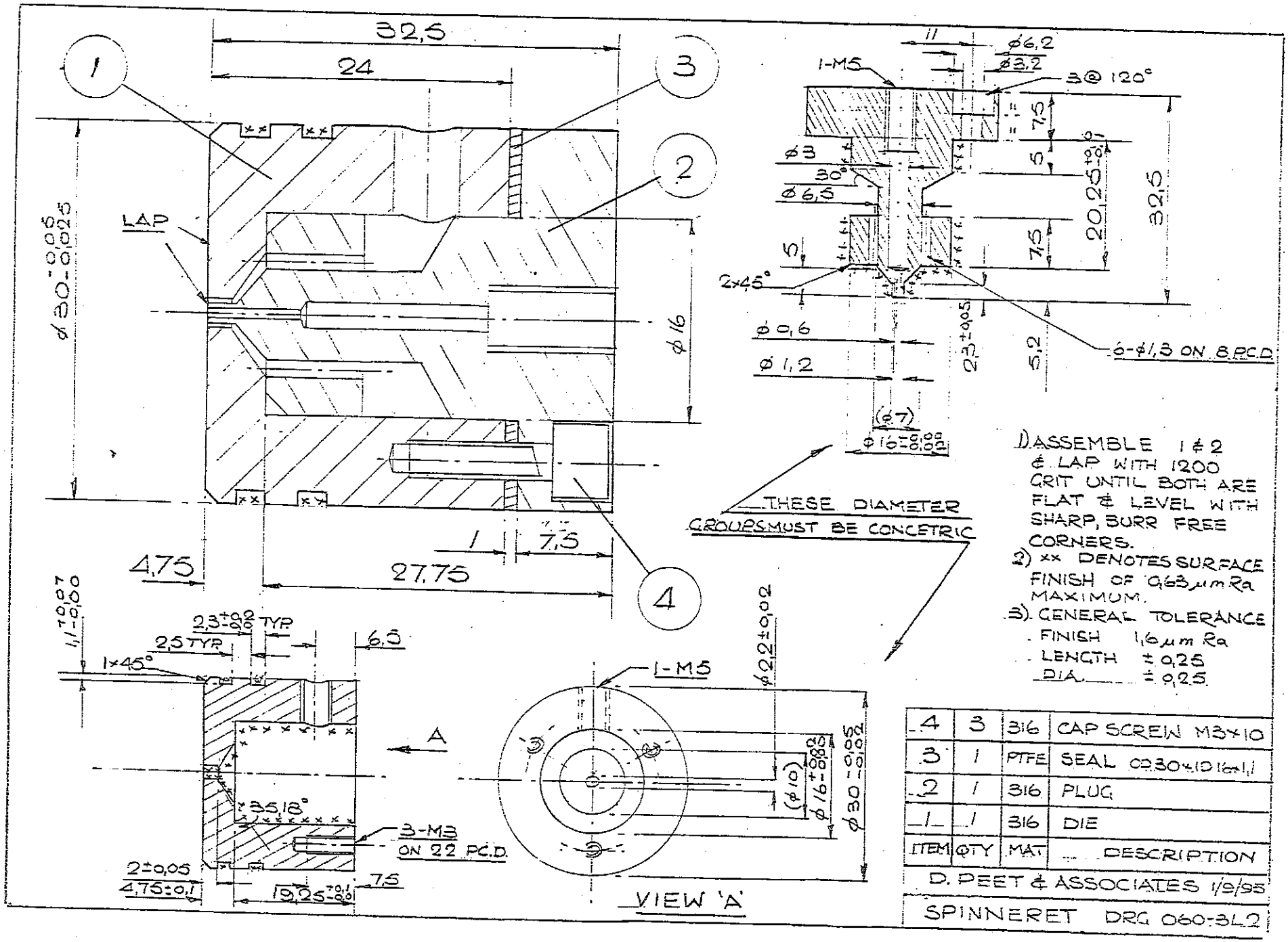
The centre needle of the spinneret often gets damaged during cleaning. Lining-up of the centre needle within the spinneret is simple, and only the centre-piece must be remachined if the needle is damaged

2.4.3 Coagulation

One of the techniques adopted to produce membranes with an outer skin of low definition is to spin the membranes first into a contact or coagulation bath which contains a high level of a solvent for the polymer and a very small proportion of non-solvent. This step is to inhibit gelation on the outside of the membrane, and therefore skin formation, but rather to promote liquid-liquid phase separation. The membrane is coagulated from the lumen side with a strong non-solvent such as water, which leads to gelation (a necessity for skin formation), followed by liquid-liquid phase separation in the underlying structures.

The membranes lacking an outer skin were originally cast into a 1m-long precoagulation plate-glass tank with a roller situated at the bottom of the tank. The height of the idler roller within the tank was adjustable, which was a necessary requirement during start-up. The spinneret was 2,5cm above the liquid level in the tank and the membrane was spun vertically downwards into the coagulation medium (see Figure 3) where it passed over the idler roller to change direction and pass again through the precoagulation tank (a total path-length of 2m).

One problem associated with this approach was that although the membrane structure was set by the time the membrane came into contact with the roller in the bottom of the tank, the



ITEM	QTY	MAT	DESCRIPTION
4	3	316	CAP SCREW M3×10
3	1	PTFE	SEAL ID 3.0×1.0 W 1.1
2	1	316	PLUG
1	1	316	DIE

D. PEET & ASSOCIATES 1/9/95

SPINNERET DRG 060-3L2

outside of the membrane was still soft and gel-like. The idler roller disturbed the equilibrated polymer-rich and polymer-poor phases in the membrane exterior and as a result left a longitudinal smear mark on the outside of the membrane.

It was proved during burst tests that this mark did not affect the mechanical integrity of any of the low MMCO membranes that were produced during the previous WRC-funded research programme. These membranes (#748) had instantaneous burst-pressures well above 2 000kPa and were structurally very strong. (Sets of these membranes have been operated continuously in the field for more than 24 months without structural failure). Figure 6 show a cross-section of the #748 membrane; the blemish mark can be seen in the top section of the membrane.

The situation has been quite different for the high-flux medium-MMCO polysulphone membranes which are under development. The instantaneous burst-pressures of these membranes are not only much lower (1 600kPa), but the membranes are mechanically less robust and split along the seam-line if overpressurized. With these membranes the seam-line constitutes a structural flaw and must therefore be eliminated.

It was hoped to solve the problem if the time interval before the membrane passed over the first roller in the bottom of the tank could be increased. It was considered impractical to increase the height of the precoagulation tank to allow more time in the precoagulation tank before the membrane came into contact with the roller. A new glass tank was constructed instead. This tank was made longer so as to allow the membrane to hang from the spinneret in a loop in the tank and pass over a roller only once it leaves the precoagulation tank. In this way the membrane remained in the tank for the same duration as previously, but the time to traversing the first roller was doubled. Although the seam-line flaw was reduced (Figure 7), the problem, however, was not completely overcome.

The problem with the seam-line was finally solvent when the extrusion die was positioned at the bottom of the aqueous precoagulation tank and the extrusion process inverted. The membranes that have been made after the alteration are completely concentric and unblemished on the outside. (See Figure 8). The height of the 1m-high precoagulation tank is sufficient to allow complete definition of the exterior membrane at the point of exit.

