TRANSVERSE-FLOW MODULE FABRICATION DEVELOPMENT

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TRANSVERSE-FLOW MODULE FABRICATION DEVELOPMENT

Final Report

to the Water Research Commission

by

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Executive summary

Introduction

Membranes are incorporated into devices referred to as *modules* to allow them to be engineered into a process. In the case of capillary membranes, there are two conseptually different module designs available. The one design, by far the most commmonly encounted, is the so-called axial flow device. In this design, which resembles a tube-within-tube arrangement, the feed flow is directed either axially along the lumen of the membranes, or axially along the outside of the membrane. Depending on the design of the membrane, filtration may occur either from the inside to the outside, or from the outside to the inside.

In transverse-flow modules, the flow is directed perpendicular to the membrane axis. Figure 1 shows a photograph of a transverse-flow module. The feed flow is directed along the central channel, and the permeate is collected in the four permeate manifolds at the edges of the module. This project involves the development of techniques to produce transverse flow membrane modules and methods to characterise such modules.

The incorporation of membrane technology to complement biological treatment of industrial and municipal effluent is one of the most rapid areas of membrane technology development. RSA once had the edge with their anaerobic digestion ultrafiltration (ADUF) process that was developed in the late 1980s. This project considered the development and characterisation of a special housing for capillary membranes (the transverse-flow bioreactor) for use in laboratory scale experimentation with bioprocessing.

Project aims

The programme had the following objectives:

- The development of transverse-flow membrane bioreactors (MBRs) useful for the small-scale point-source treatment of biodegradable effluents, the production of enzymes for the treatment of non-biodegradable noxious effluents or contaminated soil, or the biotransformation of objectionable species in effluents into useful products.
    - The work will concentrate on the development of MBR fabrication technology that will enable MBRs of different design to be manufactured without incurring expensive retooling costs.
    - The fabrication approach adopted will enable membranes of various diameters and materials of composition to be incorporated into the module.
    - The fabrication approach developed must lend itself for the large-scale production of both laboratory and larger sized modules.
    - The MBR end product must be simple, reliable, low in cost, robust, leak-proof and sterilisable.

Module design

Two conceptually different transverse-flow modules were experimented with. In the one design the fibres were affixed in a urethane matrix. These matrices were referred to as

Figure 1: Photograph of a transverse-flow module with capillary membranes in the background.

membrane discs, and a module is constructed by stacking the discs atop of each other. The discs may be arranged such that all the membranes either uni-directional (in-line or staggered) or cross-wise (in-line or staggered), with the membranes in every alternating disc lining up.

The spin-moulding technique that was developed to produce the discs can accommodate fibres of different diameters. All the membranes used in the modules reported on have outside diameters in the region of 1.8mm. However, membranes with outside diameters of 0.6mm have also been built into discs to test the technique.

In a second embodiment of the transverse-flow module concept, fibre ends were cast into u-PVC tubes. These modules are fully immersed into bioreactors and the membranes are free-floating. The membranes act as a dewatering device under a static pressure driving force or by applying a vacuum to the lumen side of the modules. Narrow bore membranes are specifically suitable for use in bioreactor applications, because if a narrow bore membrane should break, the biomass in the solution will effectively plug the membrane lumen. Figure 2 shows a photograph of one of the research assistants constructing such a module, and Figure 3 shows a bank of these modules in a vessel.

Membranes

Two types of membranes were installed in the membrane reactors. The one membrane is the so-called outer skinless polysulphone capillary membrane that was specifically designed for use in the gradostat reactor. This gradostat reactor concept allows the continuous production of enzymes from filamentous fungi. A micrograph of the membrane is shown in Figure 4.

The transverse-flow modules are very suitable for application in the gradostat reactor, since it is necessary to remove excess biomass from time to time by scouring the membranes with moist air. For that reason, it was necessary to produce membrane discs with different spacing between individual membranes in order for the module not to become clogged with cell debri.

If, however, the membranes are used as a diffuser to supply molecular oxygen to the reactor, our research showed that rates of gas transport accross the membranes are very low. This is because water penetrates the microvoids from the outside. This large body of stationary water causes a very large resistance to mass transport into the bulk flowing fluid. For cases where a biofilm is grown on the membrane outside, it was necessary to adapt the membrane formulation and provide the membrane with a more pronounced skinlayer on the outside. Figure 5 shows the cross-section of the membrane that was developed for bio-film type reactors. The outer skin is very porous and adds little resistance to gas transport. To reduce the tendency of water to penetrate into the membrane and again restrict transport of gas into the flowing bulk, the outside of the membranes were coated with a very thin layer of a polyamide-polyether block copolymer. The results showed that this material had much better coating properties than silicone rubber that was initially used.

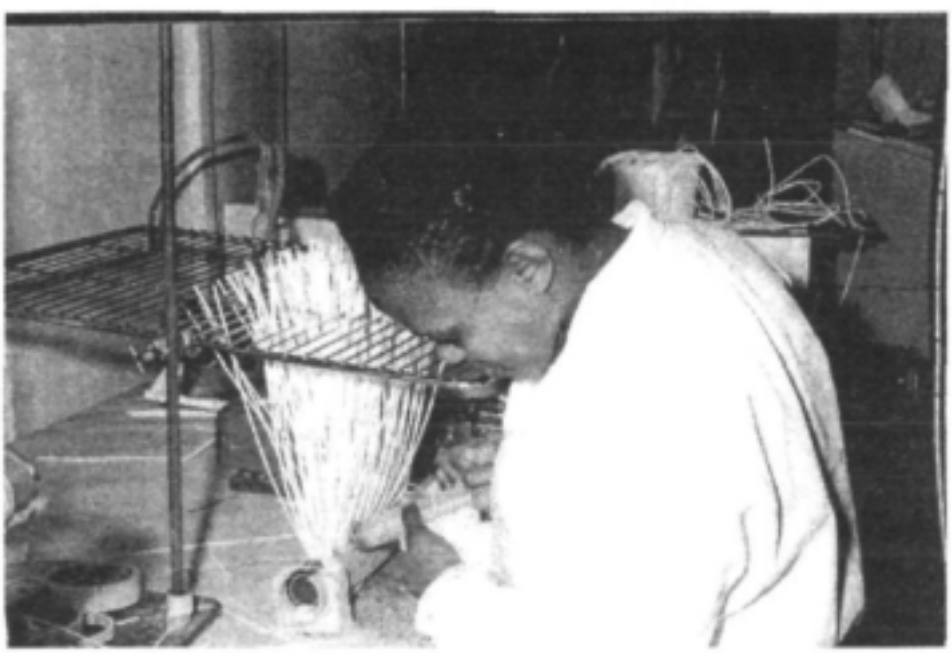

Figure 2: Construction of a curtain-type membrane module.

Module characterisation

The performance of disc-type transverse-flow modules were characterised in gas transport studies. One use of transverse-flow modules in bioreactor applications could be to provide oxygen to the bioreactor in a bubble-less operation and capillary and hollow-fine fibre membranes provide an ideal vechile because of their high surface to volume packing ratios.

Mass transfer correlations were derived for oxygenation and deoxygenation of water, as well as carbonation and carbon dioxide abstraction. These correlations were initially establised for the smaller reactors and later verified for the larger sized reactors. Figure 6 shows a range of membrane discs that were built into reactors during this study.

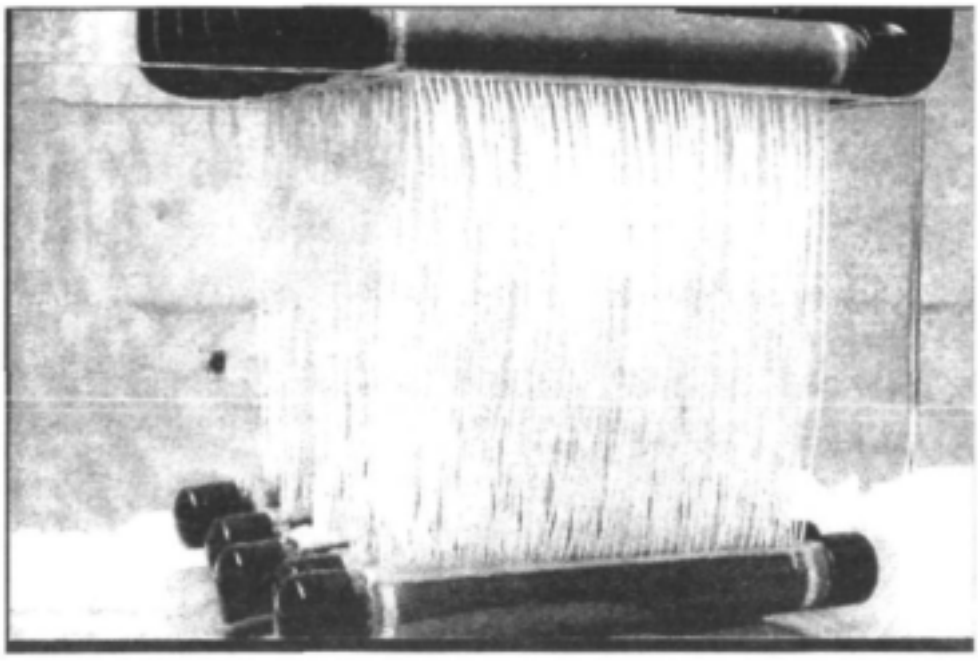

Figure 3: Array of equally spaced capillary membranes immersed in a membrane reactor.

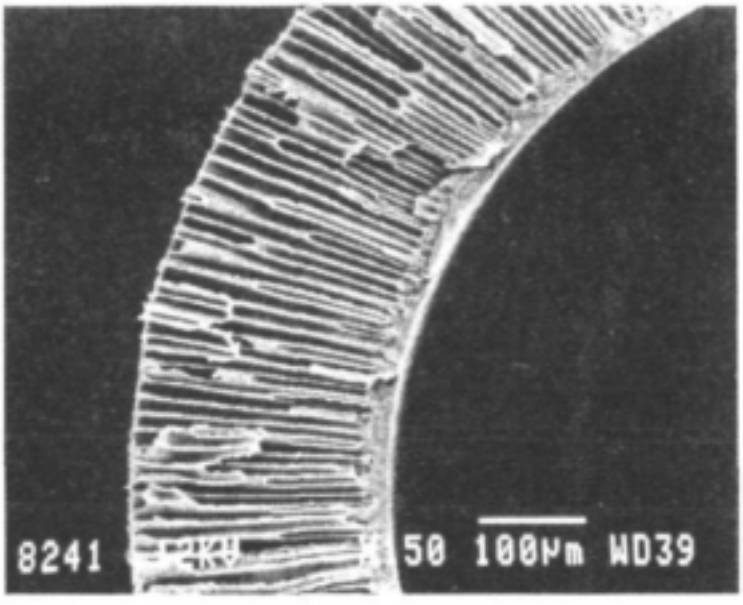

Figure 4: Cross-section of an outer skinless membrane.

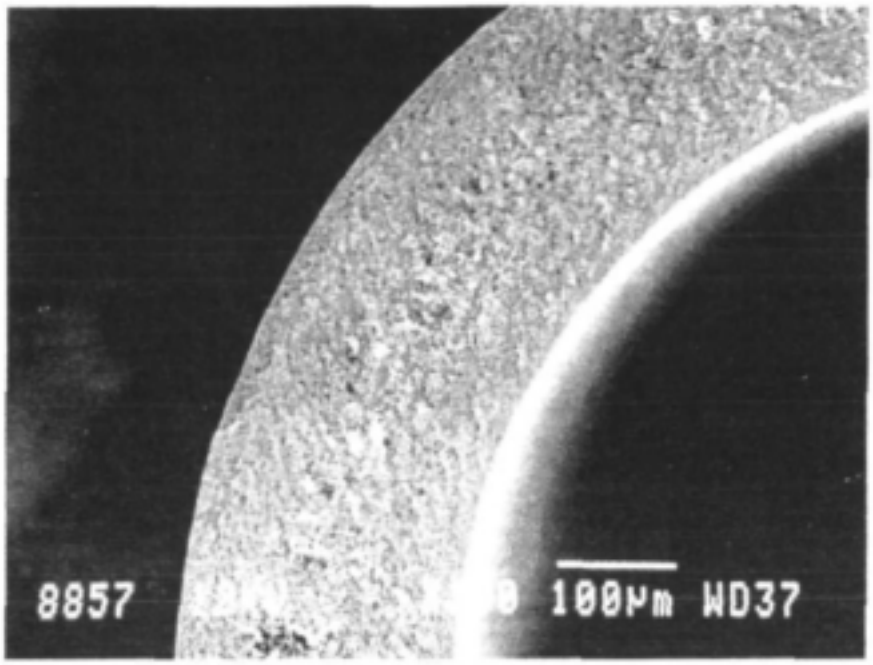

Figure 5: Cross-section of the double-skinned membrane used during oxygenation and carbonation of water.

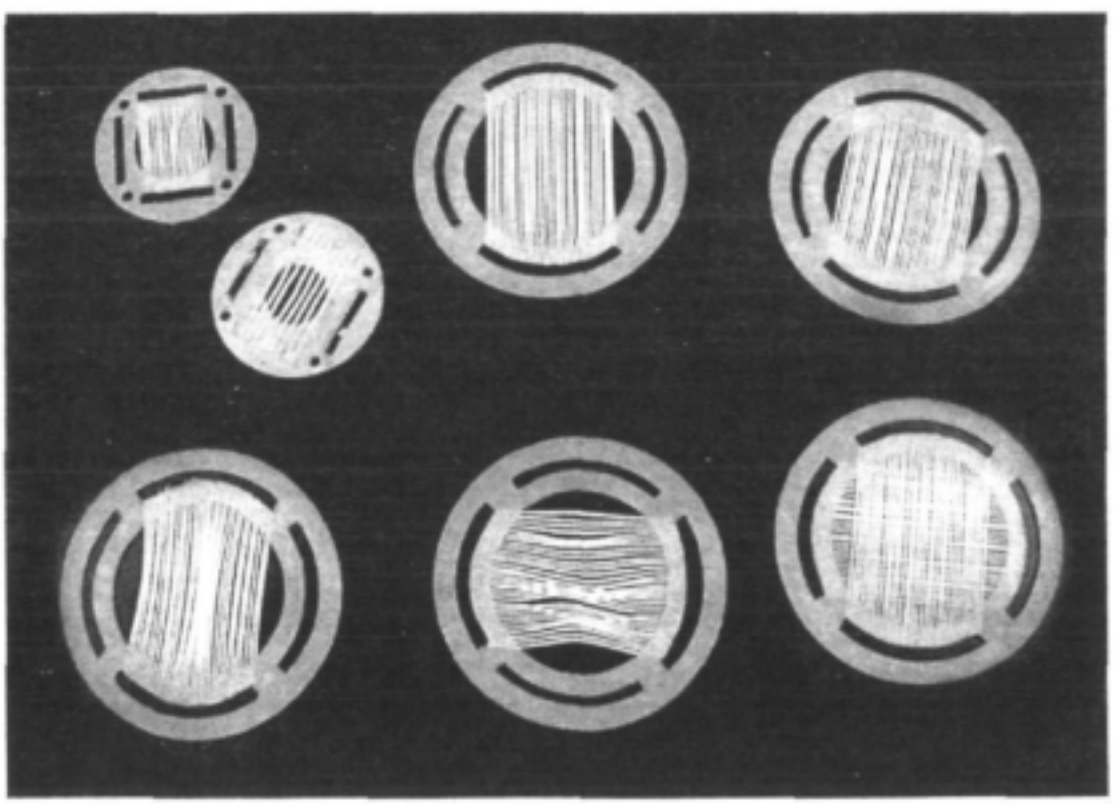

Figure 6: Various transverse-flow membrane wafers used during gas transport studies.

Conclusions

The project managed to develop various experimental membrane contactors for use in bioreactor application studies. Most of the work concentrated on the development of suitable membranes and techniques to improve gas transport into and out of water. A series of mass transport correlations were establised to quantify oxygen transport into and out of water as

well as carbon dioxide transport into and out of water. This work is documented and available to laboratories for use.

The research indicated that scale-up of the disc approach is not without problems and serious reconsideration should be given to materials and wafer design in order to achieve a more robust system for large-scale use. However, for small-scale laboratory work, the systems developed has potential for use in membrane bioreactor application studies.

The method developed to construct transverse flow membrane discs can be used for membranes of different sizes and different materials. The material costs (membranes and sealant) to produce one of the membrane discs shown bottom right in Figure 6 is in the region of R6.90.

Recommendations

Many different types of membrane bioreactors have seen the light over the past few years and have found wide-spread application in the treatment of industrial and domestic wastewater and in bioconversion. Although the technology is reasonably young, strong evidence already exists that these versatile reactors outperform the more conventional aerobic and anaerobic type reactors with respect to the residual chemical oxygen demand and clarity of the final effluent.

This project was an initial attempt to provide a research tool to microbiologists to study potential applications in membrane bioreactor technology. When one considers the development of a new membrane bioreactor process and applications technology, it is clear that engineers cannot proceed without the assistance of microbiologists and *vice versa*. Such research should be approached as a team. However, the development of the system hardware (membranes, reactor configuration, operation and control) has to proceed to a point of semi-finalisation before any serious bioprocessing and the involvement of microbiologists on the process side can be considered. It is recommended that if future considerations are given to the development of membrane bioreactor technology, the work be partisioned into two stages: (a) membrane and systems development and process operation and (b) the development of the biotechnological protocol. The first stage should be conducted by engineers of different disciplines, but under the supervision of microbiologists knowledgeable of wastewater treatment. Stage two should primarily be the responsibility of microbiologists, but should be conducted with close co-operation of the engineering contingent that did the intial development of the system.

The information obtained through this study is directly applicable to immersed membrane bioreactors making use of membranes to supply oxygen in bubbless form to the biofilm immobilised on it. This class of membrane bioreactor are referred to as membrane aeration bioreactors and can be operated in anaerobic or aerobic modes of operation. Such reactors are highly efficient since the concortia of microorganisms that will develop in the reactor (free floating and immobilised in biofilms) is much more diverse that that found in conventional systems.

Technology transfer

The research on the project was principly divided along biotechnology and engineering lines. Engineering involved the development of the membrane reactors, membranes and establishment of mass transport of gases. This work was conducted within the membrane laboratories of the Institute for Polymer Science at the Univesity of Stellenbosch. The

Biotechnology group, Rhodes University, concentrated on the use of the reactors and membranes in bio-applications, in conjunction with the Chemical Engineering Dept of Peninsula Technikon.. Membranes and reactors were furthermore also provided for free to any of the many pre-graduate and post-graduate students working on aspects of membrane bioreactor technology, but who were not officially part of the project. These students were from the Dept of Biochemistry and Microbiology of Rhodes University and from the Chemical Engineering Departments of ML Sultan Technikon, Peninsula Technikon and Cape Technikon.

All the membrane reactors were initially constructed within the Stellenbosch membrane laboratories. However, by teaching students some of the basic principles of membrane reactor constuction, the situation has now developed whereby membranes only are supplied and reactors are now being constructed by those involved with the bioreactor studies themselves. This has lead to the development of some very unique and costom-built reactor designs.

Me Anel van der Walt, who was responsible for the development of the centrifugal fabrication protocol of the membrane wafers, successfully concluded her M-Eng (chemical) studies. Part of her research is summerised in the report. She was also primarily involved with the characterisation of the transverse-flow modules by means of gas transport studies.

Mr T Mokrami, Peninsula Technikon M-Tech student in chemical engineering, also studied gas transport phenomena in axial flow devices. Mr Mokrami was not involved with the project *per se*, but had regular contact with the engineering contingent of the group.

Dissemination of results

Design and characterisation of a transverse-flow membrane module for gas transport operations, A van der Walt, M-Eng (chemical), March 1999, Stellenbosch.

International Association on Water Quality, Cape Town, 8-10 September 1997
Design of membrane contactors for water oxygenation and deoxygenation
A van der Walt, DG Bessarabov, EP Jacobs & C Nel;

2nd WISA-MTD Workshop, Aventura Spa Badplaas, 21-24 October 1997
Characterization: transverse flow membrane contactor for water oxygenation & deoxygenation
A van der Walt, EP Jacobs & C Nel;

The removal of aromatic compounds from solutions by the fungus *Trametes (Coriolus) versicolor* immobilised in a novel membrane bioreactor
DR Ryan, WD Leukes, W Edwards, A Boshoff, I Russel, T Russel, PD Rose & EP Jacobs;

2nd WISA-MTD Workshop, Aventura Spa Badplaas, 21-24 October 1997
Characterization of a transverse flow membrane contactor for water oxygenation and deoxygenation
A van der Walt, EP Jacobs & C Nel;

2nd African Water Conference, Membrane processes, Gallagher Estate, Midrand, 3-5 September 1996
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 & PD Rose.

Acknowledgements

The Steering Committee responsible for this project consisted of the following persons:

The Steering Committee:	Dr G Offringa, Chairman
	Mr R Olivier, Secretary
	Mr G Steenveld, Alternative Chairman
	Prof RD Sanderson, University of Stellenbosch
	Prof PD Rose, University of Rhodes
	Mr G Lok, ESKOM
	Mr B Hendry, Peninsula Technikon
	Dr VL Pillay, ML Sultan Technikon
	Prof TE Cloete, Pretoria University
	Mr C Nel, University of Stellenbosch

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The competent assistance of Mr Doug Peet with spin-mould design and machining thereof is appreciated.