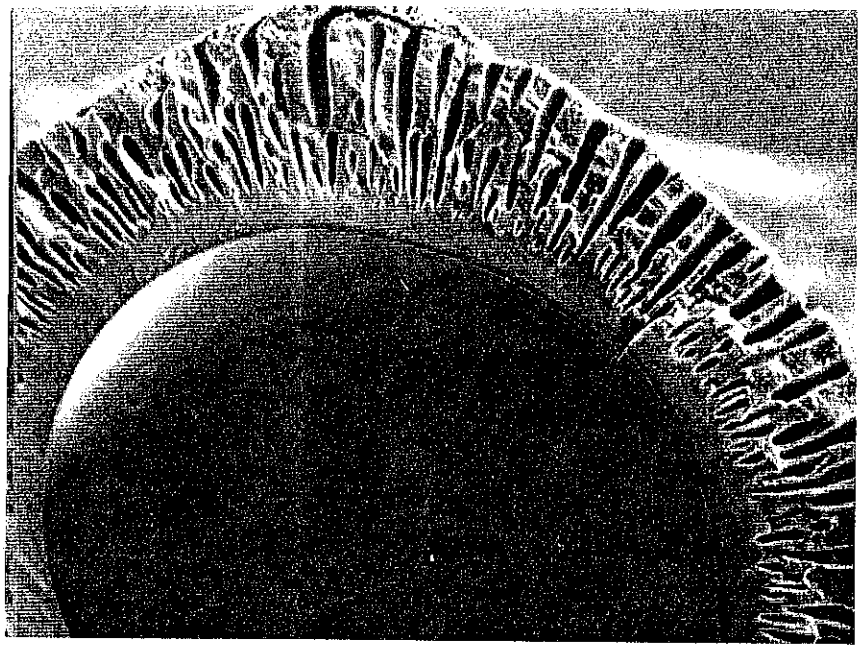


Figure 6: Cross-section of membrane coded #748/1

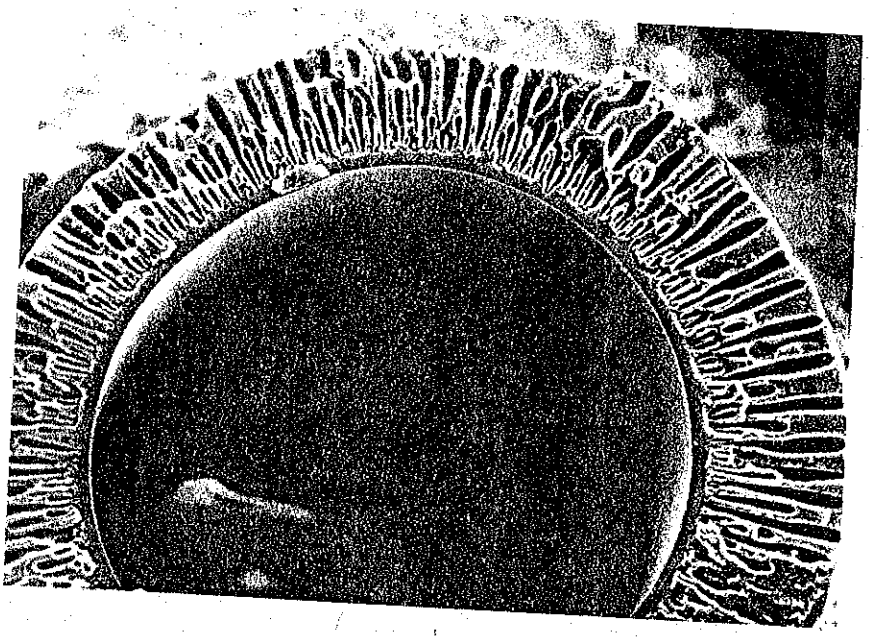


Figure 7: Cross-section of membrane coded #748/2

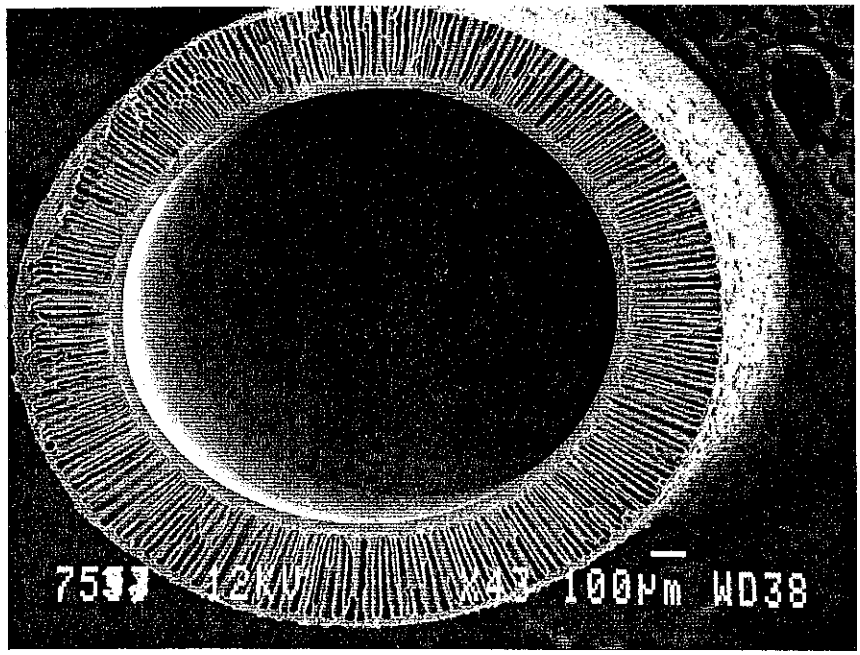


Figure 8: Concentricity of membrane exterior and absence of blemish line

As was mentioned earlier, the membrane structure is set after it has passed through the first precoagulation contact tank. However, the polymer in the outer shell of the membrane is still in semi-solvated state and still very liquid. The coagulation process in the exterior parts of the membrane must be completed gently to prevent gelation and skin formation at that stage of the membrane-formation process. The exterior structure is therefore fixed by drawing the membrane though a high-humidity zone in a column situated above the precoagulation tank. After this step the membrane is drawn through the second non-solvent bath that serves to rinse solvent remnants from the membrane (see Figure 3).

This step was successfully introduced and PSf membranes that have a flawless exterior could be made. What is more important, however, is that there is no skin whatsoever on the outside of the membrane. This is quite unique since by introducing a simple vapour coagulation step after the precoagulation step, we have achieved what is generally considered not possible with PSf, namely, the formation of a membrane lacking an outer skin and with uniform microvoids in the wall structure.

2.4.4 Membrane winding and bundling

Membranes are currently taken up on a perforated stainless steel take-up drum where they are kept wet by water sprayed onto them. The take-up drum causes two problems. First, the membranes are removed from the drum by slitting the bundle, and removing the membranes in a string. The membranes in the bundle are 1,4m long due to the fixed diameter of the take-up drum. Membranes are therefore wasted from time to time if shorter lengths are needed for experimental use. Also, the membranes remember the shape of the take-up drum and the bottom section of a membrane is always curved. This constantly causes problems during module preparation, in that it is difficult to achieve a high packing density if the membranes do not lie parallel to each other.

The problem of curved bundles was overcome by incorporating a slitter, coupled to a timer, to cut sections of the membrane at specific time intervals from a tilting and moving belt conveyer. In this way any membrane length of up to 1,4m could be cut accurately. The membrane was dispensed into a storage tank by the tilting action of the belt conveyer. A counter allowed bundles of fixed numbers of membranes to be prepared. The approach, however, did not solve the alignment problem of individual membranes within a bundle and another approach had to be devised.

As mentioned earlier, membranes assume the shape of the take-up device if they are wound onto the device in a semi-plastisized state. However, membrane module packing densities could be increased considerably if the membranes could be wound into well-packed and circularly shaped bundles, ready for use in tube-in-shell axial flow modules. This could be accomplished with the aid of a servo-controlled plane (beam) winder which in turn is controlled by a personal computer to maintain constant tension and winding pitch.

The total membrane filtration area in a shell-and-tube-type membrane module is calculated according to the geometry of the cylindrical shell and that of the capillary membranes. This relationship is described by:

$$A = N\pi dL \qquad Eqn\ 1$$

where N is the number of membranes, d is the diameter of the capillary membrane (d_i internal diameter for internal flow, d_o external diameter for external flow), and L is the effective filtration length. The number of membranes that are packed into a membrane bundle can be related to the inside diameter of the shell by the expression:

$$PR\% = 100N(\frac{d_o}{D})^2 = 100(1 - \varepsilon) \qquad Eqn\ 2$$

where $PR\%$ is the packing density, D is the internal diameter of the shell and ε is the void space or packing density.

The specific membrane area, that is, the ratio of membrane area per packing volume, depends on how closely the membranes are packed in the module. The membranes can be arranged in one of two ways, in-line and staggered, and from the relationship below it becomes simple to calculate the theoretical minimum void space of a module (i.e. not taking into account that the shell may interfere with the packing density):

$$\varepsilon_S = 1 - \frac{\sqrt{3}\,\pi}{6}$$

$$\varepsilon_L = 1 - \frac{\pi}{4}$$

where ε_S is the minimum porosity for a staggered packing array and ε_L is that for an in-line array.

In practice there is a maximum packing density (minimum void space between the membranes) which is a function of the arrangement of membranes in the module. The maximum packing density may be calculated by taking both packing arrangements into account and by using the procedure adopted by Brinkert et al [9]:

- ❑ calculate the number of membranes that can be stacked within a radius *D/2* or the number of layers (n_L, n_S) for a half-bundle;
- ❑ calculate the length L_j of the layer *j;*
- ❑ calculate the number of membranes for each layer n_f; and
- ❑ calculate the total number of membranes N in full-circular bundle.

For an in-line array, with *E* representing the integer part of the function, we have:

$$n_L = E\left(\frac{D}{2d_o}\right)$$

$$L_j = 2\left\{(0,5D)^2 - [(j-0,5)d_o]^2\right\}^{0,5}$$

and for a staggered arrangement:

$$n_L = E\left(\frac{D}{\sqrt{3}\,d_o}\right)$$

$$L_j = 2\left\{(0,5D)^2 - \left[\left(\frac{\sqrt{3}}{2}j - 0,5\right)d_o\right]^2\right\}^{0,5}$$

from which the number of membranes per layer n_f can be obtained:

$$n_f(j) = E\left(\frac{L_j}{d}\right)$$

The total number of membranes is calculated from:

$$N = 2 \sum_{j=1}^{m} n_f(j)$$

where m is the number of layers for a half-bundle. The real maximum packing density is finally calculated by substituting N in equation (2).

The packing density of currently produced capillary membrane cartridge modules is, on average <60%, because the membranes are handled in loose bundles which make packing in any specific order extremely difficult. It was calculated that the packing ratio can be increased to >70% (i.e. $\varepsilon<0.3$) if the bundles are machine-wound. It would be a simple procedure to ensure uniform penetration of the potting compound during casting of the module tube sheet.

However, when this approach was tested, it was soon realized that an unnecessary number of membranes will be lost at either end of the beam winder where the membranes curve over each other in an ever increasing radius. The membranes also tend to shag as the diameter of the bundle increases. It was therefore decided to discard the idea of a single-beam winder in favour of a broad double-beam winder and a traversing device by which the pitch of the membranes taken up on the device could be controlled.

The devices are very simple and are illustrated in Figure 9 which shows that the membranes are wound straight and when removed from the take-up unit will remain straight. This simplified bundling and module preparation.

2.4.5 Post-treatment and conditioning

Membrane fabrication involves various steps which are currently defined as *membrane production* (i.e. extrusion, pre-coagulation, vapour precipitation and leaching) and *post-treatment* (i.e. extended leaching, solvent exchange, conditioning, drying and winding). At present all the post-treatment steps are batch processes which necessitate unnecessary handling of membranes.

Membranes are generally dimensionally unstable after fabrication, and one may find that a membrane will still densify (retention will increase at the loss of water productivity) for periods of up to two weeks after fabrication. This has been ascribed to the presence of small

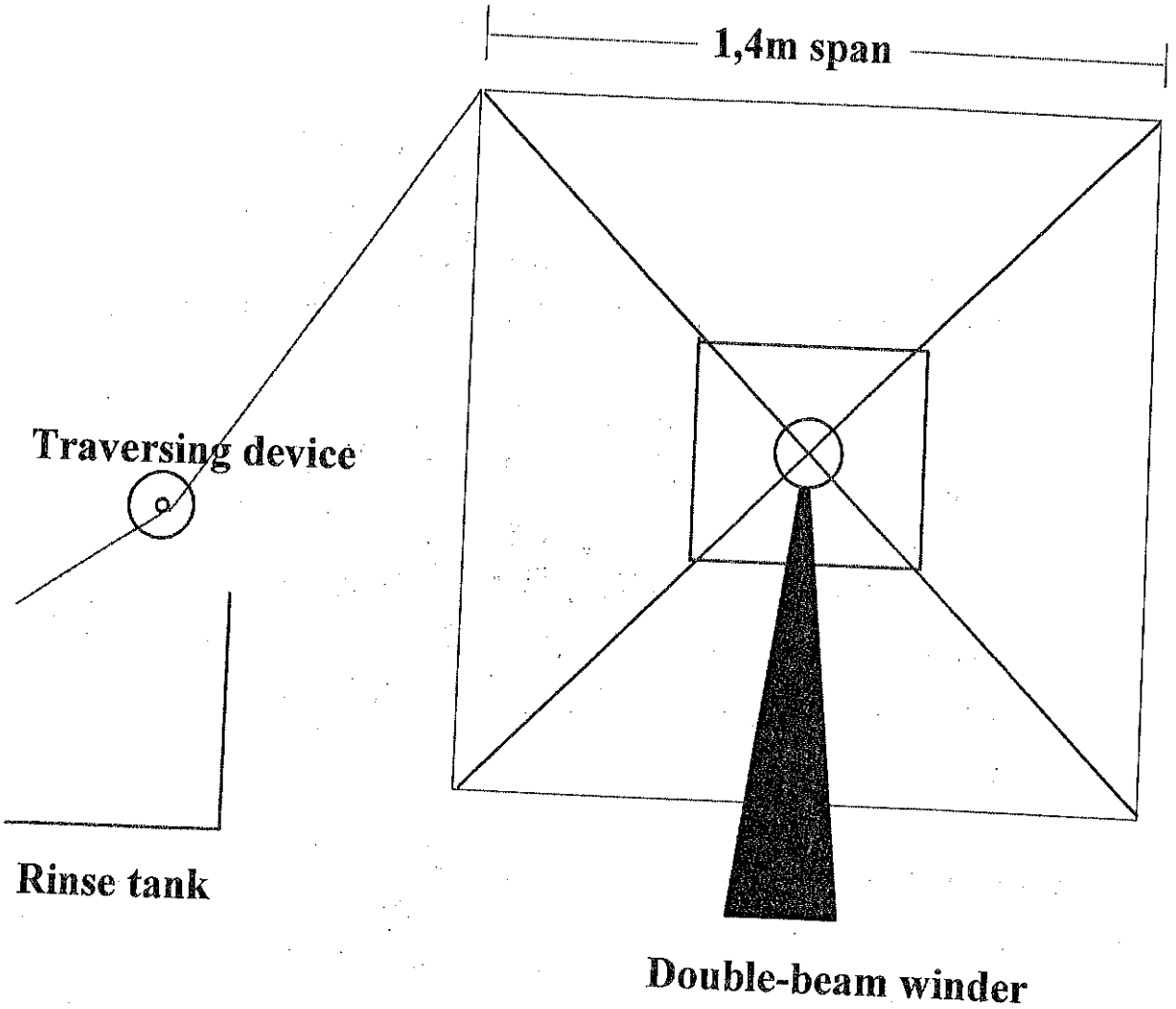


Figure 9: Double-beam take-up device and traversing feeder

amounts of solvent still trapped in dead-end pores within the membrane structure. This shrinkage may be prevented if the membranes are rinsed with hot water to remove solvent remnants before the membranes are treated before drying.

Two approaches may be followed to effect any of the post-treatment operations:

- The membranes may be wound onto a take-up device which can be removed once a certain length of membrane has been accumulated, or the membranes may be left on the take-up device while they undergo post-treatment or they may be removed prior to post-treatment. The inconvenience of several handling steps must be considered. There is also the other problem associated with winding membranes onto a reel. The membranes are not fully leached at the time when they are wound onto the take-up reel. The solvent acts a plasticizer, and the membranes tend to assume the shape of the take-up reel which as mentioned earlier, causes particular problems during module preparation.
- Another option is to incorporate the treatment step as part of the continuous extrusion process. To do this, a certain length of membrane must be accumulated at a treatment station; the total length must be calculated according to the duration of that treatment operation. If the duration of a treatment step (say thermal leaching) is 100min, it would be necessary to accumulate 500m of membrane if the membranes are produced at a rate of 5m/min; more, if the production rate is 4m/min.

The question arises as to how to do it in a way that the membrane strands (especially if double lines are spun) are to be kept apart so that they do not become entangled. In the textile industry godgets are used to transfer yarn. Fibres are drawn in the spinning process to very small diameters and to do this the fibre is anchored between two godgets running at different speeds. The godgets are heated and for this heat to be transferred to the yarn, the yarn is passed several times over the same godget. This is achieved by passing the yarn over a second separator roller which is fixed at a compound angle to the godget.

A treatment station using this approach was designed to accumulate capillary membranes. Figure 10. The unit was designed such that it could be used for thermal treatment of the membranes or as a solvent exchange treatment stage within which the non-solvent in the

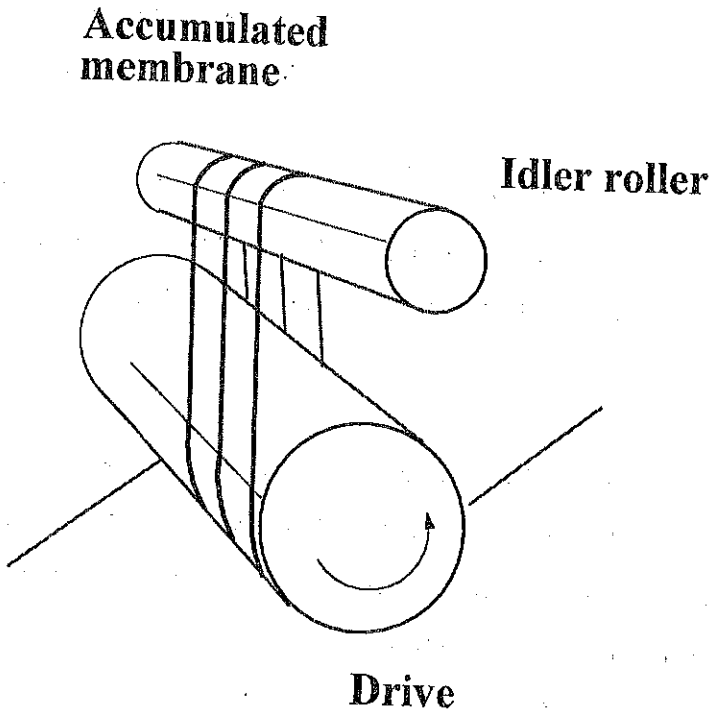


Figure 10: Godget and the separator device to serve as the accumulator in the thermal treatment station

membrane is exchanged with a low-surface-tension solvent prior to drying. The unit was designed and constructed, but was never commissioned because of various manufacturing problems which arose during the course of the programme.

2.4.6 Conditioning and storage

Solvent removal during an extended thermally assisted leaching step is necessary to ensure a good quality membrane with consistent pure-water flux performance. Capillary membrane extrusion rates are normally around 4m/min. However, as 50°C contact times of up to 45min are necessary to remove traces of solvent, up to 180m of membrane-length must be accumulated, which is a considerable length if four lines are to be spun simultaneously.

Membranes are still conditioned in a 1:1 aqueous glycerol solution for 48h before they are hung in a high humidity cabinet for drying out slowly over a period of days at a controlled ambient temperature of 22°C. The membranes appear to re-wet completely when allowed to dry out slowly, and do not lose performance.

Glycerol is, however, biodegradable and care must be exercised to prevent fungus from growing on the membranes during the one to two weeks drying-out period. Formaldehyde fumes, from a dilute solution of formaldehyde placed in a beaker at the bottom of the drying cabinet ensure sterility and arrest fungal growth.

The membranes are hung in bundles of 300 for module preparation.

2.5 RESULTS

2.5.1 First attempts at producing skinless membranes

Previous development work concentrated on the development of a productive medium-molecular-mass poly(ether sulphone) capillary membrane. The emphasis has now moved away from those membranes as a commercially acceptable product was developed. In the work described here, emphasis was placed on the development of an internally skinned medium-molecular-mass cut-off PES membrane with no skin layer on the outside (i.e. macroporous outer surface). The large surface area on the outside of the membrane should make it not only suitable for the attachment of micro-organisms in bioreactors, but the

absence of the skin would also lead to a reduction in the resistance to permeate flow and therefore higher water permeability rates.

Table 2 gives a clear indication of the water fluxes that were attained with the initial PES membranes that were produced. Typical burst pressures of these medium-molecular-mass cut-off membranes are given in Table 3.

The three-fold increase in pure-water flux between the membranes from production lot 763/114 and the remainder of the series 763 membranes (i.e. 763/115 to 763/120) was merely the result of the high-humidity contacting set that was introduced to coagulate the already phase-separated liquids on the outside surface of the membrane. The only noticeable difference between these two sets of membranes, apart from the performance, was the presence of a noticeable skin layer in the case of membrane 763/114.

Table 2: Performance of poly(ether sulphone) capillary membranes

Membrane code	Pure-water flux [Lmh]		UF performance (PEG35K) 200kPa	
	200kPa	400kPa	Retention (%)	Flux [Lmh]
763/114	373	714,00	60,3	57,9
763/115	966	1 541	46	66,2
763/117	832	1 240	58,3	71,8
763/119	844	1 323	n/a	n/a
763/120	710	1 170	n/a	n/a
748/074	163	348	90	44,7
748/078	159	348	91,3	43,3

To illustrate, membrane Code 748 (Table 4, Figure 11) was spun from a solution containing poly(ether sulphone) in an NMP solvent system, directly into an aqueous solvent bath containing 80% NMP. The internal coagulant was water, and the draw-off rate was 4m/min. Figure 11 shows not only the regularity in the spacing of the microvoids, but also the thickness of the inner membrane skin-layer. Furthermore, gelation is no longer the formation mechanism of the outer membrane layer, as many of the microvoids extend all the way into the periphery of the membrane, as can be seen in Figure 11.

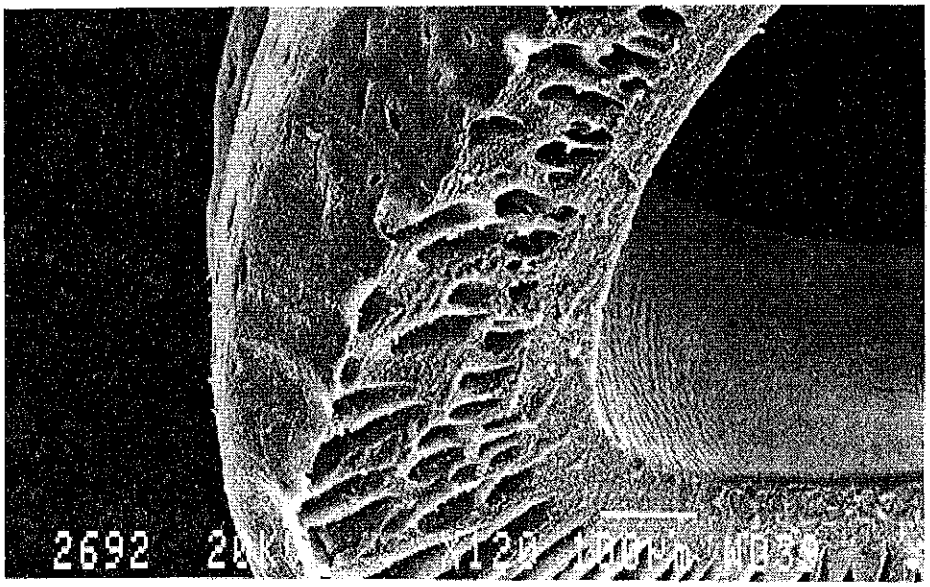


Figure 11: Electron micrographs of the cross-section of membrane #748

Table 3: Typical burst-pressures of high-molecular-mass cut-off membranes

Membrane code	Burst-pressure [kPa]
763/114	1 750
763/115	1 500
763/117	1 460
763/119	n/a
763/120	n/a
748/074	1 900
748/078	2 100

Membrane code 767 (Table 4, Figure 12) was an adaptation of membrane formulation #6 (Table 1). When the apparent subsurface and skin-layer densities are compared with membrane #748 (Figure 11), it is evident that membrane code 767 would have the higher flux rates. The flux values for the above two membranes are compared in Figure 13.