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We are also appreciative of the assistance provided by Sophie Houtman, Deon Koen, Anel van der Walt, Calvin Maart and Wade Edwards.

1 Transverse-flow membrane modules

Membranes are incorporated into devices referred to as *modules* to allow them to be engineered into a process. In the case of capillary membranes, there are two conseptually different module designs available. The one design, by far the most commmonly encounted, is the so-called axial flow device. In this design, which resembles a tube-within-tube arrangement, the feed flow is directed either axially along the lumen of the membranes, or axially along the outside of the membrane. Depending on the design of the membrane, filtration may occur either from the inside to the outside, or from the outside to the inside.

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    - The work will concentrate on the development of MBR fabrication technology that will enable MBRs of different design to be manufactured without incurring expensive retooling costs.

    - The fabrication approach adopted will enable membranes of various diameters and materials of composition to be incorporated in the module.

    - The fabrication approach developed must lend itself for the large-scale production of both laboratory and larger sized modules.

    - The MBR end product must be simple, reliable, low in cost, robust, leak-proof and sterilisable.

With the above in mind, several experimental MBR designs were considered and constructed. These prototype modules were made available to the MBR research groups at Rhodes University (Depts of Biotechnology and Microbiology) for evaluation on different applications. Those results are not reflected in this report, but will be reported on in other WRC research projects. The work reflected in this report are essentially along the objectives indicated above and centres to a large extent on the development and characterisation of a membrane disk suitable for use in a laboratory-sized MBR.

1.1 Introduction

Originally, hollow fibre membranes and modules were developed and used for filtration purposes. However, already in 1960, Schaffer and his co-workers[1] saw the potential of membrane films as gas-liquid contactors, and investigated the absorption of gas into a liquid through a membrane film. Since then, several researchers have investigated the use of flat sheet and hollow fibre membranes as gas-liquid contactors in gas absorption and removal processes in membrane bioreactor systems.

The membrane acts as a fixed interface between the gas and liquid phases and keeps them separated while the transport of gas takes place through the membrane. Bubble-free transfer is achieved when the gas is transported through the membrane and goes directly into solution on the liquid side. Gas transfer takes place because of a driving force, such as a concentration difference, across the membrane.

Previous mass transfer investigations were mostly carried out with hollow fibre modules in axial flow. All cases of transverse flow mentioned refer to a parallel fibre bundle placed transversely to the feed flow direction, that is, the feed flows in a direction perpendicular to the fibre axes (Figure 1.1). This study focuses on a regularly packed transverse flow arrangement, where the fibres are packed equidistantly, and either in a parallel or crossed arrangement (Figure 1.2). This configuration has originally been used in cross flow heat-exchangers and was first introduced in mass transfer operations by Strand.[25,26]

Although some results will be given to show the usefulness of the membrane contactors in bioreactor applications, the modules were essentially characterised by studying gas transport across membranes as examples of mass transfer processes. These processes find application in waste water treatment[11] and in membrane bioreactors.[4,11] (The use of membranes for oxygenation of bioreactors, for example, has the further advantage that CO_2 and CH_4, for example, can be removed simultaneously).

1.2 The use of membranes for mass transfer

In order to create optimum conditions for mass transfer across a membrane and to minimize concentration polarization, the geometry of a successful membrane module should provide proper hydrodynamic flow distribution on both the feed and the permeate sides of the membrane.

Hollow fibre or capillary membranes are generally housed in modules of the tube-within-shell design, where the process stream is normally directed axially along the lumen of the membranes. Another membrane module design, which allows for good hydrodynamic flow distribution, is the regularly packed transverse flow module.

The principle of transverse flow, where the flow is perpendicular to the fibre axis, has for many years been applied successfully in cross-flow heat exchangers. (In membrane technology, however, the term *cross-flow* has a different meaning[27,28], as is illustrated in Figure 1.1, and the term *transverse-flow* is preferred). The application of transverse-flow in hollow fibre membrane modules, in which the membranes are in a regular cross-packed configuration, was first patented by Strand in 1964[25] and 1967[26], and was later also investigated, on a laboratory scale, by other researchers (Futselaar et al.[27,28,37], Knops et al.[38], Wickramasinghe et al.[29], Smart et al.[39], Baudet et al.[40,41], Bayer[42], Côté et al.[43], Glassford[44], Inacio and Nilsson[45], Ter Meulen[46], Nichols et al.[47,48], Saida[49], Stam[50], and Mockros and Leonard[3]). Transverse flow over randomly packed parallel fibre bundles was

investigated by Yang and Cussler,[5,8] Côté et al.,[7] Vaslef et al.,[18] and Lipski and Côté.[23] However, to date, no commercial transverse flow modules are available, and modules for large scale industrial applications are still in the development phase.[51,52]

The regularly cross-packed transverse-flow module is ideal for use in separation processes such as microfiltration, ultrafiltration, reverse osmosis, pervaporation, gas separation and gas-gas/gas-liquid/liquid-liquid extraction processes. Futselaar et al.[27,28] investigated the usefulness and potential of such a module for reverse osmosis, ultrafiltration, microfiltration and dialysis, while Knops et al.[38] studied its use in microfiltration. Côté et al.[43] patented a cross-packed transverse flow module and demonstrated its application to microfiltration, low pressure reverse osmosis, pervaporation and aeration. Gas transfer in these modules was also investigated by Wickramasinghe et al.[29], while Yang and Cussler[5,8], Côté et al.[7] and Vaslef et al.[18] only studied gas transfer in randomly packed fibre bundles placed transversely to the flow. Futselaar et al.[37] and Smart et al.[39] used the regularly cross-packed transverse-flow module for the pervaporation of volatile organic compounds (VOCs), while Lipski and Côté[23] investigated pervaporation with randomly packed fibre bundles in transverse flow.

Transverse-flow modules may also be a superior design for use in membrane bioreactor applications as result of higher mass transfer rates and good flow distribution properties of such module designs. Not much reference could be found in the literature on the use of such

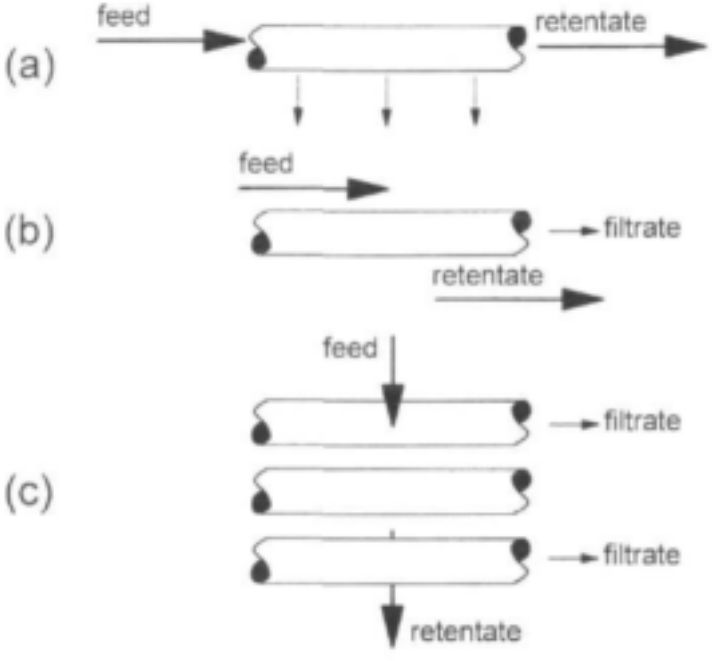

Figure 1.1: Filtration modes showing, (a) axial flow with feed on lumen side, (b) axial flow with feed on membrane outside and outside-in filtration, and (c) transverse-flow with feed on the outside of the membranes

modules in membrane bioreactor applications. Direct measurements of mass and momentum transfer in cross-packed tube banks, resulting in reliable design correlations, have not been reported until recently. Futselaar et al.[27] and Knops et al.[38] used correlations originally derived for heat-exchangers to predict mass transfer and pressure drop in membrane modules. Futselaar[28] and Wickramasinghe et al.[29] derived correlations for mass transfer and pressure drop for cross-packed tube banks in transverse flow.

Hollow fibre membrane contactors have some advantages over conventional mass transfer equipment, such as packed towers and bubble columns for gas treatment and centrifugal extractors, spray towers and mixer-settlers for liquid-liquid extraction.

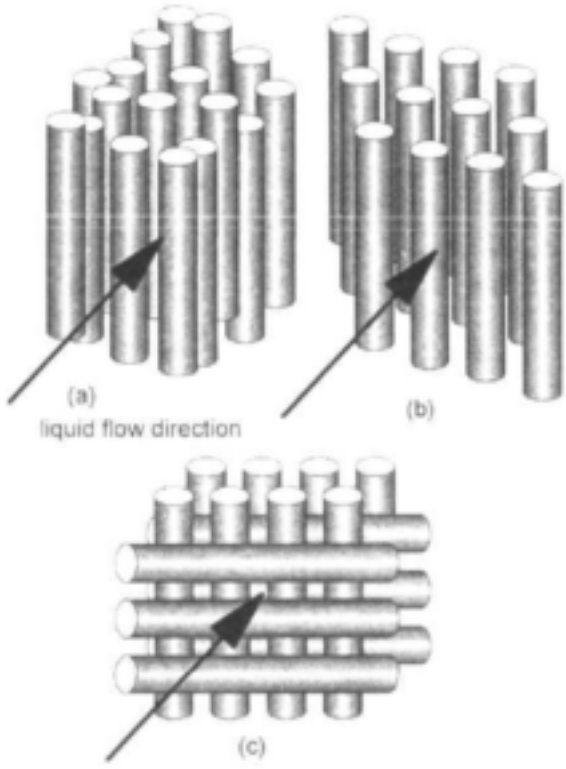

Figure 1.2: Transverse-flow arrangements: (a) parallel bundle of fibres, (b) regularly parallel-packed tube bank, and (c) regularly cross-packed tube bank.

The higher mass transfer efficiency of hollow fiber modules, compared to conventional mass transfer equipment, is mainly due to the module's large ratio of surface area per unit volume, which can be has high as 8 000 m^2/m^3.[53] (In bubble columns, sieve trays and packed towers, the maximum specific contact area between gas and liquid is about 800 m^2/m^3 [54,55]). Hollow fiber contactors thus offer the possibility of increased mass transfer rates in smaller reactor volumes because of high membrane packing densities.[5,29] For example, acid gas treatment with hollow fibres can be done at a rate which is more than ten times higher than that achieved in packed towers[5] and for gas absorption the mass transfer rate per unit volume of equipment is about 30 times higher than in packed towers.[29] When capillary membranes are used, the rate of liquid-liquid extractions can be increased two orders of magnitude over that otherwise achieved in spray towers[5] and up to 600 times higher than in mixer settlers.[29] The rates of liquid-liquid extractions achieved with capillary membranes may be comparable to those resulting from the use of centrifugal extractors, but equipment costs of the former are much lower. Mass transfer coefficients for the removal of VOCs in a membrane system are at least an order of magnitude higher than those obtained in packed towers.[10]

The contact area for water and gas in a hollow fibre membrane module is determined by the membrane area, thus it is constant and independent of gas and water flow rates. Because the membrane separates the gas and water streams, their flow rates may be varied independently, in order to maximize solute removal or minimize the amount of sweep gas used. In the case of gas absorption, when gas is contained in the membrane system, the gas-liquid contact time

is increased and 100% gas transfer can be obtained. Further, since the water and gas streams are not in direct contact with each other, mist elimination is not required.[4,9]

Hollow fibre membrane modules are also not subject to the loading, flooding and channeling phenomena, which often compromise the performance of more conventional equipment.[56] Mass transfer in hollow fibre membrane modules are also is not sensitive to factors that affect the size and residence time of bubbles in conventional aeration systems.[4]

Conventional liquid-liquid extraction involves dispersion of a solution as drops in an immiscible solvent (or *vice versa*), followed by separation and coalescence of the dispersed phase after extraction. Coalescence is often a severe problem, and can be eliminated by using a membrane system.[57]

Hollow fibre membrane contactors can also successfully be used as aerators in bioreactors. Traditionally, oxygenation of bioreactors is achieved by air sparging, coupled to a variable speed impeller. Energy costs are high and damage can be caused to shear-sensitive organisms. Changes in the viscosity of the medium can cause a decrease in oxygen transfer rates, which can only be overcome by enhanced agitation. Further, the addition of defoamers can cause complications during downstream processing. Oxygenation by means of membranes eliminates all these problems and has the further advantage that CO_2 and/or formed biological products can be removed simultaneously.[6] With hollow fibre contactors, the gas pressure is independent of the aeration tank depth, and larger mass transfer driving forces can be created by increasing the applied oxygen partial pressures, even in shallow tanks.[4]

For the removal of VOCs from waste water, membrane pervaporation has advantages over more conventional processes such as air-stripping and carbon adsorption.[23] For carbon adsorption, the rate of removal is dependent on the availability of active sites, while in pervaporation, organic compounds can freely adsorb onto the entire membrane surface on the liquid side and are continuously removed on the vacuum side. Spent carbon must be disposed of or regenerated, while pervaporation does not consume reagents or exhaustible sorbents. Air-stripping is limited to organic compounds with a high Henry's law constant. Iron oxidation and/or carbonate precipitation causes severe fouling in air-stripping columns and reduces the process efficiency drastically. Off-gases cannot be emitted directly into the atmosphere, but must go through an additional treatment step to prevent air pollution. In pervaporation, the organic compounds permeating through the membrane are contained by condensation.

With membranes, gas stripping and absorption steps can be carried out simultaneously in the same apparatus.[21,22]

Apart from all the advantages that membrane contactors have, the membrane itself may in some cases contribute to the total transfer resistance and retard mass transfer. However, if the membrane is carefully chosen, so that membrane resistance is practically negligible, mass transfer can be controlled and accelerated by changing the module configuration.[5]

Because of their high surface area to volume ratio (specific area), hollow fibre (d_i=50 to 500μm) and capillary membranes (d_i=0.5 to 2.5mm) are most suitable for use in mass transfer operations. Hollow fibre and capillary membrane modules have specific areas that range between 1 000 and 10 000 m^2/m^3 and between 600 and 1 200 m^2/m^3, respectively, compared to other module configurations such as tubular (20 to 200 m^2/m^3), plate-and-frame (100 to 400 m^2/m^3), spiral-wound (800 to 1 000 m^2/m^3), pleated cartridge (800 to 1 000 m^2/m^3) and rotating cylinders (10 to 200 m^2/m^3).[27,28]

1.3 Advantages of transverse-flow over axial-flow

Most of the conventional and commercially available capillary and hollow fibre membrane modules are of the axial flow type. Similar to shell-and-tube heat-exchangers, they consist of a bundle of fibres which are potted within a cylindrical shell. In ultrafiltration and microfiltration operations the feed solution usually flows through the fibre lumens, while the permeate (product) is collected outside of the membranes, on the shell side. The feed solution can also flow on the outside of the membranes, and parallel to, the fibre axis, as in pervaporation or gas separation.

Axial flow configurations have some disadvantages in water filtration applications. These will be briefly discussed:

- Maximization of the membrane surface area, for optimum transfer performance, can be achieved by using long fibres with small diameters. However, long fibres are susceptible to damage, and the longer the fibres, the greater the susceptibility.[43] Large pressure drops may also occur in the lumens of long fibres.[28]
- The small diameters and the long lengths of the capillary membranes prevent them from being installed into a regular configuration in axial flow modules, a type of arrangement which is needed to provide a well-defined flow distribution on the shell side of the module.[28] Channeling in the shell-side feed, due to uneven distribution of the fibres, will result in poorer performance of the module than would be the case if the feed flowed evenly over the surface of each fibre in the bundle.[43]
- Although the diameters of the capillaries should, on the one hand, be small enough to ensure high packing density, it should, on the other hand, be large enough not to cause unacceptable high pressure drops in the membrane lumens.[28]
- High packing densities (for maximum transfer area) also cause high pressure drops across the module when the feed flow is on the shell side.[43]
- The maintenance of an effective driving force across the membrane wall, such as a concentration or pressure differential, requires high pressures and feed flow velocities. Membranes may burst easily, if over-pressurized from the lumen side.[28,43]
- For shell side feed, the flow chooses the path of least resistance, which is through the largest void volumes. Liquid also tends to collect in these void volumes from which flow is impeded, forming stagnant volumes, and causing concentration polarization.[43]
- Concentration polarization, deposition of retained material on the membrane surface, and clogging of the membranes result in a decrease in permeate yield.[28]
- With lumen flow it is not possible to increase the rate of mass transfer by means of conventional turbulence promoters, such as fluidizing particles (used in tubular modules), static mixing elements (used in tubular modules), spacers (used in spiral-wound and plate-and-frame modules), or corrugated membranes.[27,28]
- The problem of low mass transfer rates can be overcome by disrupting the boundary layer by increasing turbulence at the membrane surface. One way of doing this is to use higher linear feed flow velocities, which can lead to unacceptably high energy costs.

A considerable enhancement in mass transfer rate can, however, be obtained by changing the module design in such a way that the fibres are positioned perpendicular to the feed flow direction, that is in a transverse flow arrangement. This arrangement results in turbulence promotion by the fibres themselves, thus improving the mass transfer rates.[27,28] The development of a stable boundary layer or an uninterrupted deposit layer consisting of retained material, can be prevented by continuous interruptions of the boundary layer on the membrane surface. The overall result is a higher mass transfer coefficient on the feed side.[28,37]

Other advantages of the transverse flow arrangement include:

- the regular arrangement of the fibres prevents maldistribution of flow over the cross-section of the module on the shell side of the capillary or hollow fibre membranes;[28,37]
- the improved flow distribution and absence of channeling ensures the optimal use of all the installed membrane area;[28,37] and
- high packing densities are achieved.[28]

1.4 Analogy between heat transfer in cross-flow heat-exchangers and mass transfer in transverse flow membrane contactors

The principle of transverse flow, the flow being perpendicular to the fibre axis, has for many years been used successfully in the design of cross-flow heat-exchangers, and is now also being investigated for use in membrane modules.

Extensive research has been done on the transfer of heat in transverse flow tube banks. Attention was especially given to the parallel-packed configurations, and general heat transfer correlations for $1<Re<10^6$ were published by Gaddis and Gnielinski.[58,59] Cross-packed configurations were also investigated[60-63], but no general correlations for heat transfer have been derived in the low Reynolds number regime ($Re<10^3$). Reported heat transfer correlations for cross-packed configurations are only valid in the transition flow regime ($10^3<Re<10^5$). However, Futselaar et al.[27] proved experimentally that heat transfer correlations for the parallel staggered configuration can be used as a reasonable approximation for cross-packed tube banks in the laminar flow regime.

Heat and mass transfer correlations are analogous in that the †Sherwood (Sh) and ‡Nusselt (Nu) numbers vary in the same way with the Reynolds (Re) number. The general forms of the dimensionless heat and mass transfer correlations are, respectively,

$$Nu = c \cdot Re^m \cdot Pr^n \cdot a^p \cdot b^q$$

and

$$Sh = c \cdot Re^m \cdot Sc^n \cdot a^p \cdot b^q$$

where

$$Pr = \frac{\nu}{\alpha}$$

$$Sc = \frac{\nu}{D}$$

A complete analogy between heat and mass transfer is only possible if the Re numbers are of the same order (m) and if the Lewis number (Le=Sc/Pr) equals one. In reality such a complete analogy does not exist, because in a liquid medium the mass diffusion coefficient (D) is

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† Sherwood dimensionless number: Ratio of mass diffusivity and molecular diffusivity

‡ Nusselt dimensionless number: Ratio of intensity of mass flux at interface and specific flux by pure molecular diffusion in layer of thickness L.

usually much lower than the thermal diffusion coefficient (α). Therefore, the analogy proposed by Chilton and Colburn[64] is more often applied (when $Le \neq 1$): $Nu/Sh = (Pr/Sc)^n = Le^{-n}$ in which the exponent, n, usually has a value of 1/3.[28]

Futselaar[28] carried out mass transfer experiments on parallel-packed tube banks in order to check the heat-mass transfer analogy of Chilton-Colburn. He found that experimentally obtained mass transfer results correlated well with theoretical results obtained from the analogy, and it can therefore be expected that the analogy can also be utilized successfully for cross-packed configurations.

1.5 Features of a transverse-flow module

Axial flow capillary and hollow fibre membrane modules consist of a parallel bundle of fibres with the feed stream flowing either through the membrane lumens or on the outside of the fibres, parallel to their axis. However, in the transverse flow module, the hollow fibres or capillaries are positioned perpendicularly to the feed flow direction, and to the axis of the module.

1.5.1 Packing configurations for fibres

The transverse-flow membrane module contains several rows of capillaries or hollow fibres. A row of fibres, which are placed in a plane perpendicular to the direction of the feed flow stream, is called a fibre grid. A module can consist of any number of fibre grids.