Table 4: Membrane spinning formulations

Spinning solution component	Membrane formulation			
	#767	#748	#766	#763
	mass percent			
Polysulphone - *Ultrason S*	22			
Poly(ether sulphone) - *Ultrason E*		26	22	*22
N, Methyl, 2-pyrollidone	36	51	36	36
Methyl cellusolve	10	2	10	10
Polyethylene glycol 600	32	11	32	32
Polyvinylpyrrolidone K40		10		

*note: Poly(ether sulphone) 4800G product of ICI Pty Ltd

More striking micrographs (courtesy Wade Edwards, Dept Biochemistry and Microbiology, Rhodes University), are shown in Figure 12. This figure shows various sections of membrane code 767. It is clear from the micrographs that the microvoids extend throughout the membrane and that there is no evidence of an external membrane skin layer.

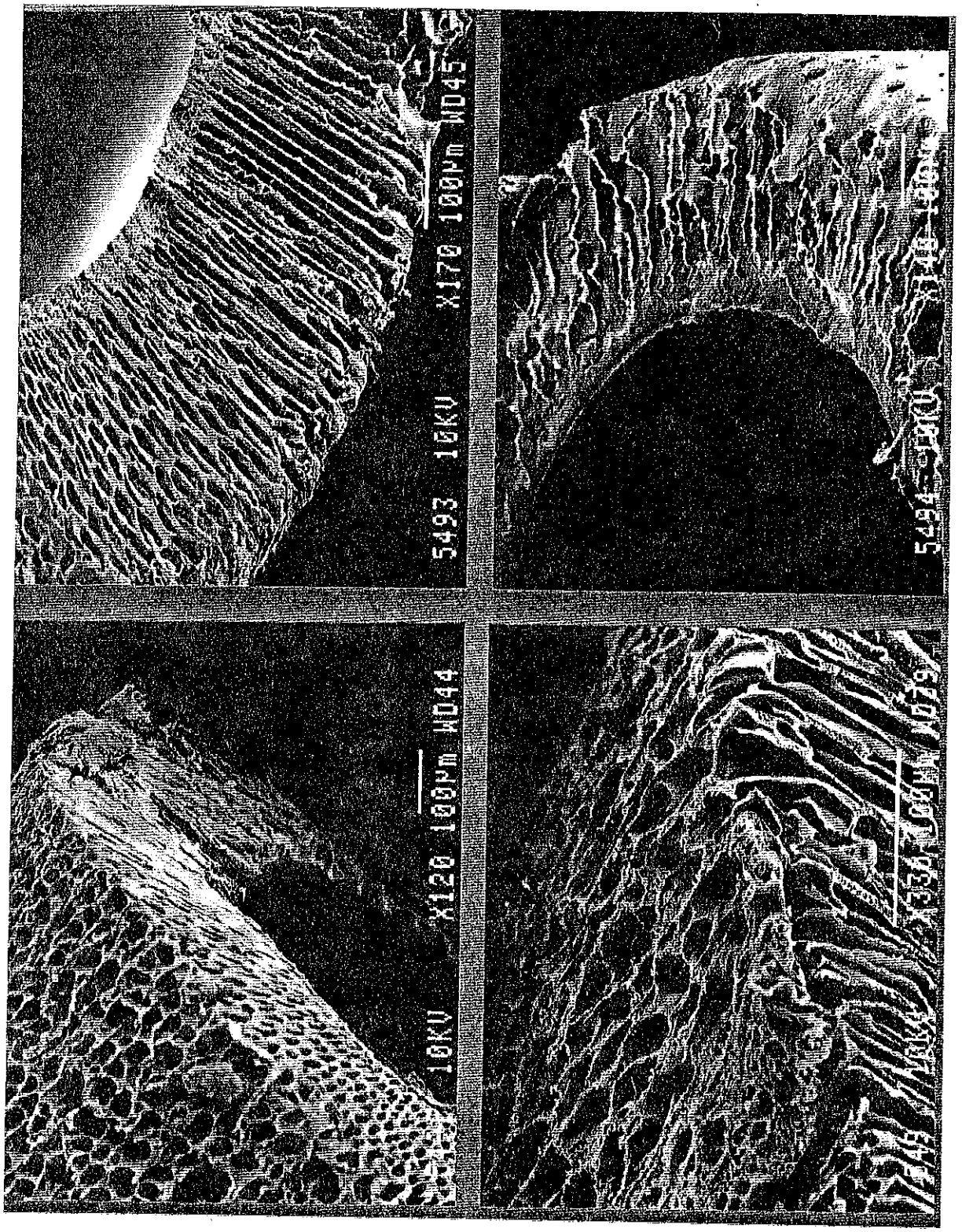


Figure 12: Electron micrograph of the cross-section of membrane #767

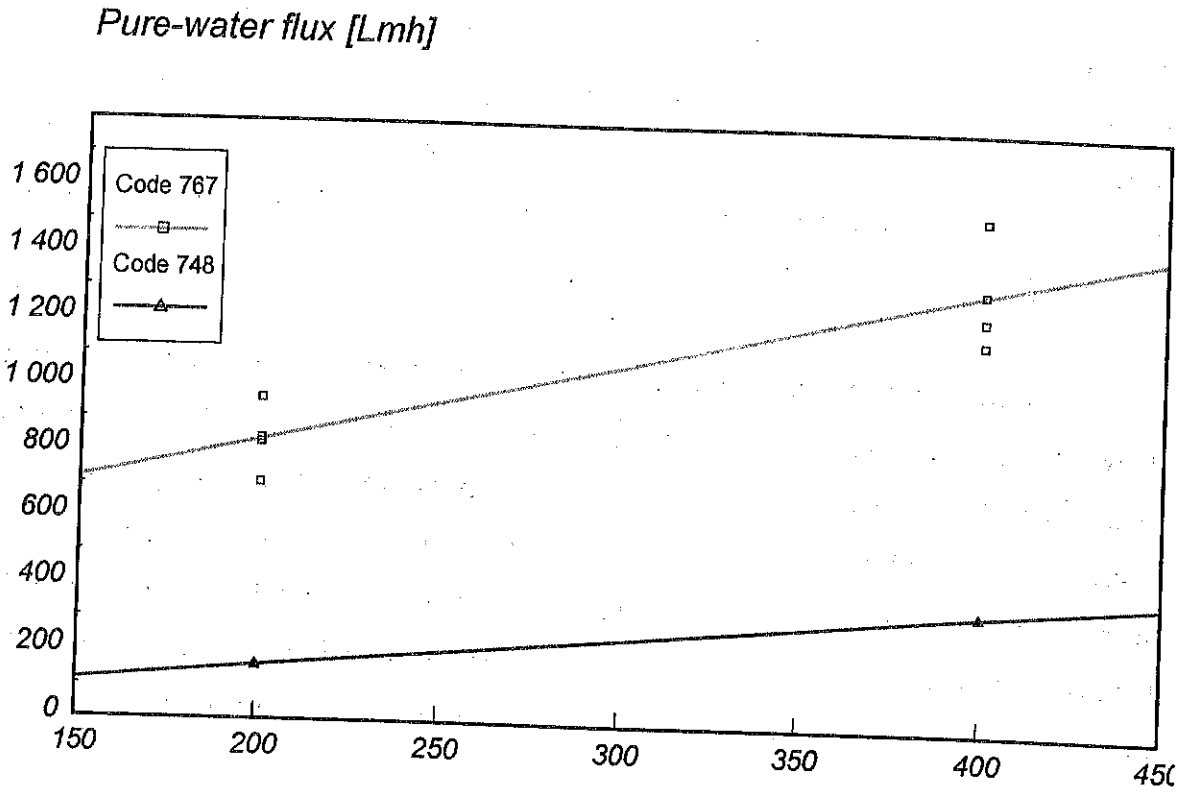


Figure 13: Comparison of the pure-water flux of membrane #748 and #767

2.5.2 Fabrication protocol for a skinless membrane

As a first approach, the membranes were spun into an aqueous external contact bath with an NMP solvent content of 80% (same solvent as that used in the spinning solution). Figure 14 shows a micrograph of the cross-section of membrane PSf-1 (formulation given in Table 5). A large number of the microvoids were dead-ended, that is, not extending the full width of the membrane wall. Figures 2d, 2e, and 2f show micrographs of the cross-sections of membranes PSf-2, PSf-3 and PSf-4 (formulations also given in Table 5). It is evident from these figures that membrane PSf-4 showed some promise for further development as the microvoids present in it were narrow and strikingly regularly spaced. The microvoids of this membrane (Figure 2f) were also fully developed and open-ended, few appearing not to extend the full width of the membrane as was the case with the other membranes shown in Figures 2d, 2e and 14.

Although some of the features of membrane PSf-4 were what was required, the membrane shown in Figure 2f required still further modification. It appeared from the figure that the cavity walls of this membrane were skinned and not microporous. The casting solution had therefore to be modified further to promote greater porosity as this was thought to be necessary for the membrane to be effective as a bioreactor. The formulation was adjusted by decreasing the polysulphone concentration and increasing the PEG600 concentration. This formulation (PSf-5), which was subsequently used in all further experiments, is given in Table 6.

It proved difficult to prevent the formation of a skin layer on the outside of the membrane, and an external skin layer is clearly visible on the micrograph in Figure 14, even though the solvent content of the external coagulant was high and therefore had little precipitation potential. However, not all membranes coagulated in the 20% aqueous NMP-solution had well-defined external skin layers, as regularly spaced cavities were prominent in most of the membranes (Figure 15).