Although it is possible to arrange individual fibres in a random fashion in a fibre grid, they are preferably positioned in a regular arrangement - parallel to and equidistant from each other, or woven into a fabric. The centre-to-centre distance between two adjacent fibres in a grid is called the transverse pitch, s_t (or in dimensionless form $a = s_t/d_t$), and is constant for the matrix. Similarly, the centre-to-centre distance between fibres in two successive grids is called the longitudinal pitch, s_l (or in dimensionless form $b = s_l/d_t$) (Figure 1.3).

The transverse and longitudinal pitches may have any value, but Futselaar[28] and Côté et al.[43] give some guidelines for preferred dimensions. Futselaar[28] recommends a transverse pitch value between 1.25 and 2.5 times the outside fibre diameter, while according to Côté et al.[43] the transverse pitch should be about 1.2 to 5 times the outside fibre diameter. The longitudinal pitch should have a value between 1 and 3 times the outside fibre diameter, says Futselaar[28], while Côté et al.[43] gives the preferred range as 1.8 to 5 times the outside fibre diameter. When the longitudinal pitch is equal to the fibre diameter, a maximum packing density is achieved and fibres in successive grids support each other optimally in the flow direction, while a larger pitch results in a higher mass transfer coefficient. Although the influence of the transverse pitch on the magnitude of the mass transfer is small,[28] it should be remembered that the packing density is inversely proportional to the transverse pitch. The values of the transverse and longitudinal pitches are also determined by the maximum permissible pressure drop over a stack of fibre grids.[28]

The consecutive fibre grids, which are placed perpendicular to the longitudinal axis of the module, can be rotated with respect to each other. The rotation angle (β) between consecutive grids may have any value between 0 and 90°. If $\beta = 0°$ the fibres are in a parallel arrangement. To obtain a crossed arrangement each fibre grid is followed by an adjacent grid rotated through 90° (Figure 1.3). London et al.[60] also investigated a random arrangement in

which two 90°-crossed grids are oriented at 45° with respect to the neighbouring pair of crossed grids.

In membrane modules the cross-packed configuration is preferred above the parallel configuration for mechanical reasons. Unlike the stiff tubes in cross-flow heat-exchangers, membrane fibres are easily bent in the flow direction by the feed stream. If the fibres in successive grids are in a crossed configuration, the fibres support each other with a minimum of touching, whereas in the parallel-packed configurations the fibres can touch each other over their entire length.[27,28] Futselaar[28] suggests that a stiff tube be placed behind a fibre in each grid or a warp thread can be woven into the grid for support in the direction of flow (both types of reinforcement preferably in the middle of a grid). In the case of a fibre fabric, the woven structure will provide dimensional stability.

The parallel and crossed configurations can also be either in an in-line or staggered orientation (Figure 1.3). In the crossed in-line configuration fibres in alternate rows line up with each other. For the crossed staggered configuration the fibres in every fourth row, for instance rows 1, 5, 9, etc., line up with each other, and so do the fibres in rows 2, 6, 10, etc., 3, 7, 11, 15, etc., and 4, 8, 12, 16, etc. For the in-line configuration the staggered pitch (s_s) is equal to 0, while for the staggered configuration $s_s = \frac{1}{2}s_t$.

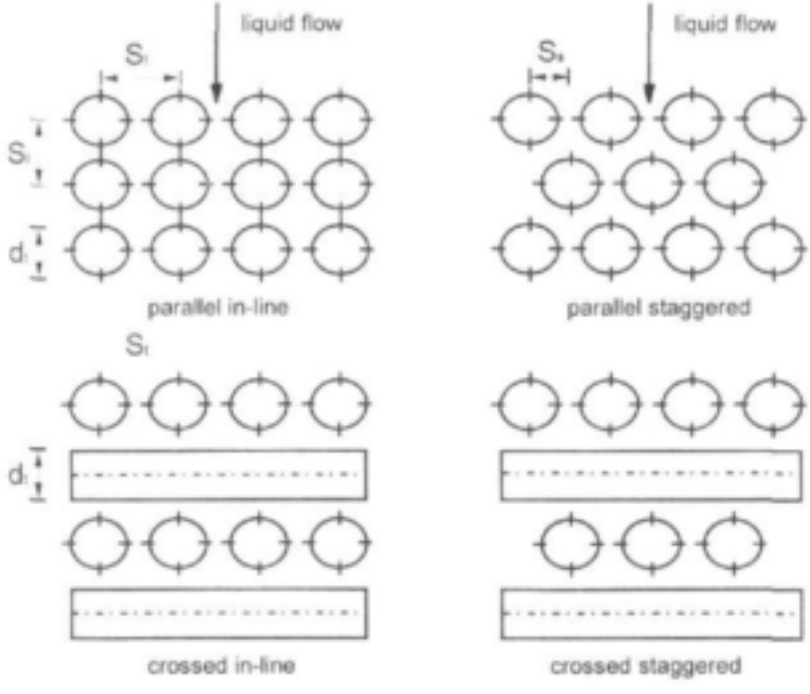


Figure 1.3: Different packing configurations for membranes in transverse-flow modules.

1.5.2 *Flow channels*

The cross-packed module has 5 flow channels - the centre channel, containing the membrane matrix, through which the feed stream flows, and four smaller outer channels in which the permeate is collected or from which a gas feed can be supplied. Two opposite lying outer channels are connected by the lumens of the membranes opening into them, while the remaining two opposite lying channels are connected by the lumens of the membranes which are in the in-between layers. In the case of the cross-packed module configuration, two different streams can be supplied through the outer channels, or a feed stream can be supplied

to half of the membranes, while a product is removed from the rest of the membranes. For example, in the operation of a membrane bioreactor where micro-organisms are immobilized on the membrane outer surface and oxygen must be supplied while a product or by-product must be removed at the same time. This can be achieved by pressurizing the one lumen channel with oxygen and providing a suction on the other to remove the product. By changing the manifold configuration, gas supplied to the outer channels can either be in dead-end or flowing mode. If the application demands it, the position of feed and gas/permeate streams may be interchanged, so that a single feed stream, or two different feed streams, is supplied to the membrane lumens, and the permeate and/or a product is collected from, or gas is supplied to, the central channel. Also, the number of outer channels can be varied by arranging the membrane grids at different rotational angles.

The cross-section of the central channel of the transverse flow module is usually circular or square, as determined by the construction techniques used. A square cross-section is, however, preferred, so that all fibres are of the same length.

The diameter of the central channel is mainly determined by the application of the module. For gas flow on the outside of the fibres, the diameter is usually larger than that required for liquid flow. However, the use of long fibres results in larger pressure drops on the lumen side. Therefore, according to Futselaar[28], the length of the fibres should not exceed half the circumference of the channel, which is normally smaller than the length of a module. This allows the use of fibres with a smaller diameter at a given pressure drop, which again results in larger packing densities (advantageous for gas separation and pervaporation). The diameter of the central channel of a transverse flow module, with liquid flowing on the outside of the fibres, may be larger than the internal shell diameter of a conventional axial flow fibre module, because, in the transverse flow module, larger mass transfer coefficients are already obtained at much lower linear flow velocities and thus larger diameters can be used for the same throughput. Diameters of the central channel may vary between 2.5 and 50cm.[28,37]

1.6 Transverse-flow module designs

Several designs for transverse flow membrane modules have been developed and patented. A brief historical overview is given below.

Strand[25,26] first patented a membrane module in which hollow fibres are placed transverse to the feed flow direction on the shell side. A square of woven membrane fabric is sealed in a frame containing a central square opening which is surrounded by four rectangular openings into which the ends of the fibres open (Figure 1.4a). Several of these square frames can be stacked to build a transverse flow membrane module with a central channel and four outer channels. The module is operated with one fluid flowing through the central channel, over the outside of the fibres, while a second fluid flows through the membrane lumens. The second fluid can either be used as a sweeping fluid and flow from one outer channel to the opposite channel through the lumens of all the membranes connecting them, or it can be passed to and fro between two opposite channels by alternately passing it through the fibres of successive frames (Figure 1.4b).

Baudet et al.[41] also made use of a hollow fibre fabric to build a transverse flow module. The module consists of a stack of circular flanges pressed together. Each flange, which is cast in a mould, contains a fabric of hollow fibres.

In another patent, Baudet et al.[40] presented a module comprising a stack of rectangular frames in which two of the opposite edges have been thinned. Hollow fibres are wound

across the frame at these thinner sections of the frame (Figure 1.4a), and are secured in position by a resin material. The fibres can either be open at both opposite edges of the frame (Figure 1.4b) or they can be U-shaped, with both open ends at the same edge of the frame (Figure 1.4c). The frames containing the wound fibres are stacked with the fibres from successive frames either parallel or perpendicular with respect to each other (Figure 1.4d). The frames are glued together and mounted in a container. A fluid stream flows outside of the fibres in the channel formed by the interior of the frames. The membrane lumens are connected to the shell side of the container, which collects either the permeate or a second

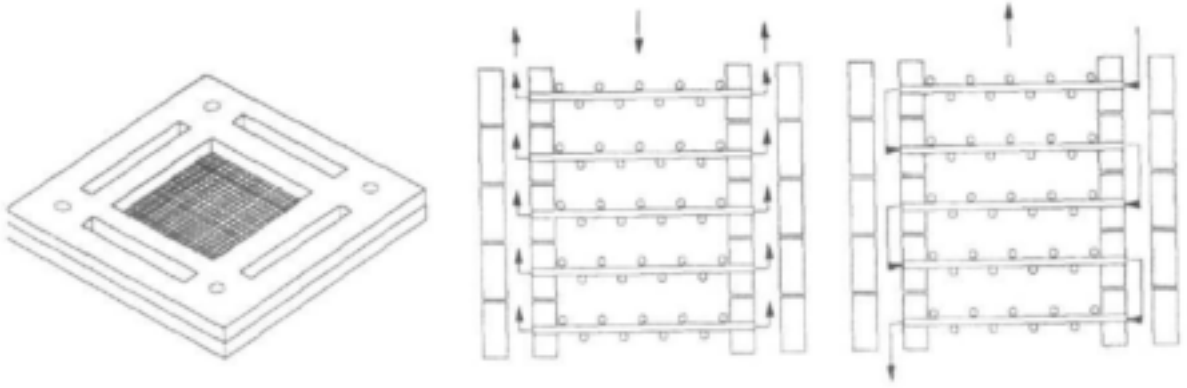


Figure 1.4a: Square frame containing woven fabric membranes and different flow configurations in the assembled module.[25, 26]

fluid(s) which flow through the hollow fibre lumens.

Both Bayer[42] and Saida[49] used a centrifugal casting technique to produce a transverse flow module. The former used a fibre fabric in which the fibres are stacked in layers, while the latter used a woven fabric fibre mesh. Circular forms are cut from the fabric of hollow fibres and a stack of circular grids are placed in a cylindrical tube. The tube is placed horizontally and rotated at high speed around its longitudinal axis while a resin is poured in at one side. After the resin has cured, the moulding tube is removed and a layer on the outside of the formed resin tube is scraped off to open the fibre ends.

A transverse flow membrane module for exchanging ions, molecules, gases, liquids and/or heat, between at least two fluid streams, is described in a patent by Inacio and Nilsson.[45]

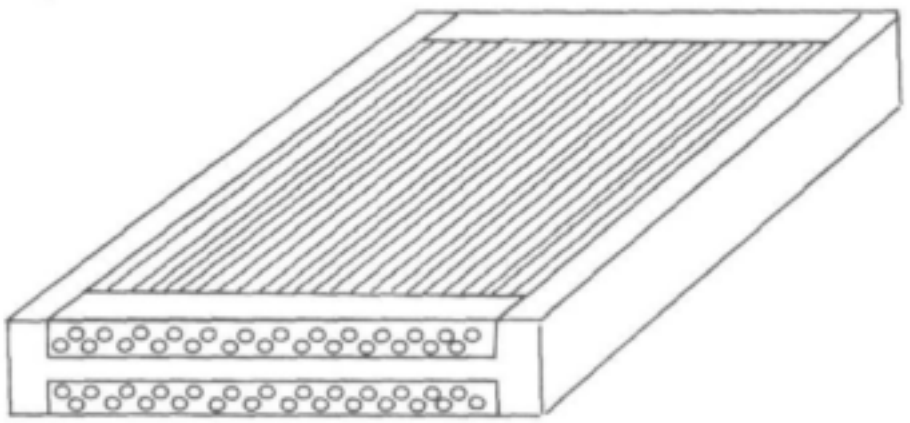


Figure 1.4b: Frames for transverse-flow module with fibres open at opposite ends.[40]

One or more fibre segments, each with its own inlet and outlet (Figure 1.5), can be inserted in a shell, also with its own inlet and outlet connections. A fluid flows on the outside of the fibres, while, in order to perform different types of exchange, different fluids can be supplied to each of the segments.

Stam[50] also used a centrifugal casting technique to produce discs for a transverse flow membrane module to be used in gas separation. Discs were mounted between two flanges to form a module, which could withstand an internal air pressure of 130 bars, and with a specific

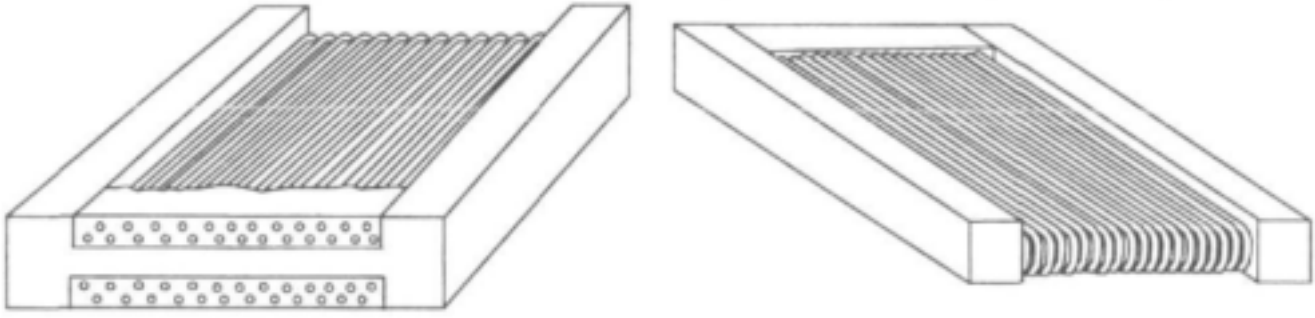


Figure 1.4c: Frames for transverse-flow module with U-shaped hollow fibres.

membrane area of approximately 30 000 m^2/m^3.

Glassford[44] used microporous hollow fibres woven into a fabric and orientated transversely to the direction of the flow in a device for the transfer of one or more gases from a gaseous mixture, or volatile components from a liquid mixture, into an absorbing gas or liquid. The gaseous or liquid mixtures flow on the outside of the fibres, while the absorbing gas or liquid flows through the lumens of the fibres.

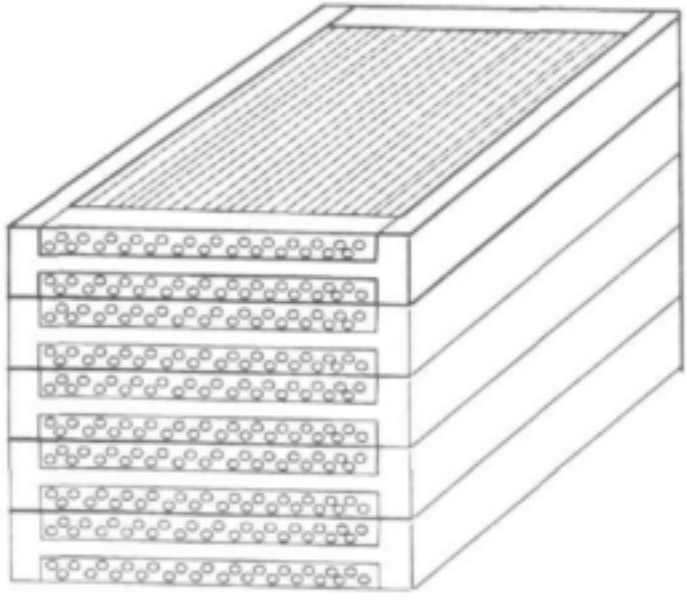


Figure 1.4d: Parallel-packed transverse-flow assembly.[40]

Nichols[47] has described another transverse flow membrane module. Arrays of parallel fibres which are held in position by a warp thread or a strip of adhesive material, are stacked crosswise in a casting mould. While the mould is rotated axially, wax is injected and forms an annular ring on the inside of the mould. A second annular ring is formed by injecting a resin. When the cast is removed from the mould and the outer wax ring is removed, an annular frame with hollow fibres crossing the central channel and with lumen openings on the outside surface of the frame is obtained. The complete module is formed by stacking several of these segments together with an O-ring seal between each segment, and the assembly is then placed in a pressure vessel.

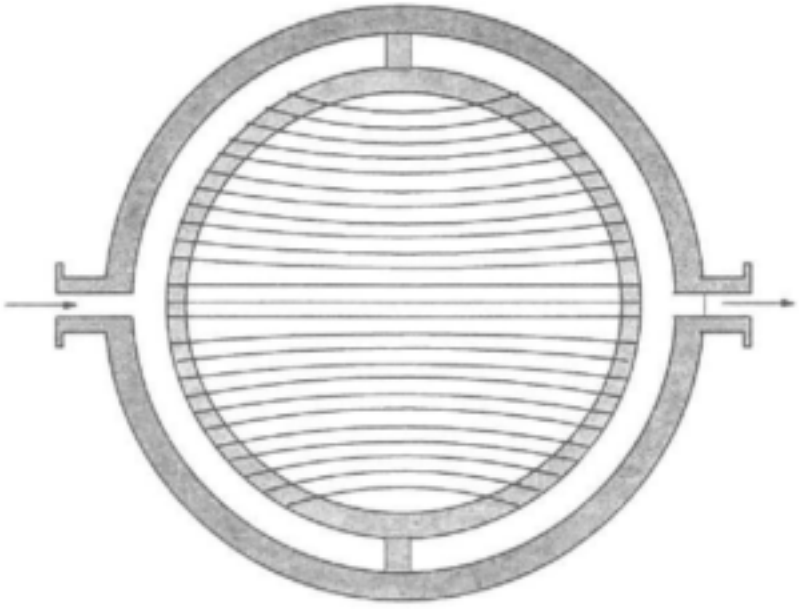


Figure 1.5: Cross-section of a two-port segment used by Inacio and Nilsson[45] to build a transverse-flow module.

In yet another patent, Nichols et al.[48] described a modification of the above mentioned patent. Instead of having only one port for the withdrawal of the permeate, several ports are provided on the permeate side of the module. Moreover, the area between the hollow fibre stack and the inside wall of the pressure vessel is divided into compartments by gaskets in the axial direction, in such a way that two permeate ports are connected with each other *via* the fibre lumens opening in these compartments. In this way one or more additional fluids can be supplied through the fibre lumens. This fluid can be either a sweeping stream or a heating fluid which adds heat to the fluid flowing on the outside of the fibres. Contrary to the design described by Inacio and Nilsson,[45] in which different fluid streams are supplied at the successive fibre segments, the different fluid streams on the inside can be alternated with every fibre grid, depending on the manner of stacking. Several variations on the multi-port construction are also described.

Ter Meulen[46] described a transverse flow membrane module consisting of several rectangular segments connected in series. Two fluid streams can be accommodated in this module. One stream flows on the outside, perpendicular to the hollow fibres, while a second stream flows through the lumens of the hollow fibres and is directed from segment to segment.

Côté et al.[43] described a transverse flow membrane module consisting of a stack of square segments. Each segment is made up of a row of parallel lying hollow fibres, which are joined in position at their ends by clamping them between two strips of flexible material. These strips are injection moulded and have parallel semi-circular grooves which fit tightly around the fibres (Figure 1.6). The strips also have stepped ends so that they interlock when the segments are stacked with the fibres in a crossed configuration. The segments are stacked upon four guide pins, to form a leak-proof channel through which the feed stream flows transversely over the fibres. One or more of these stacks can be placed in a shell to complete the module. The fibre lumens are open to the permeate zone of the module housing. The invention was tested for microfiltration, aeration, low pressure reverse osmosis and pervaporation processes.

Futselaar[28] produced circular fibre segments using the same technique as Nichols[47] and stacked them inside a shell. A gasket is inserted in the area between the fibre stack and the shell to divide this area into several compartments. By doing so, a continuous flow path is formed on the permeate side, providing a countercurrent flow path between the feed and permeate streams.

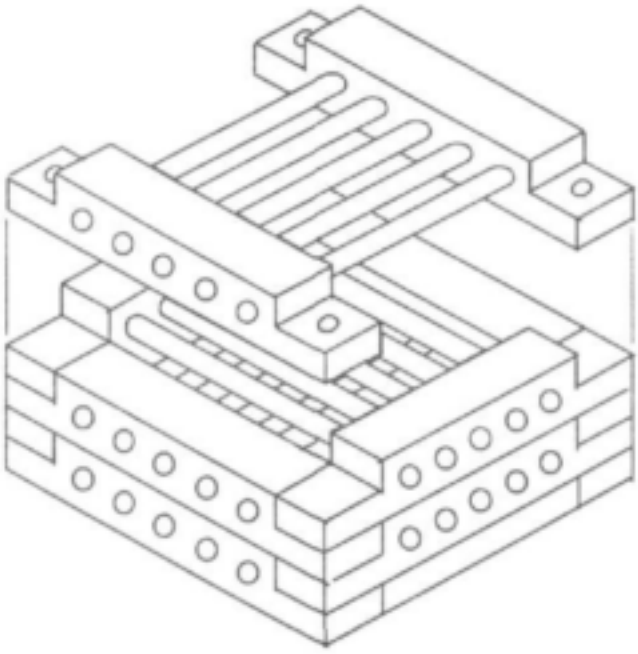


Figure 1.6: Fibre ends are clamped between two strips to form a fibre segment which are stacked to form a transverse-flow membrane module.[43]

2 Transverse-flow module fabrication and capillary membrane production techniques

The production of capillary membranes and the different fabrication techniques that were developed during this project to fabricate a range of transverse-flow type capillary membrane modules will be discussed in this section.

2.1 Capillary membrane production

Capillary membranes were produced by extruding a membrane spinning solution through the annulus of a tube-within-tube spinneret. The solution was pumped from a reservoir with a metering pump through a filter to the spinneret. The spinneret also contained a central opening for dispensing the coagulant. The volumetric rate of flow of the internal coagulant was controlled with a needle. The lumen fluid prevented the nascent membrane from collapsing before gelation took place, and also played a role in the coagulation process to determine the morphology of the inside wall.

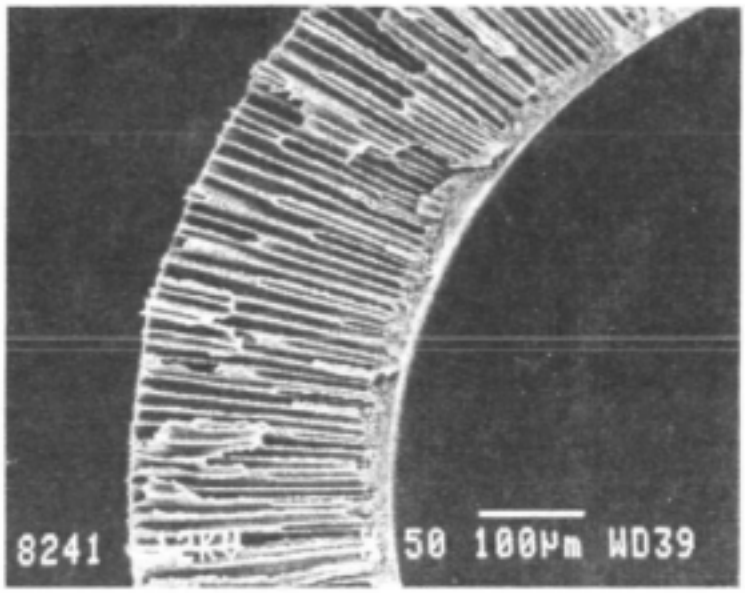
By adjusting the spinning solution formulation and composition of the internal and external coagulants, internal, external or double skinned membranes with different substructure morphologies could be produced.

Capillaries with an interior skin and an open structure on the outside were produced as follows.[65] Pure-water (a strong non-solvent) was used as lumen fluid or internal coagulant to encourage fast coagulation and the formation of thin-skinned membranes. To obtain an open structure on the outside, the coagulation process had to be slowed down. This is effected by a system comprising two coagulation baths (Figure 2.1). The spinneret was placed at the bottom of the first tank and the membrane was extruded into a 94% N-Methyl-2-pyrrolidone (NMP) aqueous solvent. When the membrane left this tank, it passed through a high-humidity chamber before entering the second coagulation bath containing water. Here the membrane passed over several polypropylene guide-rollers before it reached the rotating, perforated take-up drum. Water was sprayed onto the take-up drum to rinse the membranes. As the membrane moved through the second tank all excess solvents were also washed out.

To produce a double skinned membrane, the spinneret was placed directly above the high humidity chamber. Before entering into the pure water coagulation bath, the membrane passed only through the humid atmosphere, where vapour induced coagulation caused a skin layer to be formed on the outside (Figure 2.2).

2.2 Transverse-flow module fabrication techniques

Different fabrication techniques were used to produce transverse flow modules. First, the modules were built by stacking pre-moulded spacer templates, made of polystyrene, which contained the capillary fibres.[66] These assemblies were then embedded in an epoxy resin. As the supply of templates was depleted and no more could be obtained, a new fabrication technique had to be developed. One alternative was to replace the moulded templates by similar ones that were punched from sheets of closed-cell foam. A centrifugal casting technique was also developed to produce discs containing a single layer of fibres.



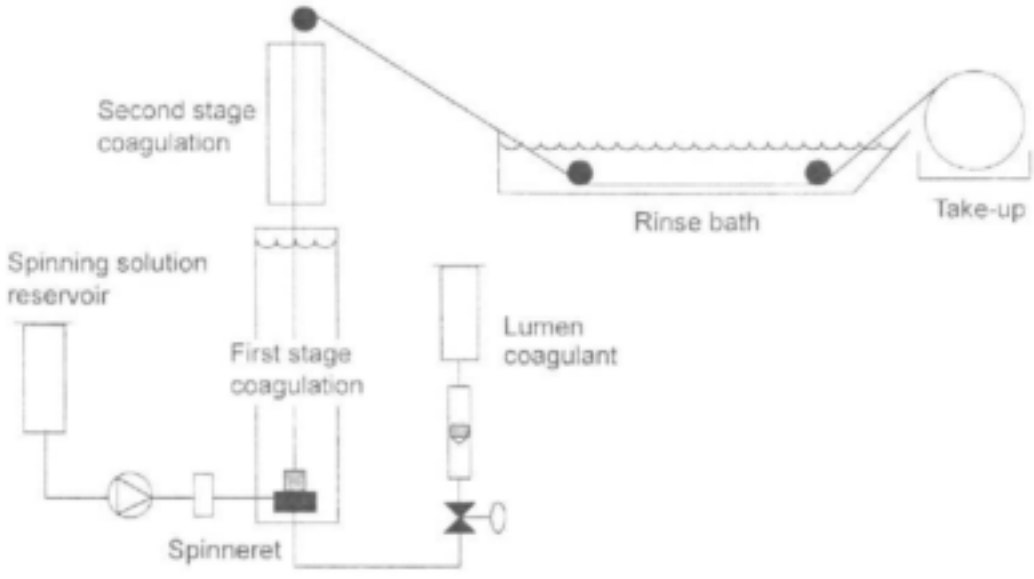


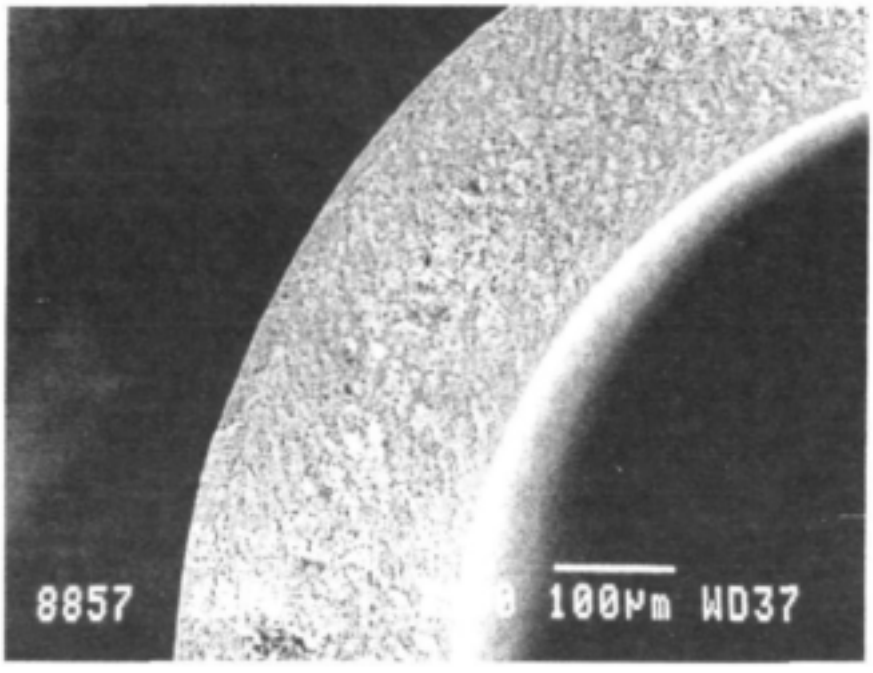
Figure 2.1: Cross-section of an outer skinless capillary membrane and a schematic representation of the spinning process by which the membrane was produced.

2.2.1 *In situ cast membrane templates (polystyrene spacers)*

The modules were built by stacking a number of spacer templates on which capillary membranes were mounted. Figure 2.3 shows a typical spacer template, injection moulded from a synthetic material such as polystyrene.

Apertures in the templates formed the central square flow channel and the four lumen channels when they were stacked to build the module. The frames which formed the individual apertures were held in place by small ribs, which were much thinner than the spacers. When the templates were stacked, a cavity was formed around the flow channels, which was filled with an epoxy casting resin. The resin surrounded the flow channels and embedded the capillary membranes, thus creating an impervious seal between the feed and

other channels. It was even possible to add more lumen flow channels by altering the design of the template.



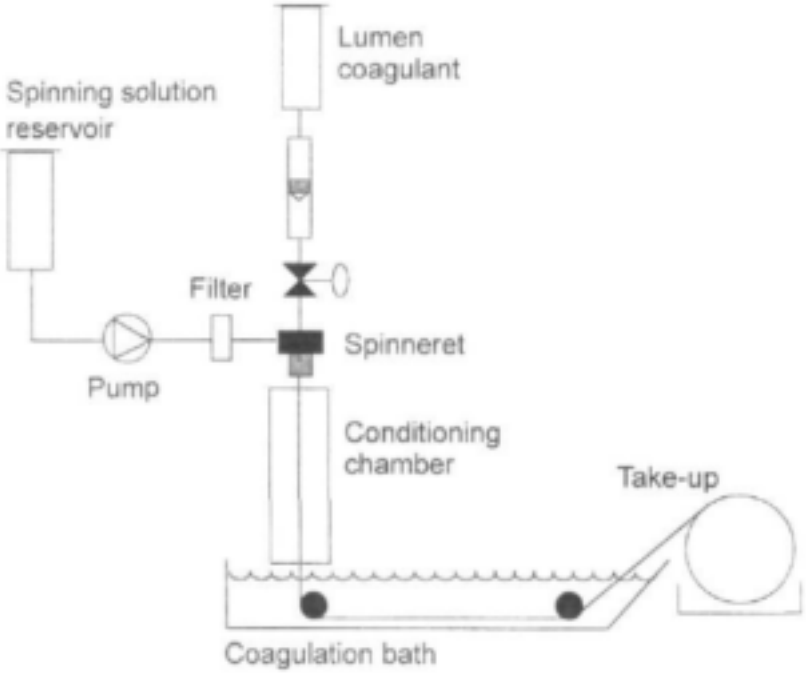


Figure 2.2: Diagrammatic representation of a capillary membrane spinning line using a one-step coagulation process to produce a membrane with a spongy substructure.

Capillary membranes were cut in short pieces and arranged in a grid, parallel to each other on the spacer templates. Grooves in the spacer templates secured their position, temporarily, before they were potted in place with a casting resin. The grooves were a ¼-pitch off-centre

so that when a spacer was rotated through 90° (cross-packed) or 180° (parallel-packed) with respect to the previous one, the capillaries were in a staggered arrangement. Thus, because of its off-centre design features, only one template shape was required to build both crossed and parallel, in-line and staggered modules. The transverse pitch could be varied by placing fibres in all the grooves or only in every alternate set of grooves and blocking the unused grooves. A drawback of this design was that only fibres of such a diameter as fits tightly in the grooves could be used. The spacer templates not only determine the transverse pitch of the membrane module, but the longitudinal pitch as well. The longitudinal pitch was varied by placing spacers without grooves in-between the fibre-containing spacers.

Any number of templates could be stacked to form a module. The stacked templates were bolted together between two blocks, the bottom one with an entry port and the top one with four exit ports which were connected to the cavity around the flow channels. An epoxy casting resin, premixed in a static mixer, was pumped into the cavity from the bottom port, while trapped air was allowed to escape through the top exit ports. When the cavity was completely filled, the resin was allowed to cure and the top and bottom sides of the module were faced.

This method provided a means to assemble a module quickly and economically, by forming the various feed and permeate flow channels in one casting operation.

One or more of these module segments could be stacked and bolted between flow distribution manifolds. A gasket was placed between segments to form a leak-proof assembly.

2.2.2 In situ cast membrane templates (closed-cell foam spacer)

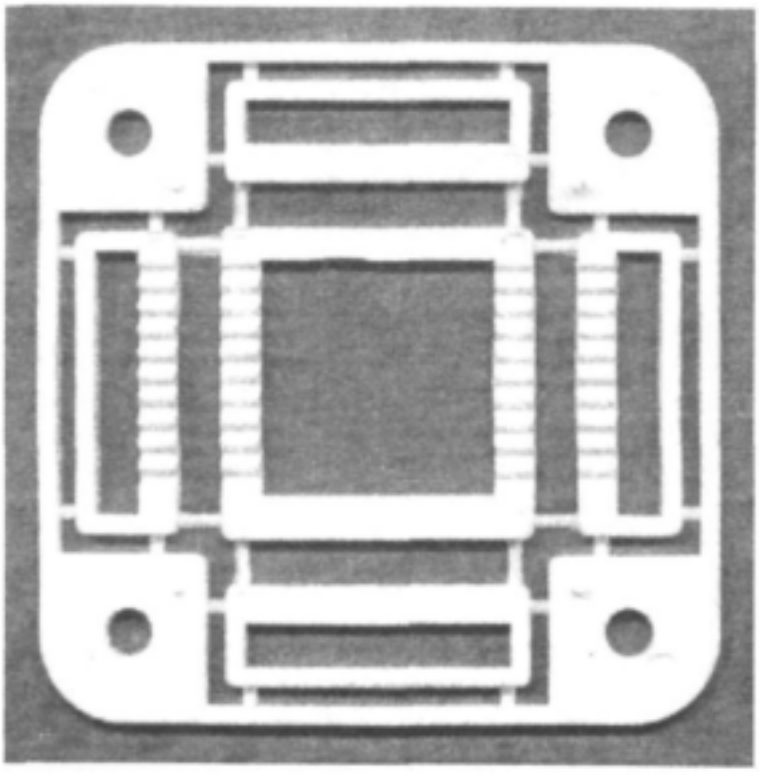
A limitation of the method described above was that separate injection moulding dies were required to produce spacer templates with central channels of different size. As these dies were very expensive, it was necessary to develop an alternative, cheaper fabrication technique.

Clicking dies could be obtained at much lower cost than the dies for injection moulding. Spacer templates, similar to the ones described in the previous paragraph, and with central channels of various diameters, were punched from sheets of closed-cell foam (SPX45 obtained from SONDOR Industries (Pty) Ltd., Cape Town). Because of the flimsiness of the foam, the frames surrounding the flow channel apertures had to be wider than they were for the rigid injection moulded spacer templates. This caused the total diameter of the templates to be larger and the resulting modules were very bulky.

The ribs connecting the frames were of the same thickness as the rest of the templates. Some of them had to be removed so that a continuous cavity was created around the flow channels, keeping only a sufficient number of ribs to support the frames. Grooves to position the capillaries were melted into the foam with the aid of a heated aluminium punch. The width of the grooves and the distance between them could be changed by using different punches. The foam spacer templates with capillaries were then stacked, and the module assembled by casting the epoxy resin in the same way as for the injection moulded templates.

Although the foam has some advantages as a construction material, the modules produced from it were not leak-proof. A material which allows for use of the same production method, but is more rigid, would be more suitable.

(a)



(a)

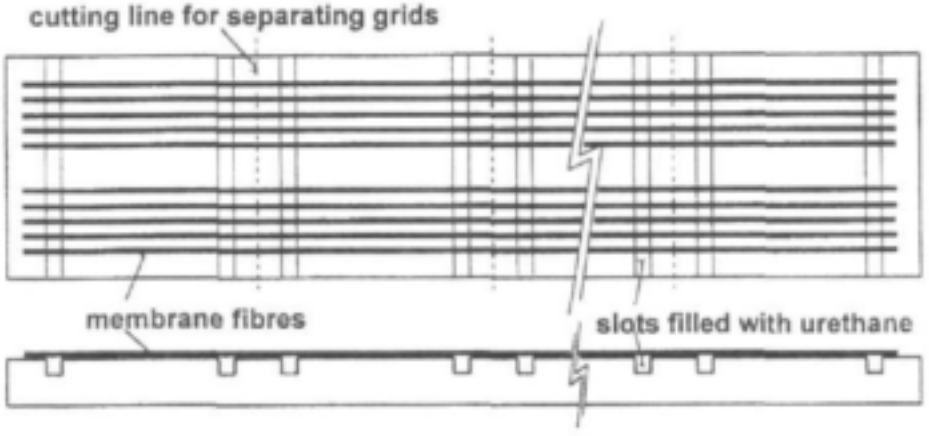
Figure 2.3:(a) Assembled transverse-flow module and (b) injection moulded spacer template used in construction.

2.2.3 *Centrifugal cast membrane templates*

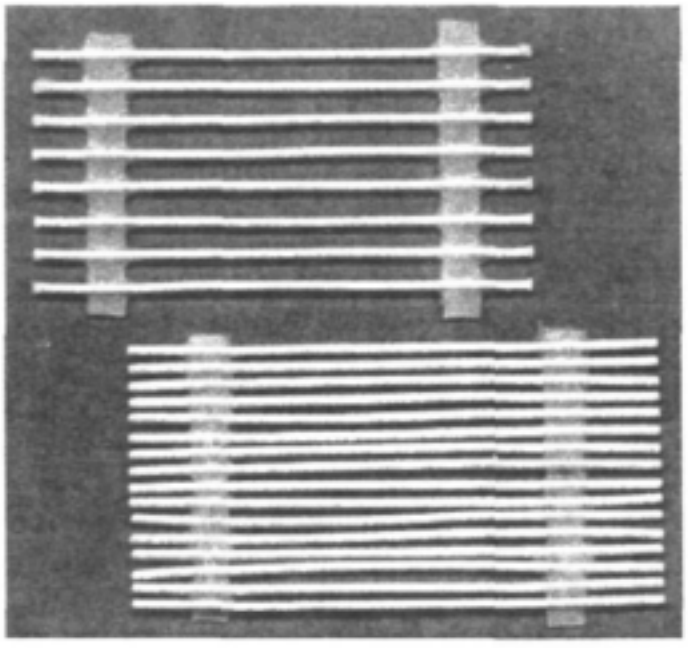
A drawback of both previous methods was that once the module was assembled, defective membranes cannot easily be detected or removed. A new construction method was devised

whereby the capillaries were embedded into separate spacer templates and the resulting discs assembled into a module.

Firstly, grids of evenly spaced, parallel aligned fibres were made. A chosen number of fibres were spanned parallel to each other on a poly-ethylene surface with slots perpendicular to the fibres. Spacers were used to obtain the precise centre-to-centre distance between the membranes and thus the desired transverse pitch. With this technique, any transverse pitch was possible, in contrast to the injection moulded templates where the pitch was fixed, *a priori*, by the moulded grooves. The fibres were bonded together in a grid by pouring urethane into the slots and allowing it to cure (Figure 2.4a) The assembled fibres were then cut into separate grids and removed from the surface. Figure 2.4b shows completed fibre grids.



(a)



(b)

Figure 2.4: (a) Fabrication of fibre grids, and (b) fibre grids with different transverse pitches.

The discs were fabricated by a centrifugal casting technique. The resin used for casting the discs should, after curing, bond well to the membrane fibres to ensure a leak-proof construction. The cured resin must be flexible enough for the finished discs to seal on each other, but rigid enough to withstand pressure when the discs are clamped together. It should also have a sufficiently long pot-life to enable its injection into the mould and have a low viscosity while it is injected. The curing temperature must be low enough not to damage the fibres, preferably room temperature. Urethane (compounds 6123 and 9333.1, obtained from Polynates (Pty) Ltd., Cape Town) was found to be a suitable casting resin.

The centrifugal casting mould assembly consisted of several circular disc moulds (Figure 2.5a), a distributor plate (Figure 2.5b), a cover plate (Figure 2.5c) and a split-housing, all made from poly-ethylene.