If earlier assumptions regarding skin-formation were correct, the aqueous content of the external coagulant had to be reduced considerably, to below the 20% level, to prevent gelation, nucleation or phase-separation by any of the mechanisms. However, the lower-limit aqueous content of the external bath was that point at which the coagulant actually started to redissolve the nascent membrane. To determine this point, 50g of membrane PSf-5 spinning

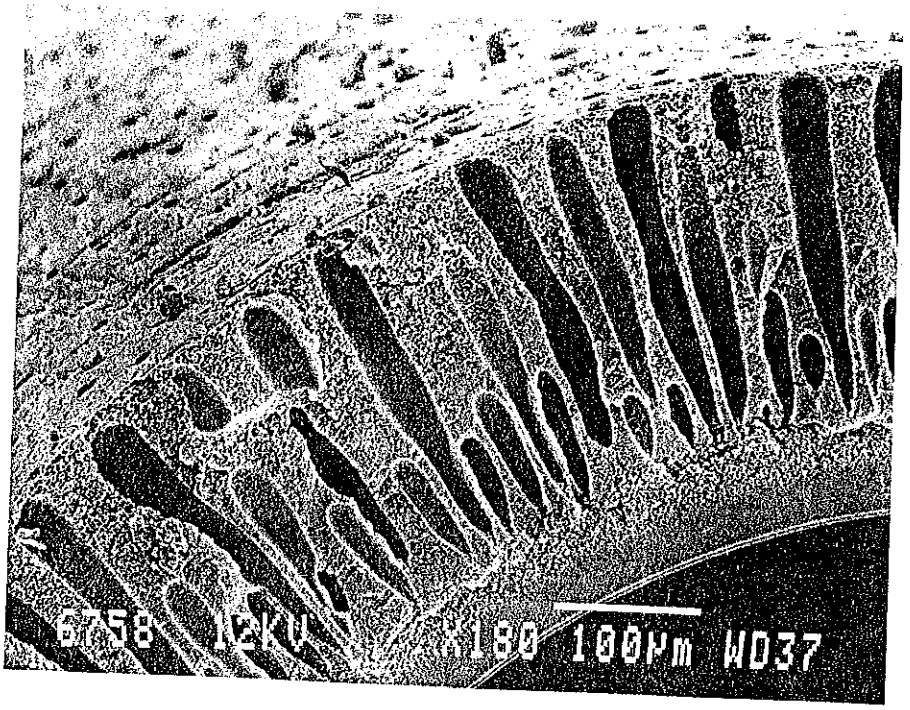


Figure 14: Electron micrograph of the cross-section of membrane PSf-1

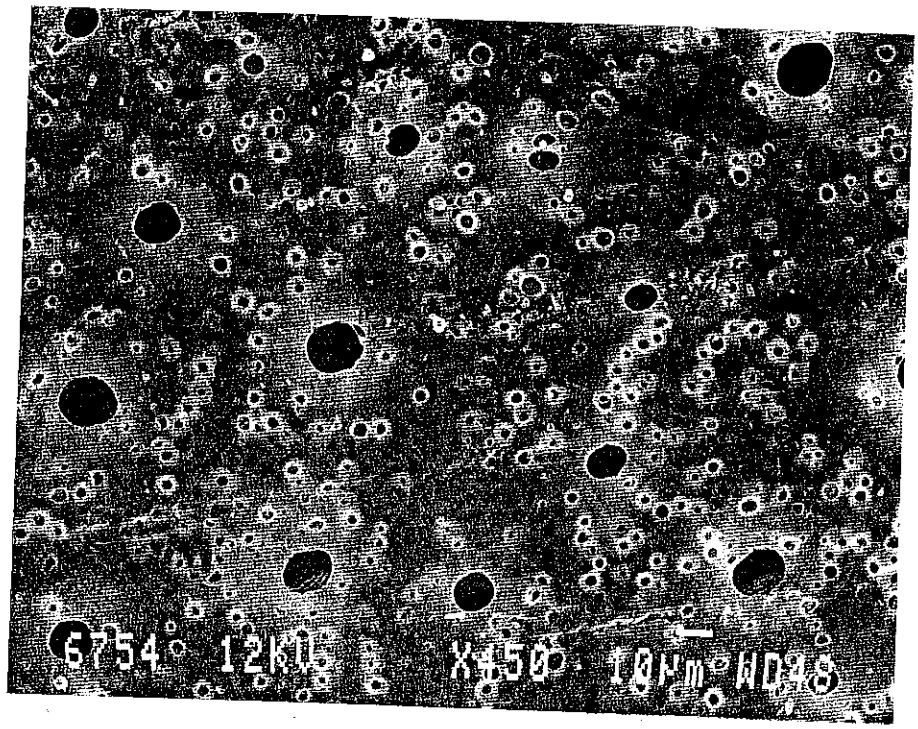


Figure 15: External skin-surface of polysulphone membrane coagulated in a 20% aqueous solvent coagulant

solution (Table 6) were shaken up with an equal amount of aqueous solvent mixture at 22°C. The casting solution dissolved without any sign of cloudiness in aqueous mixtures containing up to 8% water, although dissolution of the casting solution became progressively slower at higher water contents. The first sign of cloudiness appeared at water concentration levels of 9% and greater. It was therefore reasoned that a water concentration level of 9% should be regarded as the upper aqueous limit for the external precoagulation bath.

The next step in the development of the bioreactor membrane was to spin the polysulphone membranes into external coagulants that contained less water than the proposed 9% upper limit. Table 7 shows the water content of three of the solvent coagulation baths that were used. The compositions of the three respective coagulation baths had pronounced effects on the exterior morphology of the membrane. Figures 16, 17 and 18, respectively, show the external surface textures of these membranes, and give a clear indication of the pronounced effect of increasing the water content. In external coagulants with low aqueous contents the outer regions of the membrane seemed to redissolve (and smudge) to form a secondary skin layer of low definition (Figures 16 and 17). At higher water concentrations gelation again occurred and skin morphologies similar to that shown in Figure 15 again become prominent.

Figure 19 shows the extraordinary cross-section of membrane PSf-5, cast into a 7,9% aqueous NMP coagulation bath. The ultrafiltration membrane had a well-defined internal skin layer and the open-ended narrow-bore microvoids which radiated from the internal skin layer were strikingly regularly spaced. It was clear from the micrograph that coagulation was initiated from the lumen side. Formation of solvent-rich nuclei below the skin layer was possibly enhanced by the controlled slight tension under which the membrane was drawn away from the spinneret. Shrinkage (outside diameter of the spinneret was 2,1mm, whereas the final membrane diameter was 1,8mm) may have played a role in sustaining exchange of non-solvent and growth of the finger-like cavities across the full width of the membrane. The composition of the external contact bath lay just outside the demixing gap on the solvent/non-solvent axis of the ternary phase diagram, and did not affect the state of the nascent membrane with which it was in contact. Surface tension within the polymer-rich phase maintained the structural integrity of the soft viscous coagulated polymer-rich phase which was finally set when brought into contact with the non-solvent vapour in the high humidity chamber.

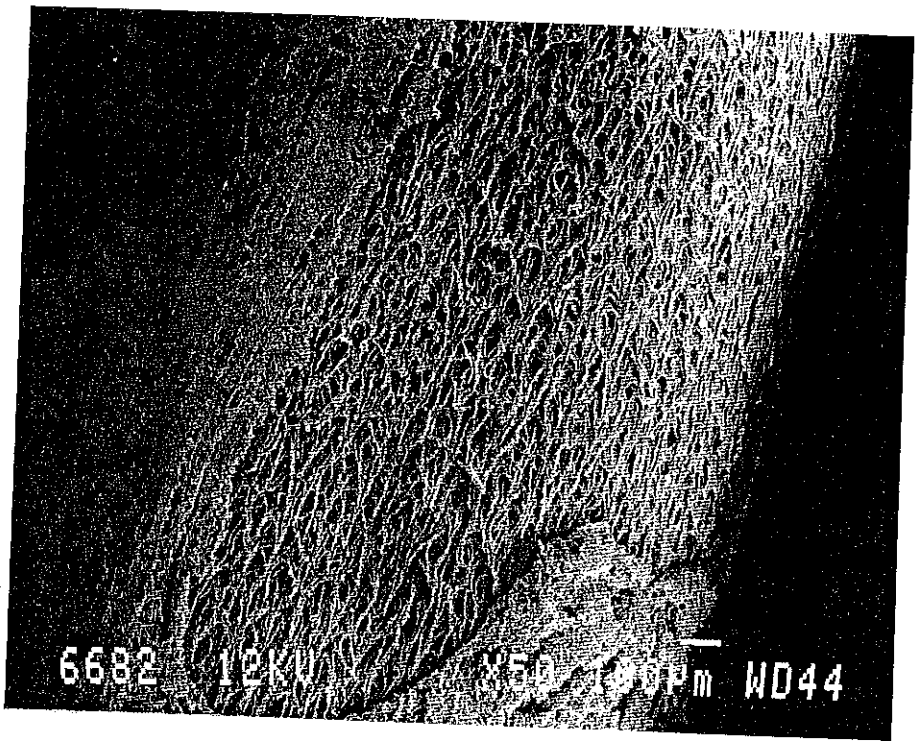


Figure 16: External surface of membrane PSf-5/1 cast into an 4,3% aqueous solvent coagulant

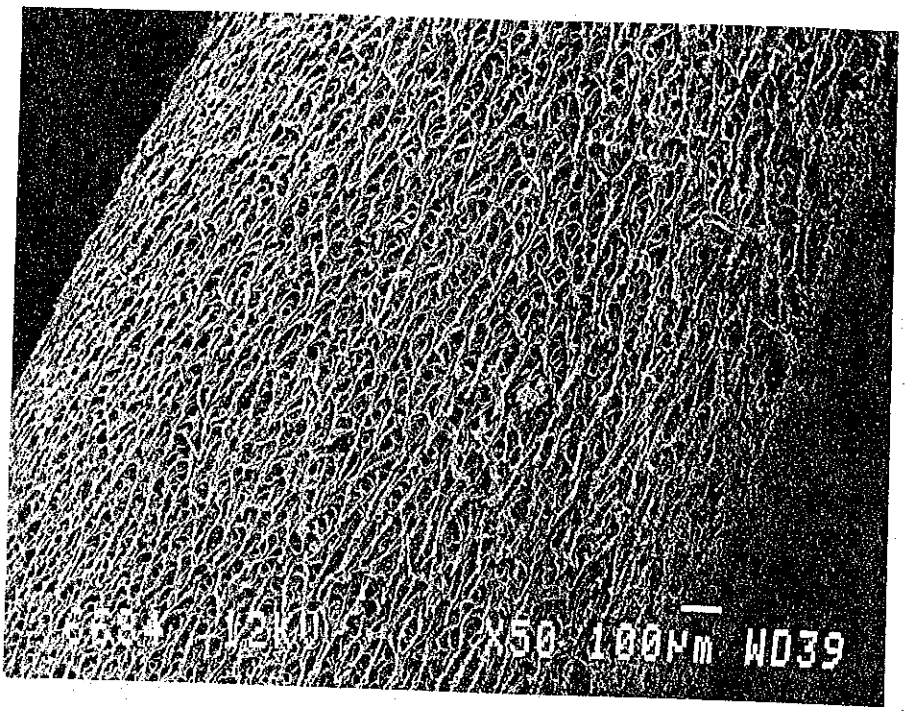


Figure 17: External surface of membrane PSf-5/2 cast into an 6,1% aqueous solvent coagulant