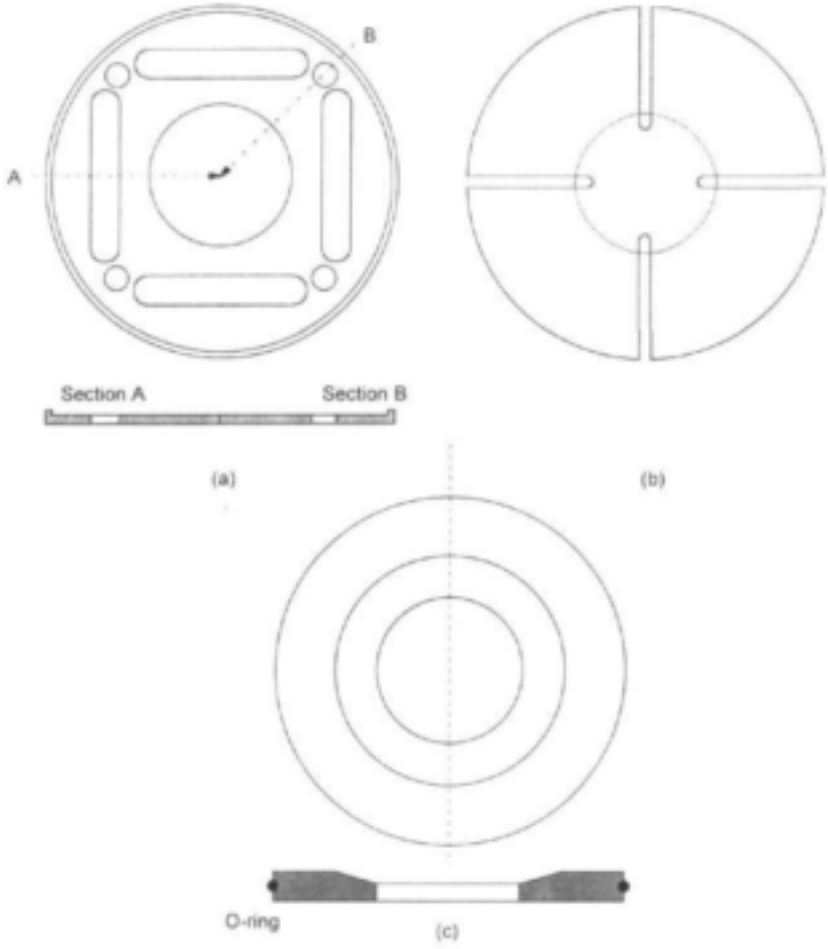


Figure 2.5: Centrifucal casting apparatus: (a) disc mould, (b) distributor plate, and (c) cover plate.

The disc moulds have a central circular opening to form the feed flow channel, four rectangular openings with rounded ends to form the lumen channels, and four openings for assembling them in the casting container and to form the bolt holes to facilitate the assembly of the final module. After the fibre ends have been sealed, either by pressing them closed or by applying a drop of quick-set epoxy, a fibre grid is placed between two disc moulds. It was positioned a ¼ pitch off-centre with the aid of a guide and secured into position. The bonding strip between the fibres act as a spacer so that the fibre grid was positioned equidistant from the top and bottom of the disc. The closed membrane ends were clamped between silicone

rubber blocks which fitted into the lumen channel apertures. The purpose of these blocks was to keep the lumen channel apertures open when urethane forms the disc around them. Similarly, silicone rubber rods were placed through the other four holes to form the bolt holes and to keep the stack of 'mould-sandwiches' in position. The distribution and cover plates were placed on top of the stack and the whole assembly was clamped together in the casting container. The container was split axially for easier placement of the moulds. The distribution plate had four slits, which overlapped with the open ends of the lumen channels, to guide the urethane into the assembly, allowing it to flow through and fill the moulds.

The casting container, housing the moulds, was clamped into a lathe and rotated horizontally round its axis at 480 r.p.m. while the urethane is injected. The urethane spread through the mould, and was deposited on the inside of the wall, by centrifugal force. The spinning process continued until the urethane was sufficiently cured (about one hour). When the urethane was completely cured, the casting assembly was dismantled, the silicone rubber blocks and rods were removed and the discs were taken out of the moulds. The sealed ends of the fibres, which were protruding into the lumen apertures, were positioned so that the fibre lumens opened into these channels when the sealed ends were cut away. Figure 2.6 shows some examples of discs with varying transverse pitches and central channel diameters.

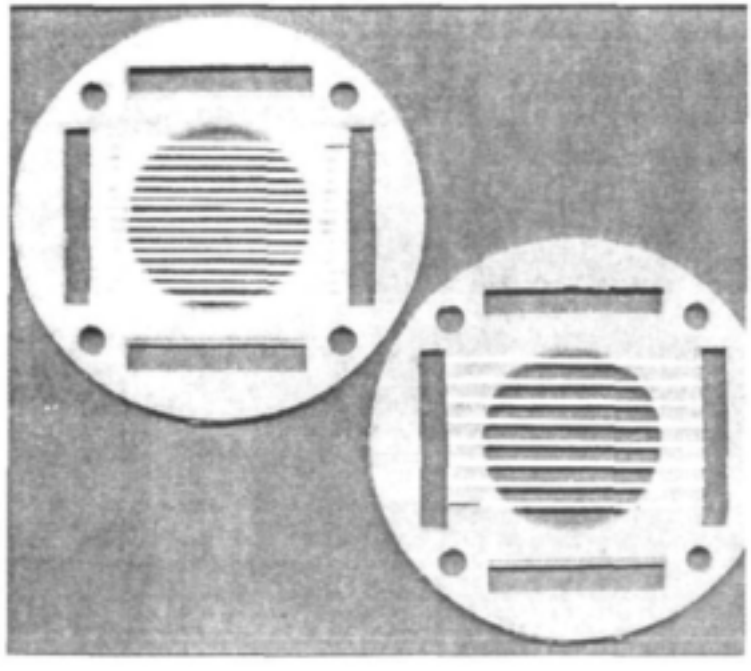


Figure 2.6: Discs of varying transverse pitch and central channel diameter.

The thickness of the discs determined the longitudinal pitch. The longitudinal pitch was increased by inserting blank discs between those containing membranes.

Before a module was assembled, the discs were pressure-tested to ensure that defective membranes were not installed into the module. Each of the apertures into which the membrane lumens open were clamped between a set of blocks. One set of blocks contained a port through which gas could be supplied to the lumens, while the other set of blocks served to close off the lumen volume. This disc assembly was immersed in water and gas was pressurized into the membrane lumens. Any defects, such as pinholes, in the membranes could easily be detected by bubbles streaming from the membranes.

Depending on the membrane area required, the module was completed by stacking any number of discs and bolting them together between two manifolds, each of which contained an entrance or exit port for the feed flow, and entrance and exit ports for the lumen channels.

This design offered greater flexibility in replacement of defective module parts and in rescaling the membrane unit. The effects of membrane fouling and failure could be minimized as the membrane-containing discs could be removed from the module at any time and replaced by others. Each segment could also be individually pressure tested to detect any defects before a module was assembled. The length of a module could be changed by simply adding or removing templates. Scale up of the templates could easily be done by merely using larger moulds, and by incorporating membrane support struts if necessary.

2.2.4 Scale-up of centrifugal cast membrane templates

During scale up the size of the Mark I templates described in the pervious paragraph, the template and mould designs were sligthly altered (Figure 2.7).

The main differences between the Mark I and Mark II membrane wafers, except for the increase in size, where the absence of clamping bolts in the Mark II design, as well as the introduction of semi-circular lumen ports. This allowed the wafer to be more compact than the Mark I design was. However, it was soon realised that much urethane was wasted as result of the distributor plate design and the mould was yet again modified see (Figure 2.8).

The slots in the original distributor plate were replaced with holes, each hole coinsiding with the outer edges of the four semi-circular lumen ports. This reduced the volume of urethane used considerably. The vent hole in the centre of the two-disk moulds was also reduced in size, to alter the size of the central fluid flow channel. Three locating and compression studs was machined to help compress the membrane wafer templates once the spin-mould was loaded. Fibre grids again have to be prepared before loading into the mould templates. A lay-up jig was again used for this purpose. Figure 2.9a shows the template used to prepare the grids and Figure 2.9b shows a completed grid, ready for loading. The method of fabrication allows for various packing arrangements. Figure 2.10 shows the standard single membrane layer, as well as a orthogonally packed membrane mat.

The Mark III wafers were housed in a module device that also differed from the previous designs. These wafers were designed so that they fitted snugly inside a 200mm class 4 u-PVC tube. The templates were clamped between two steel flanges, with appropriate holes for connecting the various flow compartments. Figure 2.11 shows a module as part of an experimental set-up used for the oxygenation of water.

The water entered into the module through the central channel at the bottom and exited at the top. A spacer was provided between the membrane wafer stack and the outer steel flange to reduce channeling of water when it entered into the module. The oxygen entered into the lumen channel apertures in the wafers and the membranes, entering and leaving at the top of the module. The three discs without fibre were used as spacers at the top so that the fittings did not touch the membranes. Steel plates sandwiched the two PVC face-plates that were machined to accommodate connectors for liquid and gas.

Proper sealing during operation was one of the main problems experienced with Mark III membrane templates. This was very much a function of the hardness of the urethane used. If the urethane were too soft, the template would buckle or distort during fastening of the clamping bolts (Figure 2.12). Harder urethanes solved this problem, but made sealing

difficult and finishing off even more taxing. The problem of material choice was never really solved. Leakage was prevented by applying a thin coat of sealing individual between individual disks. Silicon rubber worked well, but had to set first before the wafer stack was bolted by means of a torque wrench to ensure even distribution of load onto the wafers.

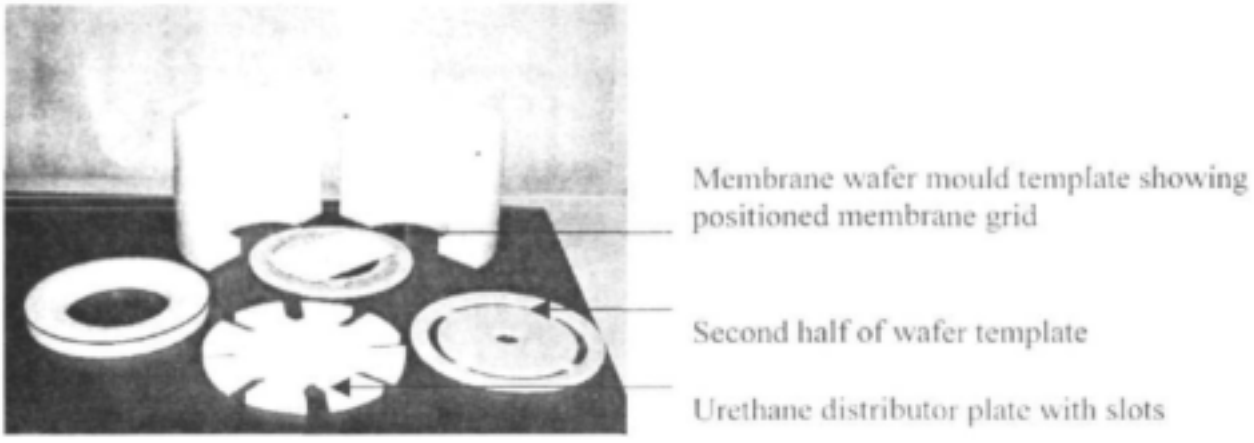


Figure 2.7: Scale-up of Mark I to Mark II centrifugal casting mould.

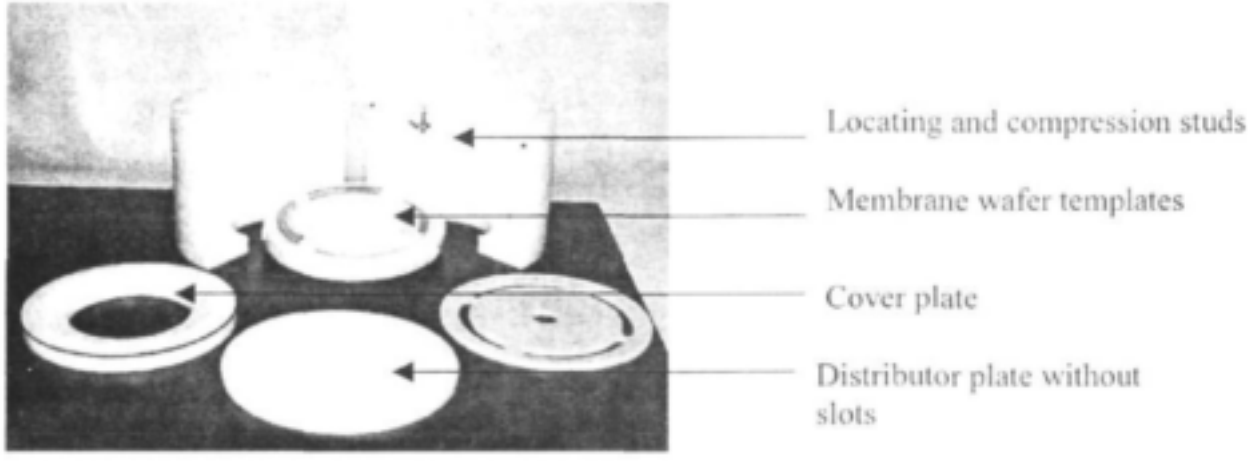
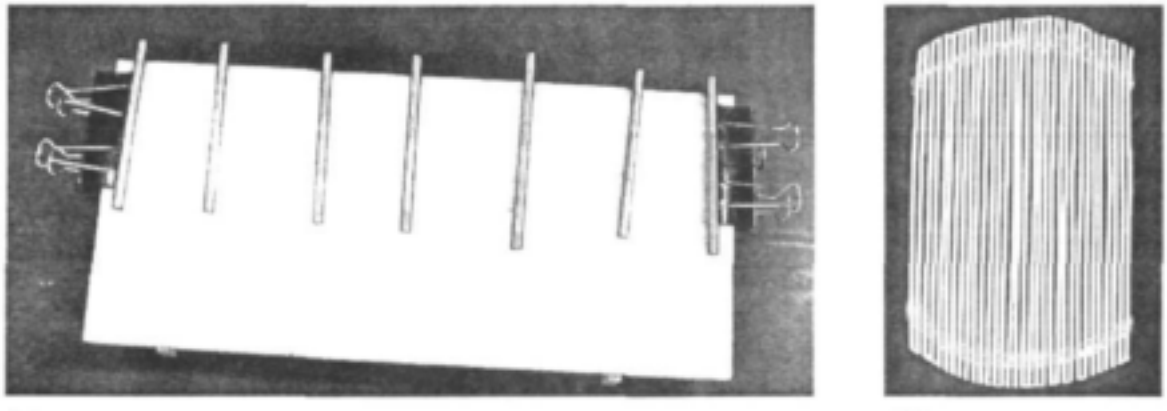


Figure 2.8: Mark III centrifugal mould.



(a) *(b)*

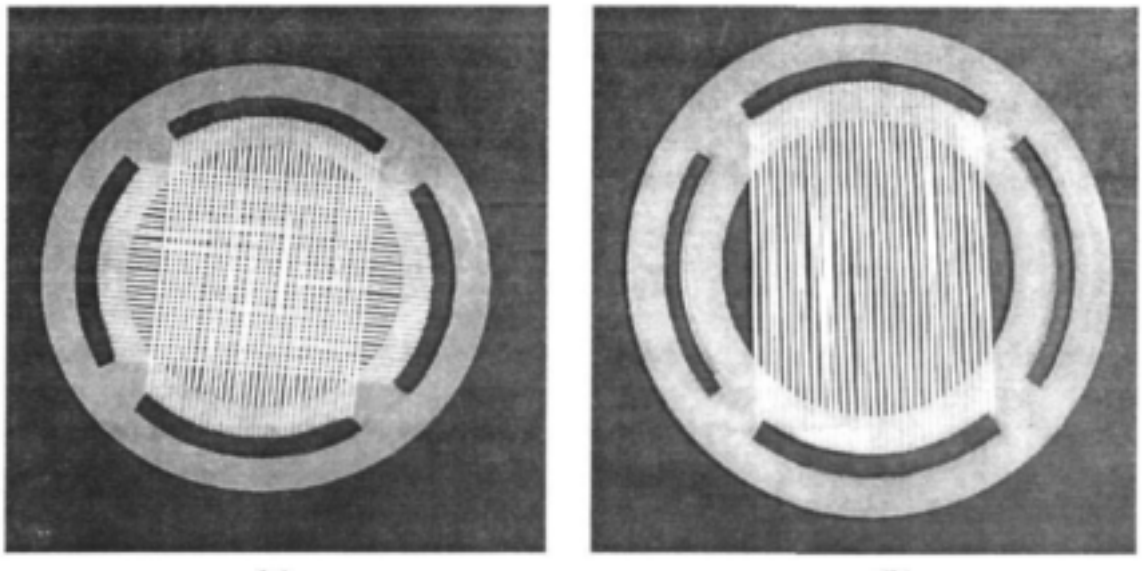
Figure 2.9: Spacing and forming jig to assist with fibre orientation during fibre grid prepration.

2.2.5 *End-manifolded modules*

A further embodiment of transverse flow modules were the immersed-type elements. These, so called dewatering elements were fully immersed in a vessel which may, for example, be a bioreactor. In this application the membranes are skinned on the outside and product is withdrawn from the reactor by applying a small vacuum to the lumen manifold.

Fabrication of equispaced membrane elements were fairly laboursome, whereas the construction of randomly spaced elements was somewhat simpler. The simple routine followed to construct the manifolded arrays was to drill a series of holes, sligthly larger than the outside diameter of the membrane, into a u-PVC tube. The pitch of these holes would depend on the spacing required. Figure 2.13 shows an example of a predrilled manifold and the mould arrangement used to encase the ends of equally spaced fibres. Figure 2.13 shows a close-up of the mould. The design of this cell was such that the epoxy was cast right around the tube manifold. The bonding between the epoxy and the u-PVC was not good, and to prevent leakage, an O-ring was provided and embedded in the casting. The membranes may be any of length, as can be seen from the examples in Figure 2.14. Figure 2.15 shows a complete, single manifolded membrane element. The lumen of the unattached membrane ends were sealed off.

A further emodiment of the design was somewhat more sturdy, and an example of this type of module can be seen in Figure 2.16. The membranes were again potted into the tubesheet at equal pitch and four bolts kept the tubesheets at fixed distance appart. The amount of free swing the membranes had could therefore be adjusted. A manifold had to be machined and bolted onto the endblocks to provide connections for the inlet and outlet ports. The module was operated either inside out or outside in, depending on the application and membranes.



(a) *(b)*

Figure 2.10: Membranes packed (a) orthogonally and (b) unidirectionally in a transverse-flow membrane wafer.

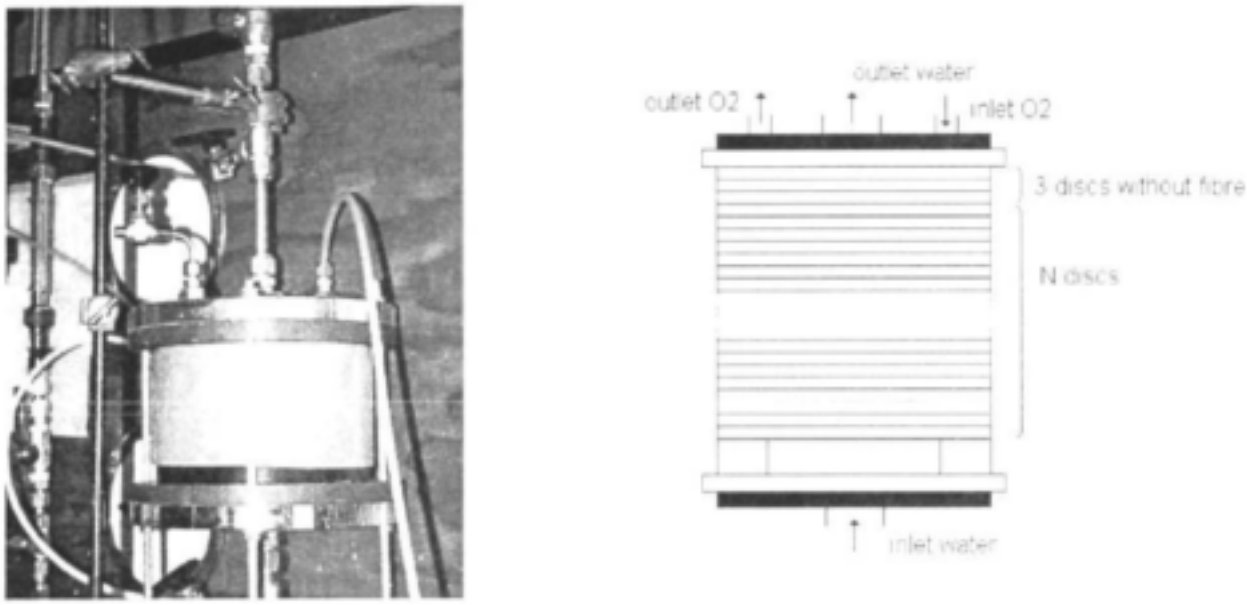


Figure 2.11: Photograph and schematic of a Mark III transverse-flow module installation used during oxygen transfer experiments.

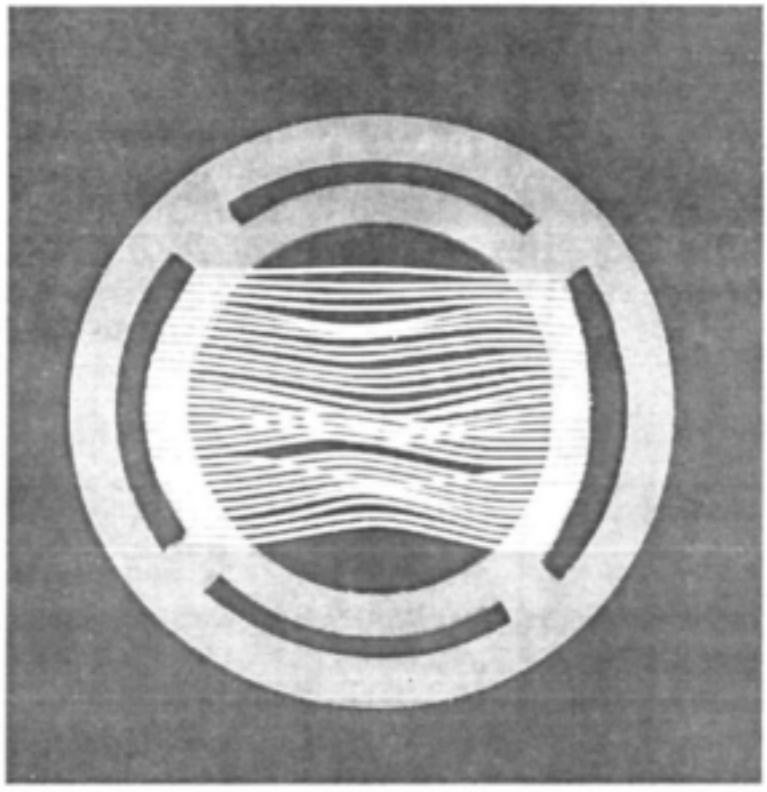


Figure 2.12: Membrane module clamping force too high, with subsequent distortion of membrane wafers in module.

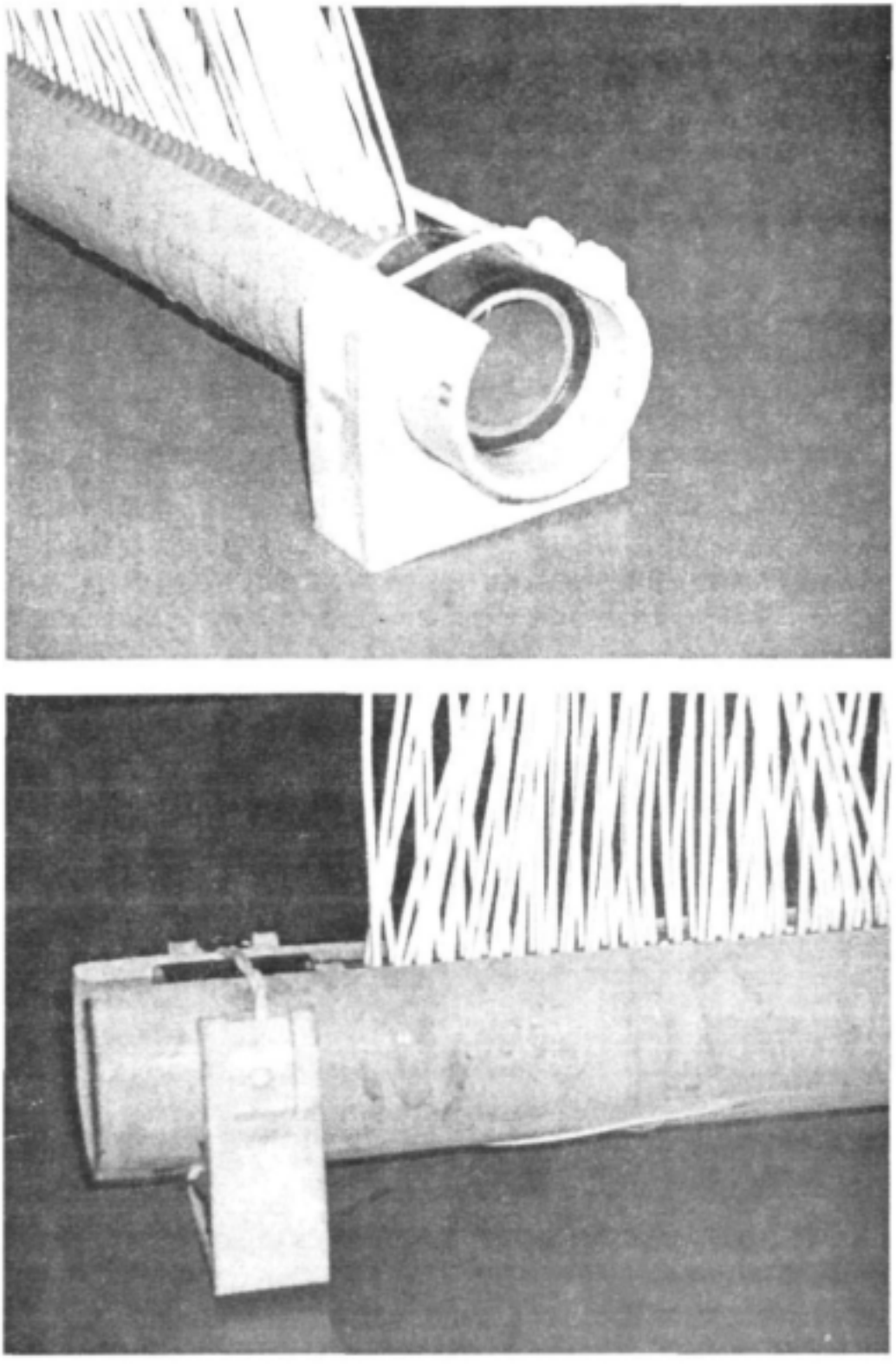


Figure 2.13: Close-up views of a predrilled manifold and the mould arrangement used ot encase equally spaced capillary membranes.

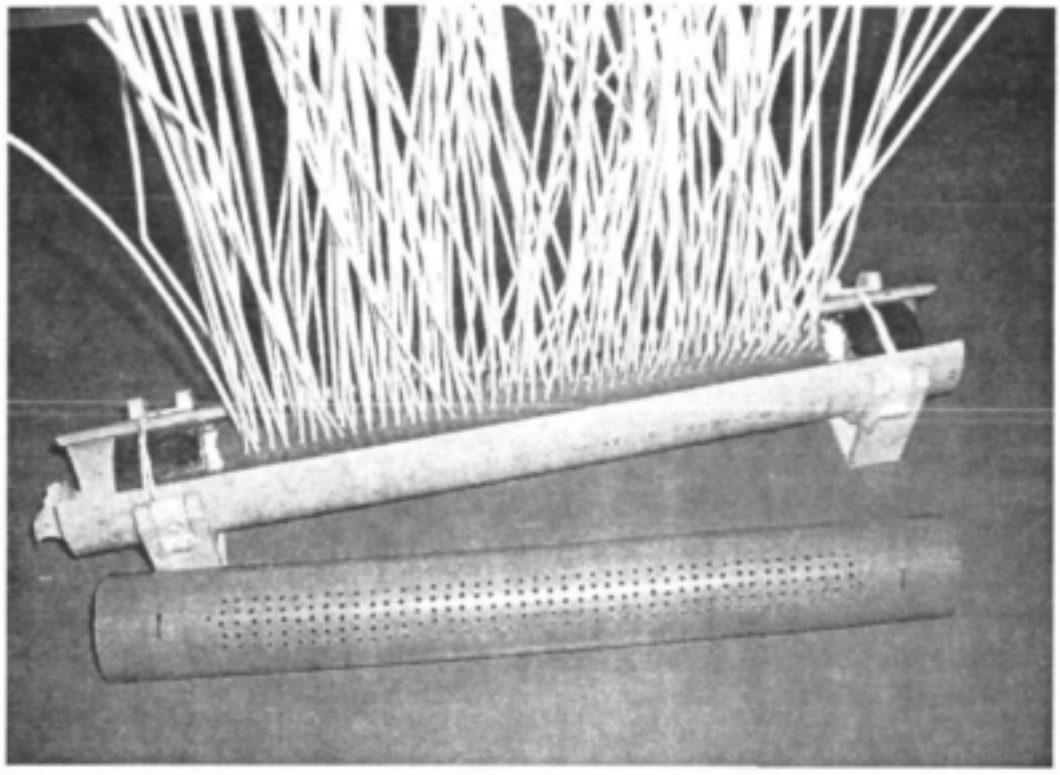


Figure 2.14: A further view of the casting mould and a pre-drilled manifold.

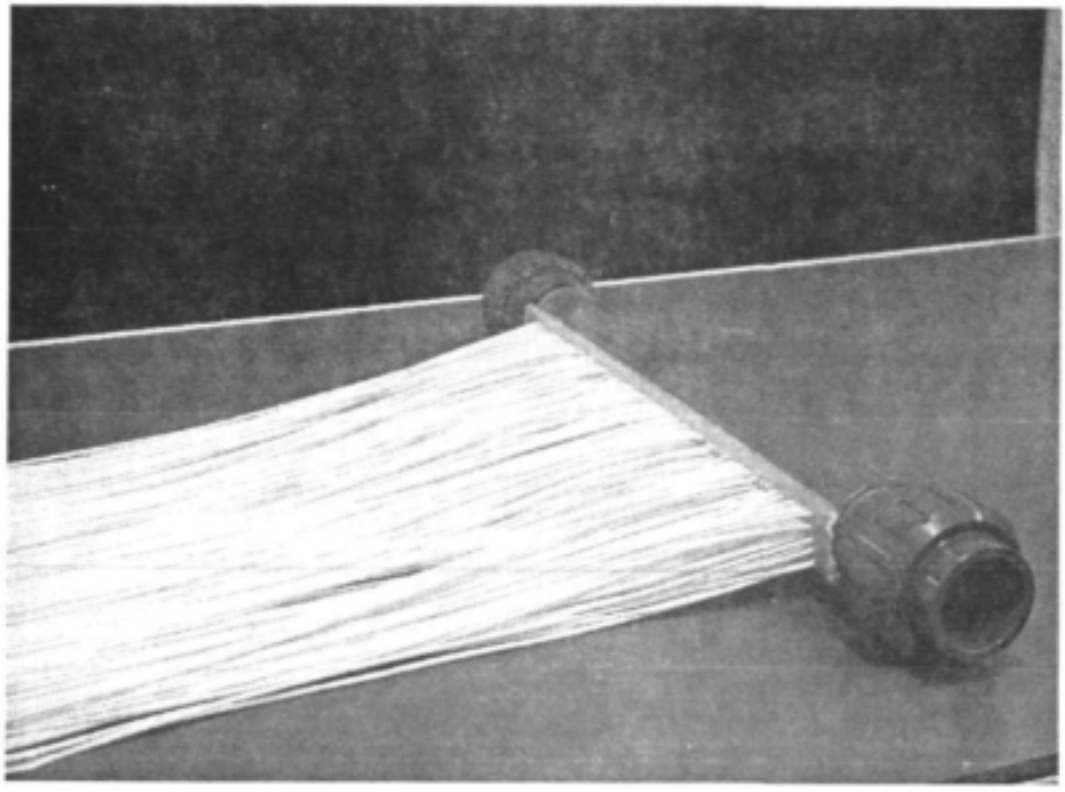


Figure 2.15: Single-manifolded filter element, complete with couplings.

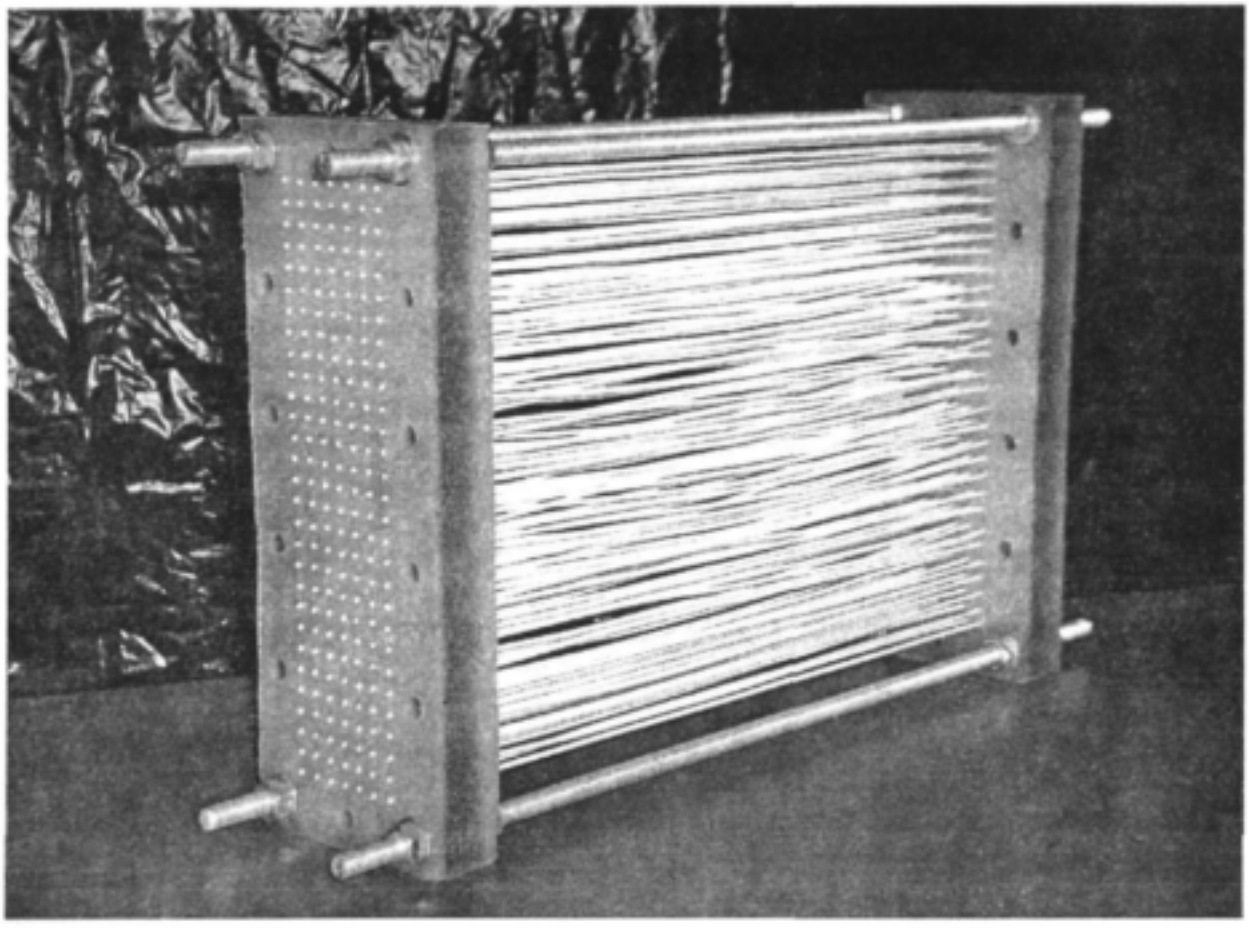


Figure 2.16: Equally spaced capillary membranes in a bioreactor, embeded into expoxy-urethane manifold-sheets.

3 Study of gas transport in transverse-flow module configurations

This section concerns the transport of gases across capillary membranes and the establishment of mass transport correlations for oxygenation, deoxygenation and carbonation for the reactors developed. Derivation of the mass transport correlations used and sample calculations may be found elsewhere.[80]

The membranes were orientated transversely to the flowing liquid stream in the reactors under study. Liquid was fed through the centre channel of the transverse-flow membrane system and therefore across the outside of the membranes. The liquid could either be recycled back to a feed reservoir, or pass through the module only once. Gas was pressurised into the membrane lumen from a gas cylinder. The gas could enter the module in either dead-end or in flowing mode (Figure 3.1). In dead-end mode only the pressure had to be controlled, whereas in flowing mode the linear flow velocity of the gas and the pressure had to be controlled.

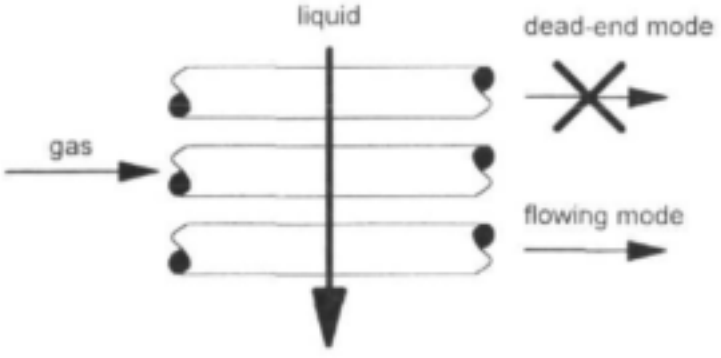


Figure 3.1: Illustration of the principle of flowing and dead-end modes of gas flow, and transverse-flow of liquid.

Dissolved oxygen concentration was measured by means of an oxygen selective electrode. Concentration levels of dissolved CO_2 was measured indirectly through pH and alkalinity measurements.

Oxygenation experiments were conducted with both pure oxygen and compressed air, under the following operating conditions:

- liquid once-through – gas dead-end;
- liquid once-through – gas flowing; and
- liquid recycle – gas dead-end.

Deoxygenation was accomplished by passing a N_2 sweep gas through the membrane lumens while liquid flowed in the once-through mode.

For carbonation, CO_2 was supplied in dead-end mode, while water was again flowing in once-through mode.

3.1 Dimensionless mass transfer correlations

Mass transfer coefficients are usually presented in dimensionless form by exponential correlations:

$$Sh = c \cdot Re^{m} \cdot Sc^{n} \cdot a^{p} \cdot b^{q} \cdot N^{r} \quad \text{(for transverse flow)} \qquad (1)$$

where:
Sh = Sherwood number = $K \cdot d^{*}/D$
Re = Reynolds number = $v^{*} \cdot d^{*}/\nu$
Sc = Schmidt number = ν/D
a = dimensionless transverse pitch = s_t/d_t
b = dimensionless longitudinal pitch = s_l/d_t
N = number of discs in module stack
m,n,p,q,r = constants
K = total mass transfer coefficient [m/s]
D = diffusion coefficient [m^2/s]
ν = kinematic viscosity [m^2/s]

d^{*} = characteristic diameter = $\left(\frac{4ab}{\pi} - 1\right)d_t$

v^{*} = characteristic velocity = $\frac{1}{\left(1 - \frac{\pi}{4ab}\right)} v_s$

v_s = superficial flow velocity [m/s]
d_t = outside tube diameter [m]

3.2 Derivation of theoretical mass transfer models

Theoretical mass transfer correlations were derived to determine the mass transfer coefficients for the different experimental set-ups investigated. All variables in these equations were determined experimentally, and the mass transfer coefficient (K) calculated.

3.2.1 Absorption of gas, with gas in flow-through mode[2]

$$K = -\frac{Q_L}{A}\left(\frac{1}{1 - \frac{Q_L}{Q_G H_c}}\right) \ell n \frac{C_{L2} - C_2^{*}}{C_{L1} - C_1^{*}} \qquad (2)$$

where:

K	overall mass transfer coefficient [m/s]
Q_L, Q_G	liquid, gas flow rates [m^3/s]
A	membrane surface area [m^2]
H_c	Henrys's law constant [-]
C_{L1}, C_{L2}	dissolved gas concentration in liquid streams (L1) entering and (L2) exiting the module [mg/L]
C_1^{*}, C_2^{*}	concentration of dissolved gas in the liquid streams entering and exiting the module which is in equilibrium with the gas phase [mg/L]

3.2.2 Removal of dissolved gas, with sweep gas[9]

$$K = -\frac{Q_L}{A}\left(\frac{1}{1 - \frac{Q_L}{Q_G H_c}}\right) \ell n \frac{C_{L2}}{\left(1 - \frac{Q_L}{Q_G H_c}\right) C_{L1} + \frac{Q_L}{Q_G H_c} C_{L2}} \qquad (3)$$

3.2.3 Absorption of gas, with gas in dead-end mode[80]

$$K = -\frac{Q_L}{A} \ell n \frac{C_{L2}}{C_{L1}} \qquad (4)$$

3.2.4 *Absorption of gas, with gas in dead-end mode and liquid in recycle mode*[80]

$$K = -\frac{Q_L}{A} \ln\left(1 - \frac{V}{Q_L} X\right) \qquad (5)$$

where

V volume of liquid reservoir [m^3]

X slope of $\frac{C_{L1}(0) - C^*}{C_{L1}(t) - C^*}$ vs. time

3.3 Development of suitable membrane structure and drying procedures

The initial polysulphone (PSf) capillary membranes used had a well-defined internal skin layer, a substructure consisting entirely of microvoids that open into the membrane periphery. These membranes had not external skin layer and were especially developed for application in a certain bioreactor, suitable for the immobilization of fungal-type micro-organisms.[65,79]

All mass transfer coefficients obtained in different transverse flow arrangements with these skinless membranes were of the 10^{-6} m/s order of magnitude. It was believed that water penetration into the macrovoids (diameter of void openings on membrane outside ~15μm) is responsible for the low mass transfer rates. From this it was concluded that the mass transfer rates could be improved by changing the membrane structure. Therefore, membranes with a skin on both sides and a sponge-like substructure were produced.