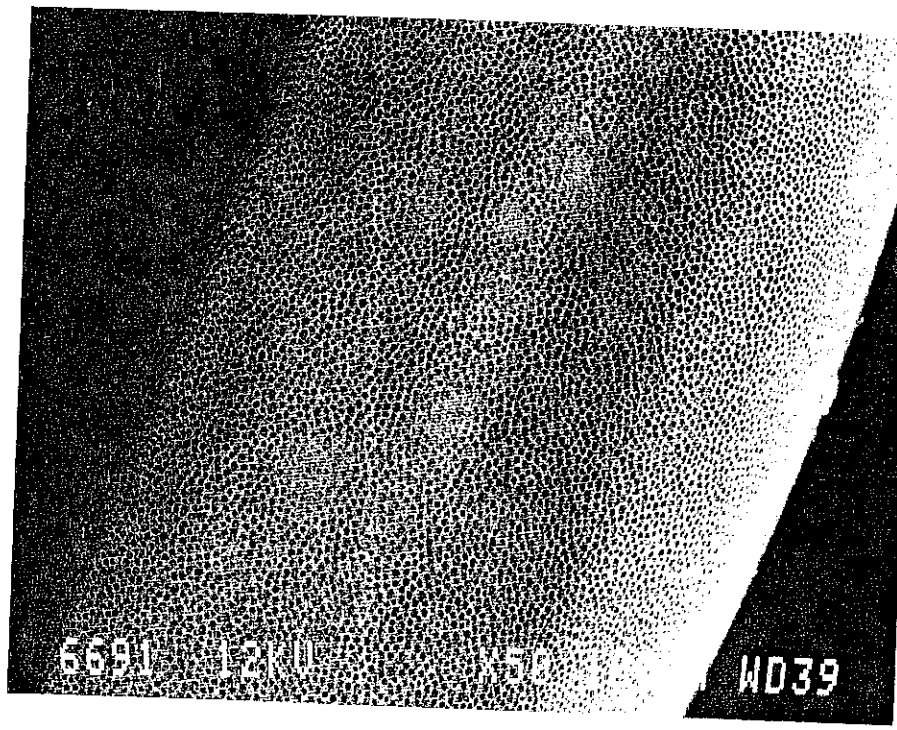


Figure 18: External surface of membrane PSf-5/3 cast into an 7,9% aqueous solvent coagulant

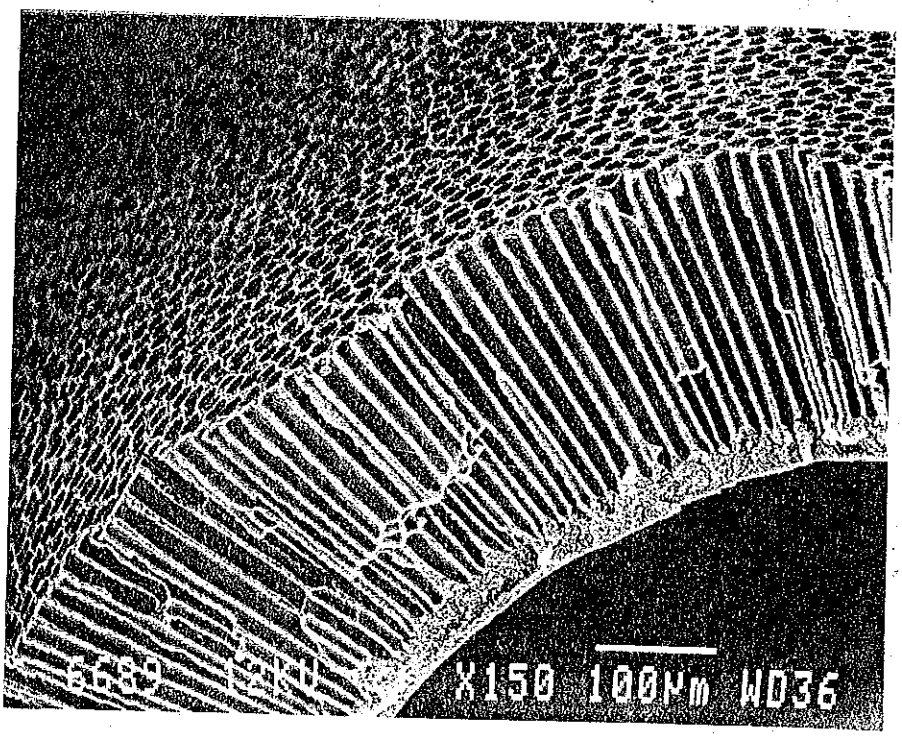


Figure 19: Cross-section of membrane PSf-5/3 showing the thin inner skin layer, porous microvoid substructure and skinless exterior

Figure 20 also depicts membrane PSf-5 and the striking uniformity of the microcells which, according to Figure 21, had highly porous walls. The average diameter of the microvoids was 20μm (Figure 22). From the micrographs, the cross-sectional diameter of the membrane was calculated to be 1,8mm and the diameter of a microvoid opening to be 25μm (i.e. including one wall thickness). On the basis of these figures, it was estimated that there were more than $9x10^6$ microvoids per metre-length of membrane.

Table 5: Spinning solution formulations designed to produce membranes with finger-like microvoids in substructure

Component	Membrane code			
	PSf-1	PSf-2	PSf-3	PSf-4
	Mass percent			
Polysulphone - *Ultrason S*	26	24	24	24
N, methyl, 2-pyrrolidone	51	46	56	36
Methyl cellusolve	2	10	10	10
Polyethylene glycol 600	11	10		30
Polyvinyl pyrrolidone K40	10	10	10	

Table 6: Modified spinning solution formulations to enhance porosity

Component	Membrane code	
	PSf-5	PES-1
	Mass percent	
Polysulphone - *Ultrason S*	22	
Poly(ether sulphone) - *Ultrason E*		22
N, methyl, 2-pyrrolidone	36	36
Methyl cellusolve	10	10
Polyethylene glycol	32	32

It is commonly observed that the presence of microvoids in the substructure of membranes does not always benefit the mechanical integrity of the membrane [10]. In the present case it was important to reduce the thickness of the internal skin layer to stimulate microvoid formation [11] and maximize the void length. Because of the resulting thinner skin-support layer, the membrane resistance, and hence the hydrostatic driving force requirements of the membrane, were also reduced. The membranes were nonetheless reasonably robust with instantaneous burst-pressures ranging from 2,3MPa for membrane PSf-1 to 1,8MPa for membrane PSf-5.

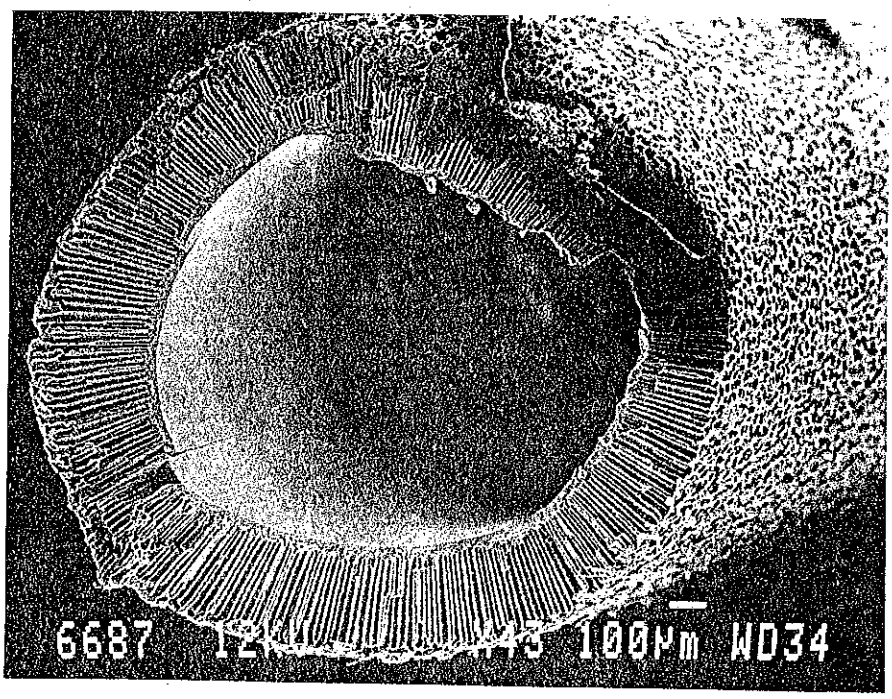


Figure 20: Striking regular spacing of the finger-like microvoids in membrane PSf-5/3

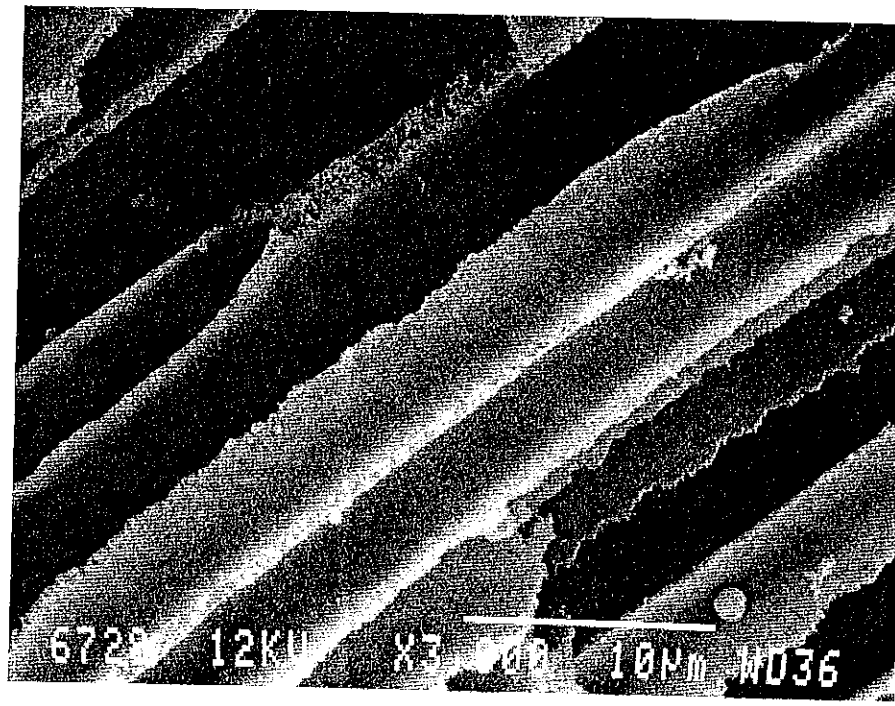


Figure 21: Close-up of the microvoids in membrane PSf-5/3, revealing the microporous morphology of the microvoid walls

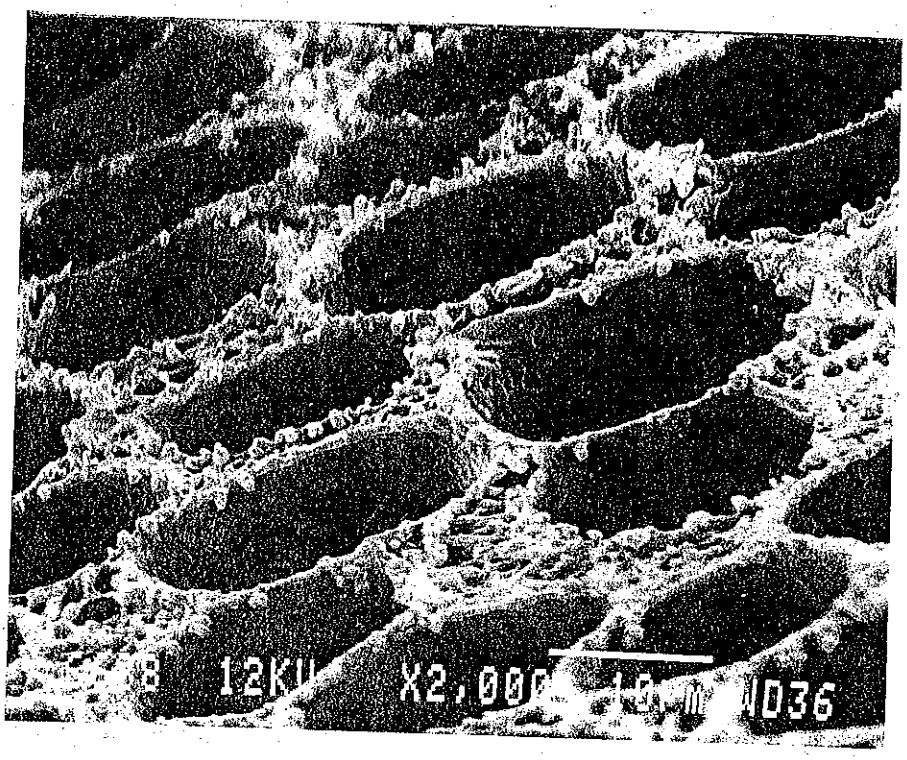


Figure 22: Close-up o the exterior surface of the bioreactor membrane

Membranes were prepared from poly(ether sulphone) by the same method, although with slight modifications to the fabrication protocol (an aqueous contact bath of higher water content was used). A cross-section of membrane PES-1 is shown in Figure 23. The micrograph shows that the morphology of the microvoids of the poly(ether sulphone) membrane was different from those of the polysulphone membranes. As the spinning solution formulations and fabrication protocol were, except for the composition of the external coagulation bath (12vv% aqueous content), identical for both membranes. The difference in morphologies could possibly be ascribed to the differences in coagulation pathways, hydrophilicity and in glass-transition temperature of the two polymer systems. However, initial results also indicated that many of the micovoids in the poly(ether sulphone) membrane were dead-ended, and therefore not nearly as regularly shaped as those of membrane PSf-5.

Table 7: Water content of aqueous NMP (solvent) external contact baths

Membrane code	Water content
	Mass percent
PSf-5/1	4.3
PSf-5/2	6.1
PSf-5/3	7.9

One very interesting aspect of membrane formulation PSf-5 was that when the internal and external coagulants were reversed, that is, pure-water was used as the external coagulation medium and a 5% aqueous NMP solution was used as the bore-side coagulant, a membrane with a finely porous substructure was produced. Figure 24 shows a cross-section of this membrane. The membrane had a very thin skin layer integrated with a perfectly asymmetric porous substructure, completely without any finger-like microvoids. The same structure was obtained when the membrane was cast on a spun-bonded fabric in either flat-sheet or tubular form. This phenomenon could support the theory that nucleation of the polymer-poor phase and microvoid formation are induced by the slight tension under which the membrane is drawn away from the spinneret and also internal stress caused by two-dimensional membrane shrinkage. Also, it was much more difficult to maintain a uniformly open outside structure when the membrane was cast vertically upwards from an immersed spinneret, than when the membrane is cast downwards into the precoagulation tank.

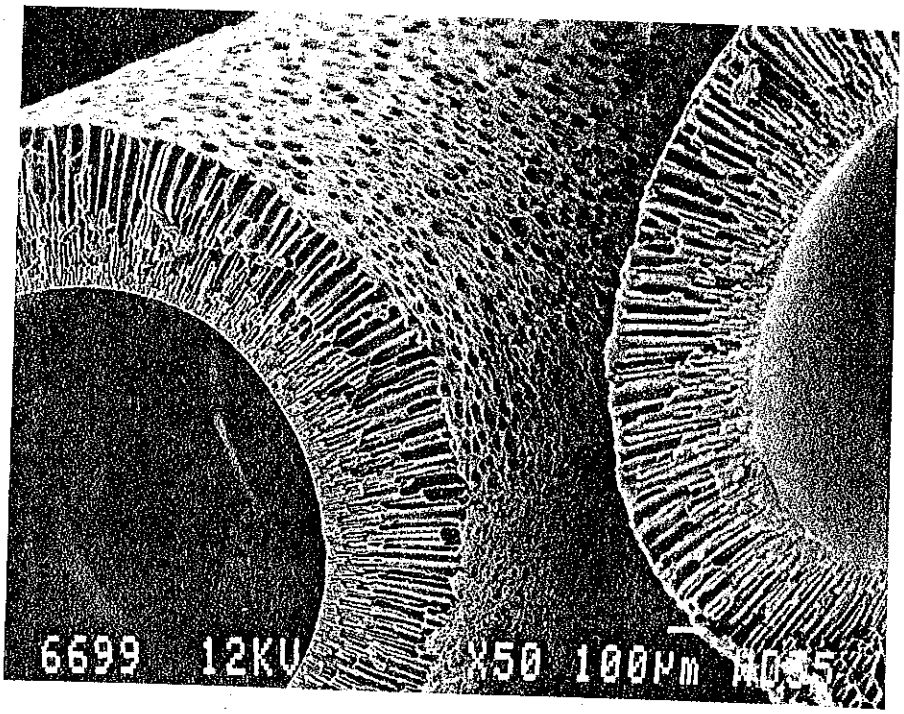


Figure 23: Cross-section of poly(ether sulphone) membrane PES-1

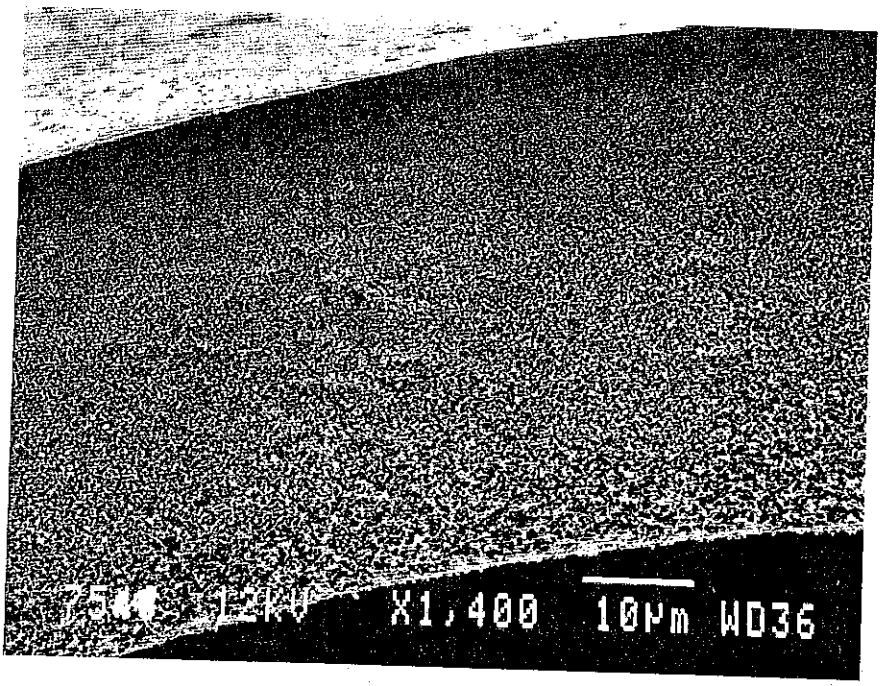


Figure 24: Cross-section of membrane with coagulation medium switched around

3.0 CONCLUSIONS

- It has been shown that an internally skinned membrane with narrow-bore microvoids extending the full width of the membrane and with no external skin layer can be produced from polysulphone and poly(ether sulphone).
- There is a very narrow region within the experimental factor space over which the skinless membranes can be made successfully.
- The membranes have good mechanical strength and unique morphological properties, which make them useful as low-pressure ultrafiltration membranes for use in water filtration for potable use and in biotechnological applications.
- The membranes were successfully incorporated into axial flow tube-in-shell-type modules.
- The membranes and modules were extensively and successfully tested in field trials as part of other research programmes where the use of these filters was investigated for water treatment for potable use.
- The membranes proved useful for the immobilisation of whole cells (fungi) and enzymes, and have been extensively used in novel biotechnological approaches in waste water remediation.