PSf is a hydrophobic membrane material. Membranes must either be kept wet or dried from solutions of very low surface tension to prevent the nano-porous pore structures of the membranes being destroyed as result of capillary forces during solvent evaporation. One approach to maintain the integrity of membrane pores is to treat the membranes with glycerol prior to drying. However, this was thought to be another reason for reduced mass transfer rates; the membrane pores and internal passages were probably filled with glycerol as a result of the treatment step prior to drying. An alternative drying procedure was proposed in which the membranes were soaked in methanol instead of glycerol. Since methanol has a relatively low surface tension and is very volatile, it will evaporate from within the membrane structure and pores and leave them filled only with air.

Mass transfer rates obtained with (▲) double skinned membranes was higher than those obtained with (◆) skinless membranes, when tested at equal trans-membrane pressures (TMP). Not even by raising the TMP across the skinless membrane to (■) 50kPa could mass transfer rates be increased above those achieved with double skinned membranes at TMP=10kPa (Figure 3.2).

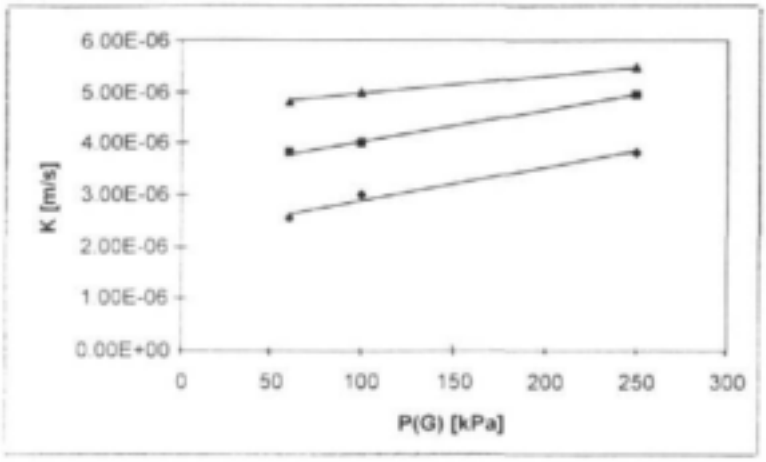


Figure 3.2: Mass transfer coefficients (K) as a function of gas pressure (P_G) to show the effect of membrane structure on mass transfer rates.
▲: double skinned, TMP=10kPa,
■: skinless, TMP=50kPa,
◆: skinless, TMP=10kPa.

Low mass transfer rates were obtained from (▲) glycerol-dried double skinned membranes. Membranes of the same structure, dried with (✖) methanol, and thus having air filled pores, yielded much higher mass transfer rates, even at lower TMP (Figure 3.3).

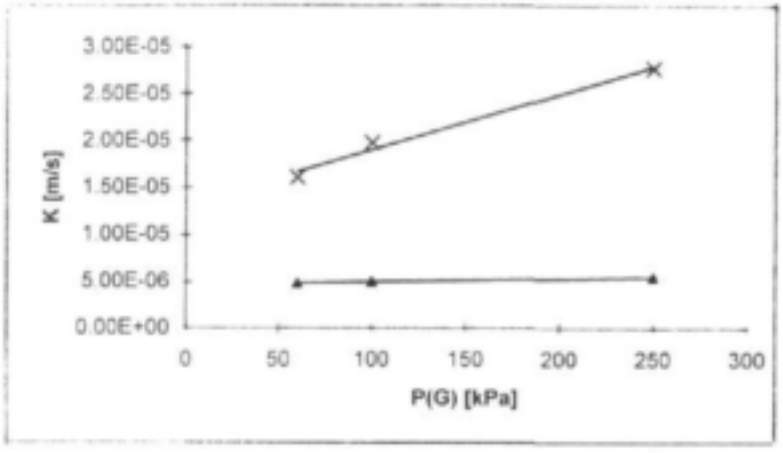


Figure 3.3: Mass transfer coefficients (K) as a function of gas pressure (P_G) to show the effect of drying procedure on mass transfer rates for double skinned membranes. (▲: glycerol, TMP=10kPa, ✖: methanol, TMP=5kPa)

From the above results, it was concluded that double skinned UF membranes dried with methanol, and thus having air-filled pores, was more suitable for use in gas transfer operations, than the skinless membranes with their large-diameter outer-pores. The double skinned UF membranes dried from methanol were used in all further experiments.

3.3.1 Coating

It was thought that by coating the membranes with a thin layer of silicone rubber, it would be possible to apply higher TMP's without bubbles forming on the membrane surface, and that this would allow higher mass transfer rates to be achieved.

Silicone rubber coated membranes could be pressurized up to a pressure of 60 kPa before bubbles started to form on the surface, compared to a maximum pressure of 20kPa for uncoated membranes. Thus, coating the membranes with a thin layer of silicon rubber was successful in reducing the membrane bubble-pressure and allowing a higher TMPs to be used during mass transfer operations.

The suitability of Pebax® (Atochem Inc. Polymers Division, New Jersey), a polyamide-polyether block copolymer, was also investigated as a coating material. A membrane coated with a (✖) 10% silicone rubber solution yielded higher mass transfer rates when tested at TMP=50kPa, than an (◆) uncoated membrane for which the maximum pressure was 20kPa (Figure 3.4). Pebax®-coated membranes (●), tested at TMP=50kPa yielded even higher mass transfer rates, and the TMP can still be increased further. So it was concluded that Pebax® is a suitable material with which to coat membranes in order to increase mass transfer rates.

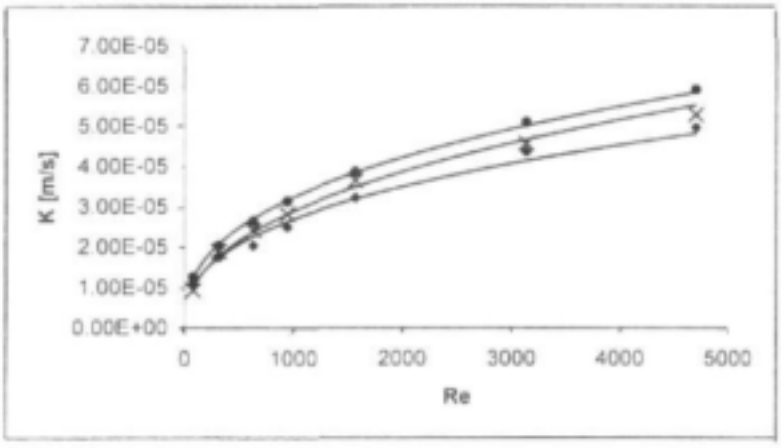


Figure 3.4: Mass transfer coefficients (K) as a function of Re number to show the effect of different coatings on mass transfer rates.
●: Pebax®, TMP=50kPa,
✖: 10% SiR, TMP=50kPa,
◆: uncoated, TMP=10kPa

3.3.2 *Final selection of membranes*

From the above discussion it was concluded that a double skinned membrane yielded better mass transfer results than skinless membranes, and this structure was therefore used in all further experiments. Membranes were dried according to the methanol technique and coated with a Pebax® layer on the outer surface.

Permeability of double skinned, methanol dried, Pebax® coated membranes for CO_2 and O_2 were determined. It was found that these membranes exhibit a higher permeability for CO_2 ($5.06 \cdot 10^{-11}$ $m^3/m^2 \cdot s \cdot Pa$) than for O_2 ($6.59 \cdot 10^{-12}$ $m^3/m^2 \cdot s \cdot Pa$).

3.4 Experimental mass transfer results

Experiments were conducted to determine the effect of operating conditions (liquid flow rate (Q_L), gas pressure (P_G), trans-membrane pressure (TMP), gas in dead-end or flowing mode, and liquid in once-through or recycle mode) and design parameters (cross/parallel packing, in-line/staggered packing, transverse pitch (s_t) and longitudinal pitch (s_l)) on mass transfer rates in the transverse flow configuration.

The general form of the notation to describe the packing arrangement of membrane wafers in transverse-flow module: **XYs_t, s_l/D,N** where:

X	cross (C) or parallel (P) packing
Y	in-line (I) or staggered (S) arrangement
S_t	transverse pitch (3 or 6 mm)
S_l	longitudinal pitch (3 or 6 mm)
D	diameter of central channel (3 or 5 cm)
N	number of discs in stack

3.4.1 *Variation of mass transfer coefficient with number of discs*

From Figures 3.5a and 3.5b it can be seen that the mass transfer coefficients became stable and independent of the number of grids after about the 15th row.

3.4.2 *Individual mass transfer resistances*

The total resistance to mass transfer consists of the individual resistances in the membrane, liquid and gas phases. The mass transfer resistance of the membrane is a function of the membrane material and structure and was determined through permeability measurements. The gas phase resistance was found to be negligible, while the magnitude of the liquid-film resistance was calculated to make out more than 99% of total resistance. The overall mass transfer rate is thus controlled by the liquid-film mass transfer coefficient.

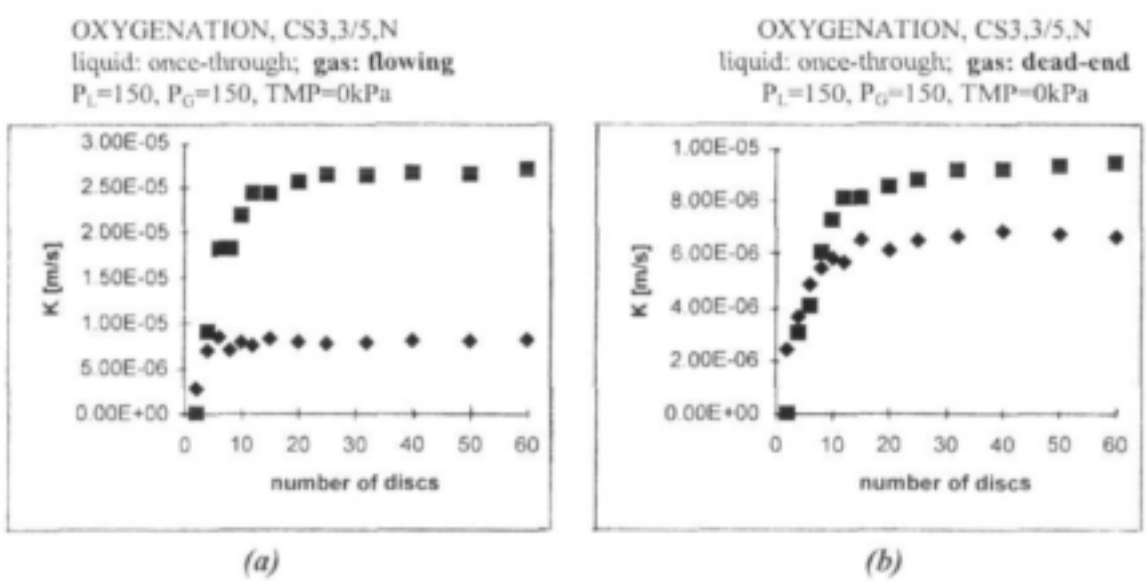


Figure 3.5: Variation of the overall mass transfer coefficient with the number of discs for gas in the (a) flowing mode and (b) dead-end mode of operation.
(◆: Re=60.5; ■: Re=302.7).

3.4.3 *Effect of gas pressure and trans-membrane pressure*

Generally, it is expected that the mass transfer coefficient will increase with increase in gas pressure, since the driving force for gas transfer arises from the concentration gradient across the membrane. A change in gas pressure also caused a change in the saturation concentration (C^*), and thus in the concentration gradient.[11,12] An increase in gas pressure caused an increase in the mass transfer rate (Figure 3.6).

The driving force for gas transfer came from the concentration gradient between the gas and the liquid phases across the membrane and the mass transfer increased with TMP (Figure 3.7).

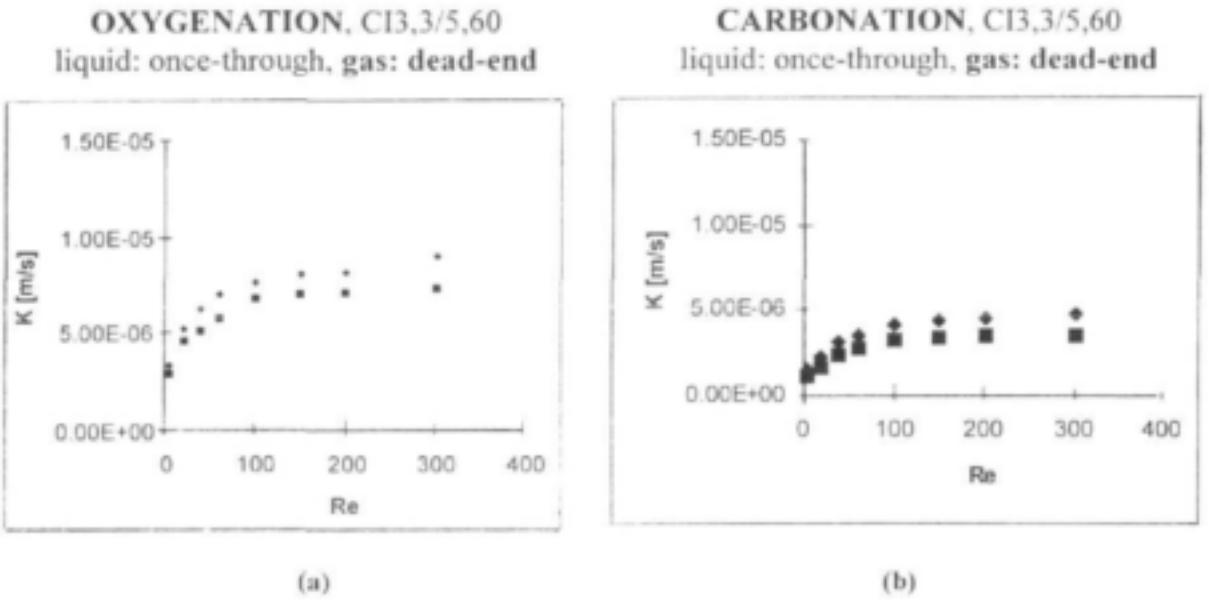


Figure 3.6: Effect of gas pressure (P_G) on mass transfer coefficients for (a) oxygenation (gas dead-end), (b) carbonation (gas dead-end).
(◆: P_G=150kPa, ■ P_G=60kPa)

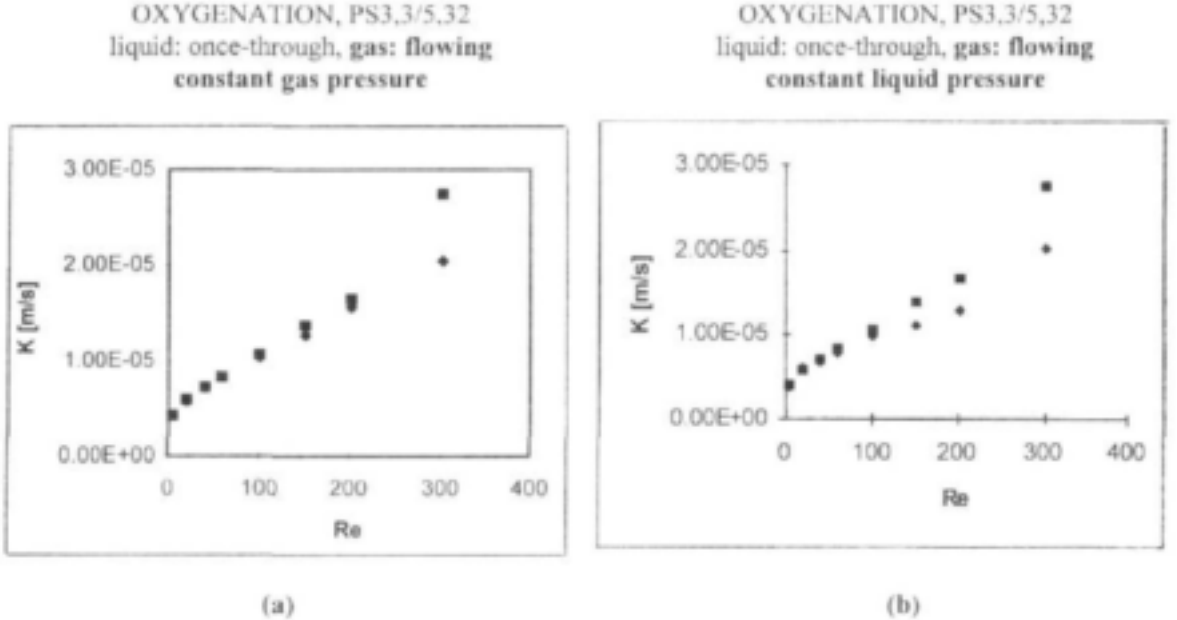


Figure 3.7: Effect of TMP on mass transfer coefficients for:
(a) constant gas pressure, varying liquid pressure
◆: P_L=150kPa, P_G=150kPa, TMP=0kPa, ■ P_L=50kPa, P_G=150kPa, TMP=100kPa
(b) constant liquid pressure, varying gas pressure
◆: P_L=50kPa, P_G=50kPa, TMP=0kPa, ■ P_L=50kPa, P_G=150kPa, TMP=100kPa.

3.4.4 Gas in flowing vs. dead-end mode

The mass transfer results obtained for flowing and dead-end modes of flow were studied (Figure 3.8). It seems that in the case with gas in dead-end mode, the mass transfer coefficient

reached an asymptotic value, which was much lower than the maximum possible value determined by the membrane permeability ($3.4 \cdot 10^{-2}$m/s for O_2 and $9.5 \cdot 10^{-3}$m/s for CO_2), whereas in the case of gas in flowing mode, the mass transfer coefficient kept on increasing with Re number over the range investigated.

The lower mass transfer performance of the membrane system when the gas was fed in dead-end mode was attributed to water vapour that possibly condensed and accumulated in the structure of the fibres, and oxygen or carbon dioxide having to diffuse through this phase. With gas in the flowing mode, water vapour was readily removed from the fibres and swept away.

Back-diffusion of nitrogen from the water was another phenomenon which could also have contributed to the decreased performance during dead-end mode of operation.

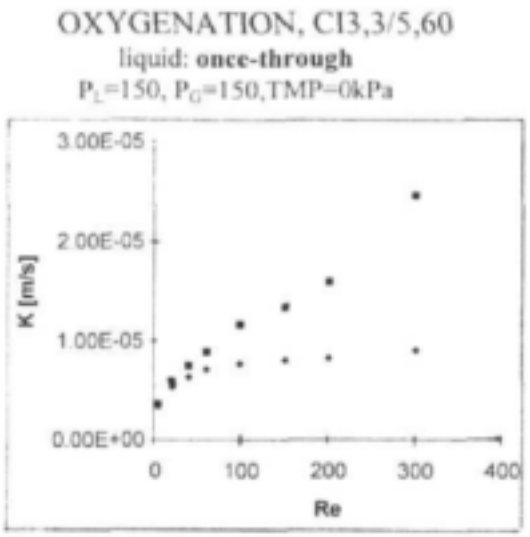


Figure 3.8: Oxygenation mass transfer results showing the difference between gas in ■ flowing and ◆ dead-end operating modes.

3.4.5 *Liquid in once-through vs. recycle mode*

When mass transfer coefficients obtained with liquid in recycle mode were compared to coefficients for liquid in once-through mode (Figure 3.9), it was found that the recycle mode yielded lower transfer rates. This may have been because of a loss of dissolved oxygen from the reservoir.

3.4.6 *Effect of cross vs. parallel packing of membrane fibres*

Albeit small, Figure 3.10 shows a benefit in mass transfer rates obtained with the cross-packed configuration. The higher mass transfer rates obtained with the cross-packed configuration were ascribed to a higher degree of turbulence created by this packing configuration.

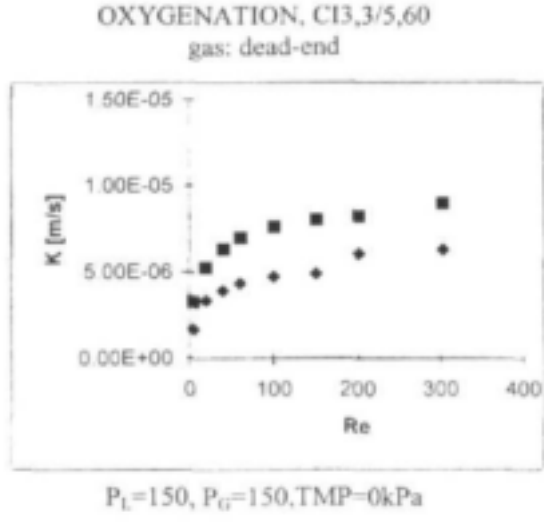


Figure 3.9: Mass transfer coefficients as a function of Re number for liquid in ◆ recycle mode and ■ once-through mode.