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APPENDIX A

Publications

- Performance of a hollow-fibre bioreactor using immobilised polyphenol oxidase for the removal of phenols from wastewater, W Edwards, R Bowes, WD Leukes, SG Burton, EP Jacobs, R Sanderson and PD Rose, submitted to Biotechnology and Bioengineering (1996).
- Formation of an externally unskinned polysulphone capillary membrane, EP Jacobs and WD Leukes, Accepted for publication, Journal of Membrane Science (1996).
- Ultrafiltration in potable water production, EP Jacobs, JP Botes, S Bradshaw & H Saayman, Water SA 23,1(1997)1-6.

Patents

- *Method of producing secondary metabolites*, WD Leukes, EP Jacobs, PD Rose, SG Burton & RD Sanderson, Assignee: Water Research Commission, SA Patent, 95/7366, 1 September 1995, European patent application 96306333.4.
- *Method of making hollow fibre membrane*, EP Jacobs & RD Sanderson, Assignee: Water Research Commission, SA Patent, 95/4846, 6 June 1996, USA patent application 08/659,744
- *Capillary membrane module encapsulation method*, SE Domröse, EP Jacobs & RD Sanderson, Assignee Water Research Commission, SA Patent 94/9427, 28 November 1994.

Oral presentation of research results

- Membranes and membrane reactors in biotransformation processes, EP Jacobs, PD Rose, WD Leukes, S Burton, W Edwards, HM Saayman & RD Sanderson, BiotechSA '97/14th Biochem, 19-24 January 1997.
- An investigation of the effects of polymerisation conditions of PAN on the properties of hollow fibre carbon membranes by means of statistically designed experiments, Macromolecule Society of South Africa, November 1996, Stellenbosch.
- New low-pressure ultrafiltration membranes in aqueous applications, EP Jacobs, VL Pillay, S Bradshaw and JP Botes, International Membrane Science & Technology Conference (IMSTEC'96), 12-14 November 1996, University of New South Wales, Sydney, Australia.
- Membrane options in food production, EP Jacobs & HA de Villiers, One-day Seminar of the Tunnel Growers Association, 8 November 1996, Welgevallen, Stellenbosch
- Ultrafiltration. A viable option for the removal of colour from South Cape Waters? EP Jacobs, HA de Villiers, P Swart & A Maartens, Seminar/Workshop on Treatment of coloured water for potable use, 21-23 Oktober 1996, Mosselbay.
- Ultrafiltration in potable water production, EP Jacobs, VL Pillay & HA de Villiers, 2nd African Water Conference, Membrane processes, 3-5 September 1996, Gallagher Estate, Johannesburg.
- Membrane morphology, EP Jacobs & D Bessarabov, Envig one-day seminar on Membranes in industrial applications, 30 August 1996, Debex, Johannesburg.

- Membrane filtration in potable water production, EP Jacobs, JP Botes, S Bradshaw and HM Saayman, , ICOM96, 18-23 August 1996, Yokohama, Japan.
- Crossflow ultrafiltration: A single-step approach to small and medium-scale rural watercare, EP Jacobs, JP Botes, HM Saayman, SM Bradshaw, Water Institute of Southern Africa, Biennial conference, 20-23 May 1996, Feather Market Centre, Port Elizabeth.
- Continuous production of lignin peroxidase by *Phanerochaete chrysosporium* in a capillary membrane bioreactor for the degradation of aromatic pollutants, WD Leukes, EP Jacobs, SG Burton, W Edwards, R Sanderson & PD Rose, Water Institute of Southern Africa, Biennial conference, 20-23 May 1996, Feather Market Centre, Port Elizabeth.
- Biotechnological application of membranes, PD Rose, EP Jacobs, SG Burton, WD Leukes, W Edwards, RD Sanderson, 33rd Convention of the SA Chemical Institute, 26-28 February 1996, UCT, Cape Town.
- Novel capillary membranes for wastewater bioremediation or potable water production, EP Jacobs, JP Botes, SG Burton, WD Leukes, W Edwards and HM Saayman, XIV National Symposium, Membranes in Chemical and Biochemical Industries, 16-17 February 1996, Indian Institute of Technology, Delhi, India.
- Biofilm dynamics of *Phanerochaete Chrysosporium* in a hollow fibre bioreactor for sustained continuous production of lignin peroxidase, W Leukes, S Burton, EP Jacobs, R Sanderson and P Rose, Biotechnology for Africa '95, 13-15 November 1995, University of Pretoria, Pretoria.
- Treatment of phenolic and cresylic industrial effluent using hollow-fibre membrane immobilized polyphenol oxidase, W Edwards, R Bownes, WD Leukes, SG Burton, EP Jacobs, RD Sanderson and P Rose, Biotechnology for Africa '95, University of Pretoria, Pretoria.
- A critical investigation into the use of *Phanerochaete Chrysosporium* in hollow-fibre bioreactor for the degradation of cresol, WD Leukes, SG Burton, W Edwards, EP Jacobs, RD Sanderson, PD Rose, Joint ASM/SGM Meeting in Bioremediation, 10-13 September 1995, University of Aberdeen, Scotland, UK.
- Dephenolisation of a synthetic industrial wastewater using hollow-fibre immobilised phenol oxidase, W Edwards, WD Leukes, SG Burton, EP Jacobs, RD Sanderson, PD Rose, Joint ASM/SGM Meeting in Bioremediation, 10-13 September 1995, University of Aberdeen, Scotland, UK.
- Recent advances in membranes for potable water provision in unserviced or underprivileged areas, RD Sanderson and EP Jacobs, 35th IUPAC Congress, 14-19 August 1995, Istanbul, Turkey
- Overview of recent advances in the supply of potable water by membrane processes, RD Sanderson and EP Jacobs, 6th International Chemistry Conference in Africa, Accra, Ghana, 31 July - 4 August 1995.
- The use of membranes in the food industry, RD Sanderson and EP Jacobs, 9th Annual Food Science Symposium, Engineering and Marketing for food in the future, 15-16 May 1995, Somerset West, RSA.

Poster presentation of results

- **BiotechSA '97/14th Biochem, 19-24 January 1997**
  Application of membrane bioreactors for the biotransformation of organic pollutants in water, A Boshoff, W Edwards, W Leukes, EP Jacobs, SG Burton& PD Rose.
  Chitosan-coated hollow-fibre membranes for phenolic effluent bioremediation, W Edwards, WD Leukes, EP Jacobs, RD Sanderson, SG Burton & PD Rose.
  Differentiation within a biofilm of *Trametes versicolor* immobilised on capillary membranes in transverse flow modules, DR Ryan, WD Leukes, W Edwards, EP Jacobs, PD Rose and SG Burton.
  Biofilm dynamics of *Phanerochaete chrysosporium* in a membrane gradostat reactor, WD Leukes, EP Jacobs, RD Sanderson, SG Burton & PD Rose.
  Evaluation of the use of membrane gradostat reactor for the degradation of certain aromatic pollutants, WD Leukes, EP Jacobs, RD Sanderson, SG Burton & PD Rose.
- **ICOM96, 18-23 August 1996, Yokohama, Japan**
  Continuous treatment of phenol-polluted waters in a novel capillary membrane bioreactor, W Edwards, A Boshoff, WD Leukes, EP Jacobs, RD Sanderson, H Saayman, SG Burton & PD Rose.

- **2nd African Water Conference, Membrane processes, 3-5 September 1996, Gallagher Estate, Midrand**
  A comparison between two parallel transverse-flow membrane bioreactor modules in terms of bioremediation efficiency using immobilised polyphenol oxidase, W Edwards, A Boshoff, WD Leukes, SG Burton, EP Jacobs, RD Sanderson & PD Rose
  The application and integration of membrane processes in biotechnology, PD Rose, W Edwards, WD Leukes, EP Jacobs, RD Sanderson & SG Burton.
  A comparison between two parallel transverse-flow membrane bioreactor modules in terms of bioremediation efficiency using immobilized *Tyrosinase*, W Edwards, A Boshoff, WD Leukes, EP Jacobs, RD Sanderson, SG Burton and PD Rose.
  Preparation of novel composite zeolite membranes, SPJ Smith, EP Jacobs and RD Sanderson.

- **Water Institute of Southern Africa, Biennial conference, 20-23 May 1996, Feather Market Centre, Port Elizabeth**
  Dephenolisation of wastewater using immobilised polyphenol oxidase in a hollow-fibre membrane transverse flow biological contactor, W Edwards, WD Leukes, SG Burton, EP Jacobs, RD Sanderson & PD Rose.
  Capillary membrane module design and manufacture, SE Domrose, EP Jacobs and RD Sanderson

- **Society for general microbiology, 1st joint meeting with the American Society for Microbiology on Bioremediation, September 1995, Aberdeen, Scotland**
  A critical investigation into the use of *Phanerochaete chrysosporium* in a hollow fibre bioreactor for the degradation of cresol, WD Leukes, W Edwards, SG Burton, EP Jacobs & PD Rose.

- **International Water Supply Association Conference, 11-13 September 1995, Durban, RSA**
  Ultrafiltration in potable water production, EP Jacobs, JP Botes, RD Sanderson, SE Domrose, HM Saayman and W Edwards.

- **Biotrans '95, 5-8 September 1995, University of Warwick, Coventry, UK**
  The effects of immobilization on polyphenol oxidase in a hollow fibre bioreactor on its monophenolase activity, SG Burton, W Edwards, WD Leukes, PD Rose, EP Jacobs and RD Sanderson.

- **1st WISA-MTD Workshop/Seminar on the Production, Performance and Practice of Permselective Membranes, 31 October - 2 November 1994, Van Stadens River Mouth, Eastern Cape**
  Hollow-fibre immobilised polyphenol oxidase for the removal of phenols from wastewater, W Edwards, WD Leukes, SG Burton, EP Jacobs, RD Sanderson & PD Rose.

- **1st International Workshop on catalytic membranes, 26 - 28 September 1994, Lyon - Villeurbanne, France**
  Removal of phenols from wastewater using a soluble and immobilised fungal polyphenol oxidase, W Edwards, W Leukes, R Lalloo, S Burton, EP Jacobs and P Rose.
  Monitoring of hollow-fibre membrane immobilised fungal enzyme production, W Leukes, S_Burton, E Jacobs and P Rose.

- **International African Water Technology Exhibition and Conference, 6 - 9th June 1994, National Exhibition Centre, Johannesburg, RSA**
  Membrane filtration devices, EP Jacobs, SE Domröse, RD Sanderson, DJ Koen and W Booysen.
  Ultrafiltration capillary membrane fabrication - Wet phase-inversion, DJ Koen, EP Jacobs, RD Sanderson and H Saayman.

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