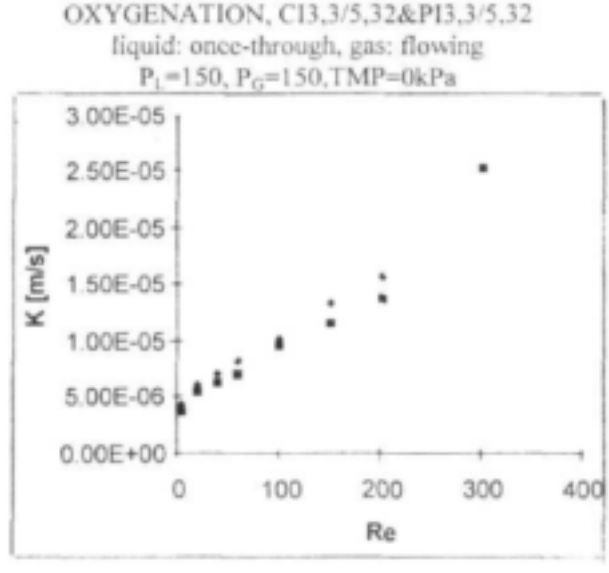


Figure 3.10: Overall mass transfer coefficient as a function Re number to show the effect of ◆ cross and ■ parallel packing of membrane fibres.

3.4.7 *Effect of in-line vs. staggered packing of membrane fibres*

The staggered packing gave slightly higher mass transfer coefficients than the in-line packing (Figure 3.11).

3.4.8 *Effect of transverse pitch*

A module with a 3mm transverse pitch yielded higher mass transfer coefficients than a module with a 6mm pitch (Figure 3.12). Futselaar[28] suggested a value for the transverse pitch of between 1.25 and 2.5 times the fibre diameter, that is, between 2 and 4mm for a fibre diameter of 1.6mm.

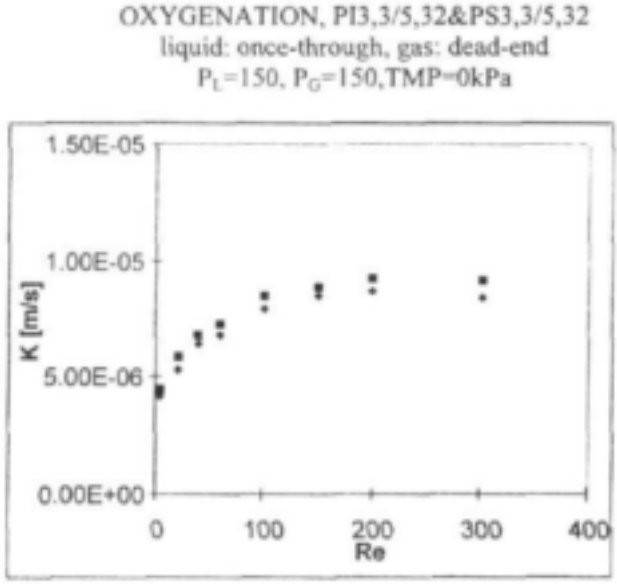


Figure 3.11: Overall mass transfer coefficient as a function Re number to show the effect of ◆ in-line and ■ staggered packing of membrane fibres.

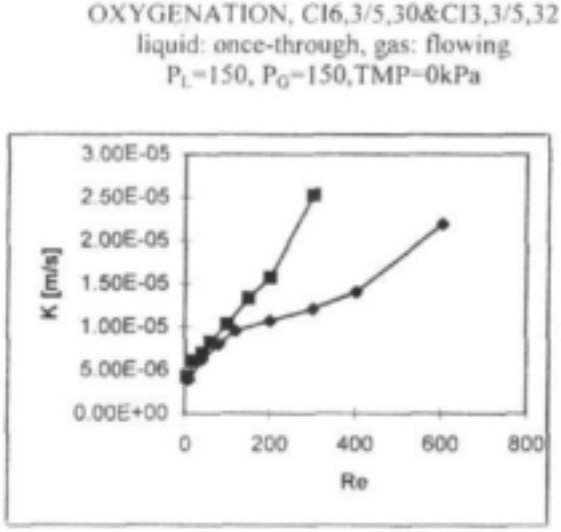


Figure 3.12: Overall mass transfer coefficient as a function of Re number to show the effect of transverse pitch on mass transfer rates.
◆: s_t=6mm, ■: s_t=3mm

1.1.1 Longitudinal pitch

A 3mm pitch yielded higher mass transfer coefficients than a 6mm pitch (Figure 3.13).

Futselaar[28] suggested a value for the longitudinal pitch of between 1 and 3 times the fibre diameter, that is between 1.6 and 4.8mm for a fibre diameter of 1.6mm.

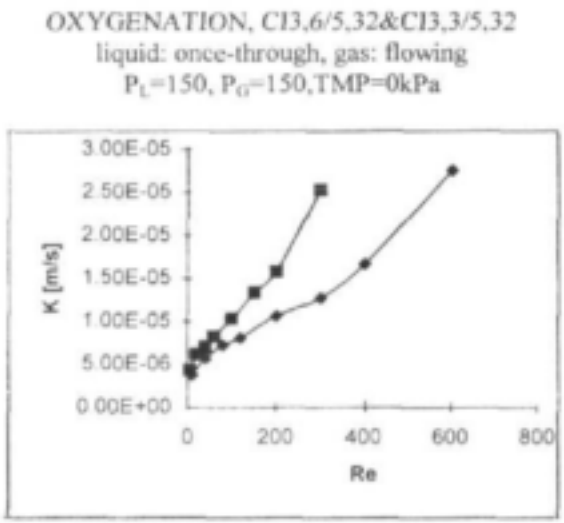


Figure 3.13: Overall mass transfer coefficient as a function Re number to show the effect of longitudinal pitch on mass transfer rates. ◆: s_l=6mm, ■ s_l=3mm

3.4.10 Transverse vs. axial flow

The performance of the transverse flow module was compared to results obtained from a conventional capillary fibre module in axial flow configuration to judge whether the transverse flow configuration is successful in reducing liquid phase resistance and enhancing mass transfer rates. Higher mass transfer coefficients were indeed obtained in the transverse flow module for corresponding Re numbers (Figure 3.14).

3.4.11 Dimensionless correlations

All the experimental data that were obtained in the different gas transfer operations were combined and general dimensionless correlations of the form $Sh = c \cdot Re^m \cdot Sc^n \cdot a^p \cdot b^q$ were derived (Table 1).

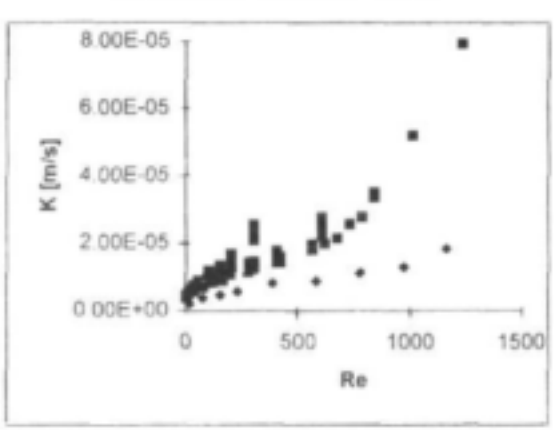


Figure 3.14: Variation of the overall mass transfer coefficient with Re number for ◆ axial and ■ different transverse flow configurations.

Table 1: Transverse flow mass transfer correlations derived for different gas transfer operations.

Gas transfer operation	Mass transfer correlation	Validity range	R^2
oxygenation			
liquid recycle, gas dead-end	$Sh = 0.396 \cdot Re^{0.26} \cdot Sc^{0.33} \cdot a^{0.52} \cdot b^{0.12}$	Re<300	0.94
liquid once-through, gas dead-end	$Sh = 0.167 \cdot Re^{0.26} \cdot Sc^{0.33} \cdot a^{1.39} \cdot b^{0.94}$	Re<600	0.97
liquid once-through, gas flowing	$Sh = 0.139 \cdot Re^{0.49} \cdot Sc^{0.33} \cdot a^{0.85} \cdot b^{0.7}$	Re<850	0.94
deoxygenation			
liquid once-through, gas flowing	$Sh = 0.231 \cdot Re^{0.28} \cdot Sc^{0.33} \cdot a^{0.97} \cdot b^{0.89}$	Re<850	0.96
carbonation			
liquid once-through, gas dead-end	$Sh = 0.101 \cdot Re^{0.24} \cdot Sc^{0.33} \cdot a^{1.61} \cdot b^{1.03}$	Re<600	0.97

3.4.12 Oxygenation with pure oxygen vs. air

A slight decrease in mass transfer performance was observed when water was oxygenated using air instead of pure oxygen. This was ascribed to the oxygen partial pressure being lower for air than pure oxygen at the same total gas pressure.

A disadvantage of using air for oxygenation was that higher total pressures were needed than in the case of pure oxygen to obtain the same oxygen partial pressure in the fibre lumens. The use of pure oxygen has the further advantage that less membrane area was required for transfer of a given quantity of oxygen, because of the higher mass transfer rates that could be achieved.

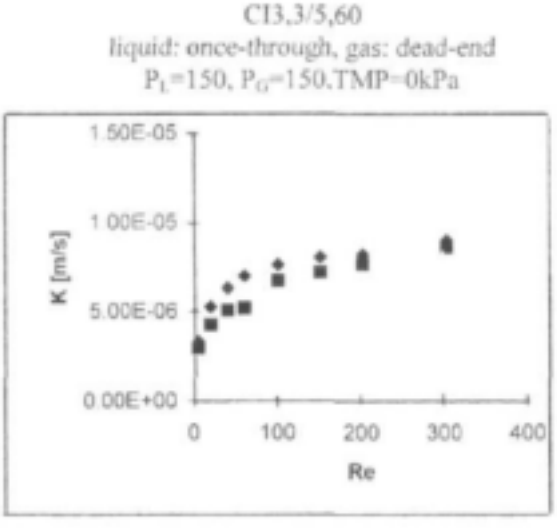


Figure 3.15: Mass transfer coefficient as a function of Re number for oxygenation with ◆ pure oxygen and ■ air.

3.4.13 Carbonation

When mass transfer coefficients for carbonation were compared to that for oxygenation under the same conditions, the oxygen transfer rates were higher than that for CO_2. A possible explanation for the apparently lower CO_2 transfer rates was the method by which CO_2 concentrations were determined. Since samples of the carbonated water were taken, and measurement was not on-line, there may have been a loss of volatile CO_2 between sampling

and measurement. The indirect method by which CO_2 concentrations were determined, might also have introduced large errors.

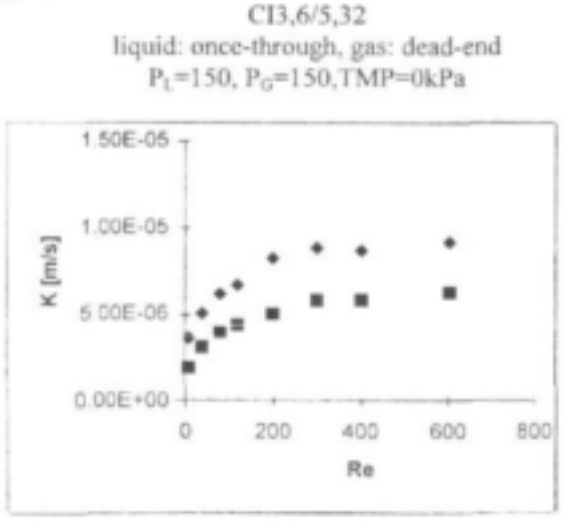


Figure 3.16: Overall mass transfer coefficient as a function of Re number to compare the mass transfer efficiency for ◆ oxygenation and ■ carbonation operations.

3.5 Pressure drop and friction coefficients

The total pressure drop across a tube-bank is a function of the liquid flow velocity, the arrangement of tubes in the bank, the number of rows in the bank and the physical properties of the fluid:

$$\Delta P = f(v^*, s_t, s_l, d^*, N, \nu)$$

A dimensionless flow friction coefficient (ξ) is associated with the pressure drop across a tube bank, and was defined as:

$$\xi = \frac{\Delta P}{N\left(\frac{1}{2}\rho v^{*2}\right)} \qquad (3.1)$$

3.5.1 Effect of packing configuration

Figure 3.17 shows that the packing arrangement, that is whether the fibres are in a crossed or parallel configuration, or in-line or staggered configuration, does not have an influence on the pressure drop across the module, or on the friction coefficients, as these data points are superimposed and fall on the same line.

3.5.2 Effect of transverse and longitudinal pitches

Figure 3.18 shows the effect of the transverse pitch on the pressure drop across the module and the friction coefficients. A smaller value (3mm) causes a larger pressure drop across the module for corresponding Re, while the friction coefficient is larger for the 6mm pitch than for the 3mm pitch. The same results were observed for the longitudinal pitch.

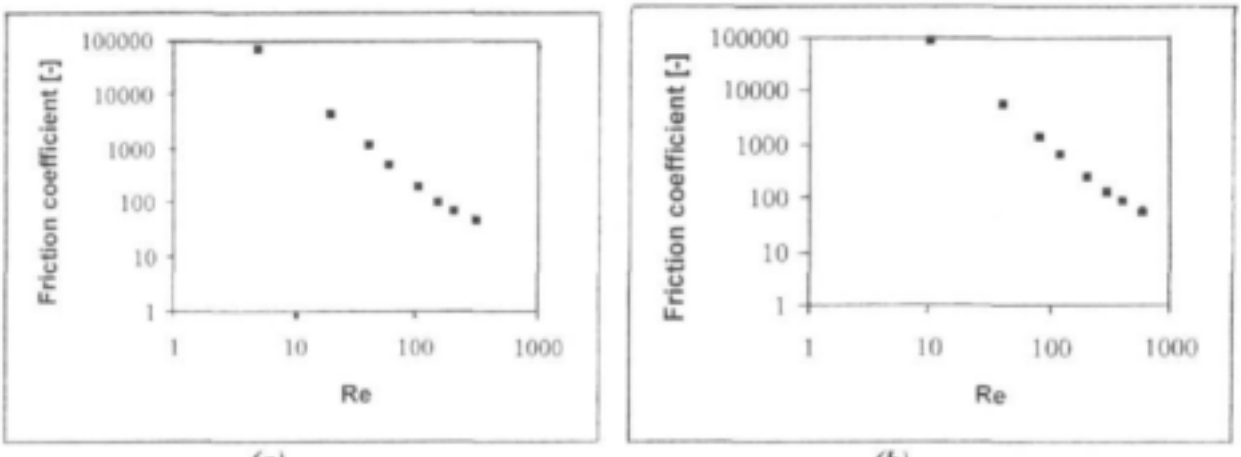


Figure 3.17: Friction coefficients (Ξ) as a function of Re number for:
(a) ◆ crossed and ■ parallel configurations, and
(b) ◆ in-line and ■ staggered configurations.

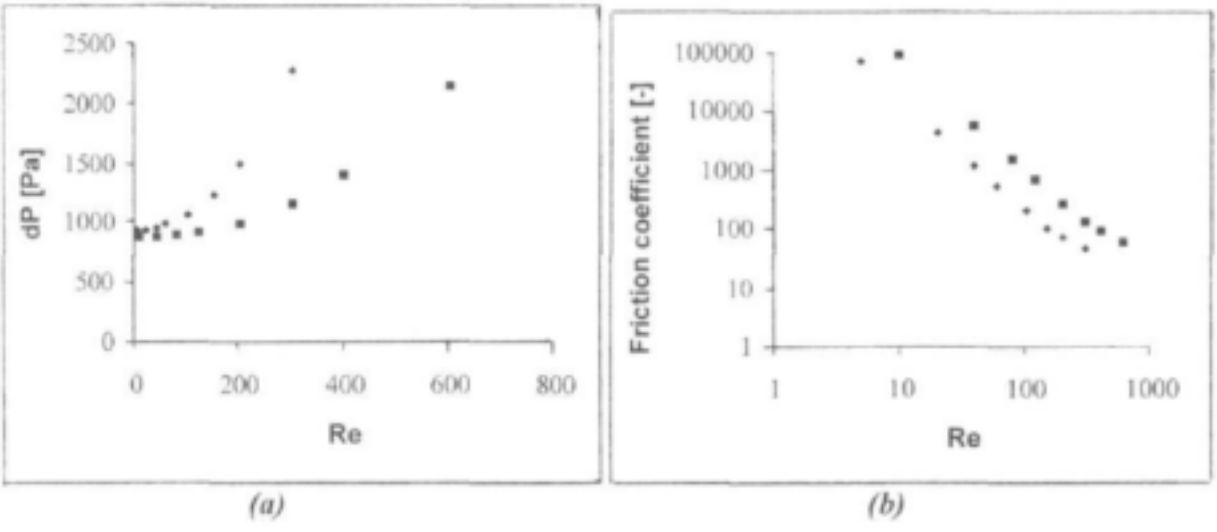


Figure 3.18: (a) Headloss across the module and (b) friction coefficients (Ξ) as a function of Re number to show the effect of transverse pitch (◆: s_t=3mm, ■: s_t=6mm).

3.5.3 Effect of number of discs

The pressure drops across a module and the friction coefficients varied with the number of discs in a stack. As expected, an increase in headloss (Figure 3.19a) and in friction coefficients (Figure 3.19b) were observed as the number of discs increased.

3.5.4 Dimensionless flow friction correlation

Friction coefficients were calculated from the measured pressure drops, and a dimensionless correlation which relates the friction factor to the liquid flow velocity, and transverse and longitudinal pitches, was derived:

$$\xi = 47948.14 \cdot Re^{-1.999} \cdot a^{2.387} \cdot b^{3.387} \quad (3.2)$$

This correlation, together with equation 3.1 can now be used to predict pressure drops across parallel- and cross-packed, in-line and staggered tube banks.

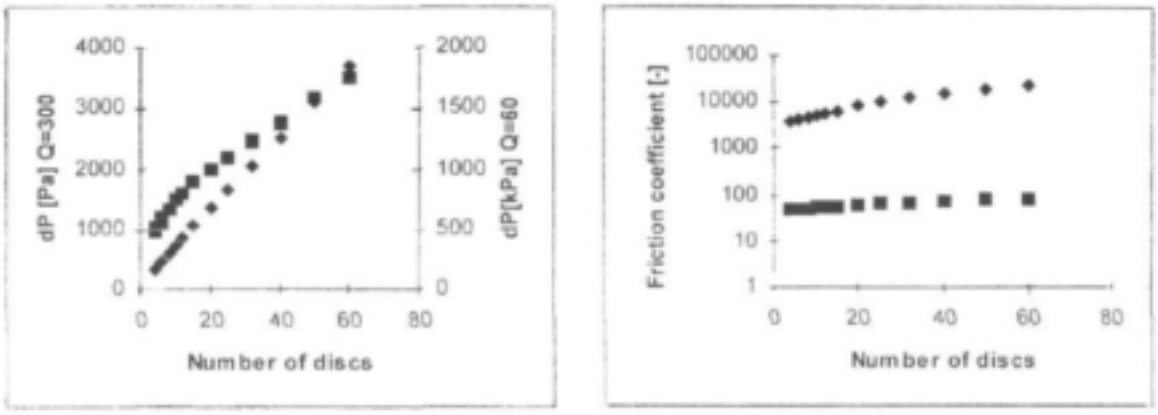


Figure 3.19: (a) Pressure drops across the module and (b) friction coefficients (ξ) as a function of the number of discs in a module stack.
◆: Re=60.5, ■: Re=302.7

3.6 Conclusions

- The calculated liquid film resistance accounted for more than 99% of the total resistance to mass transfer and therefore, transfer of gas through the liquid boundary layer was the rate-determining step.
- The new transverse-flow module configuration was successful in enhancing mass transfer rates, compared to that obtained with the conventional axial flow configuration. Cross-packed and staggered configurations both yielded slightly higher mass transfer rates than parallel and in-line configurations.
- Mass transfer coefficients measured in a module became independent of the number of grids after about the 15th row.
- Higher mass transfer rates were obtained with smaller transverse and longitudinal pitches.
- The application of larger gas pressures and TMPs can increase mass transfer rates.
- A decrease in mass transfer rates was observed when using air instead of pure oxygen to oxygenate water.
- With gas in the flowing mode, the mass transfer coefficient keeps on increasing with Re number over the range investigated. However, in the case of gas in dead-end mode, the mass transfer coefficient reaches an asymptotic value.
- These correlations can be used to design transverse flow modules for use as gas-liquid contactors.

4 Biotechnological applications

Transverse-flow type modules have great potential in biotechnological applications, where they may be used, not only as filtration and gas transport devices, but also for the immobilisation of bioactive species. One such example would be the gradostat membrane reactor.[81]

4.1 Development of gas stripping reactors

4.1.1 Module development concerns

Early experience using the membrane gradostat 'HARP' reactor configuration (Figure 2.15), deemed it necessary to radically redesign the module housing. The reason for this were centred on preventing leakages between the different compartments. Previous experience using the gradostat 'HARP' reactors showed that leakage between compartments resulted in contamination of the feed solution and feed depletion which affected the biofilm nutrient gradient. The reactor consisted of three chambers; an outer chamber to contain the media that would flow through the membranes, an inner chamber that would house 280 skinless PSf membranes, and a third media outlet chamber that could be shut off to facilitate dead-end flow. All three chambers were made of perspex and sealed with silicon rubber and perspex dissolved in acetone. The reason for using perspex rather than glass was to allow expansion of the plates at 37°C (the operating temperature used in the first application of the new module), to better withstand the pressure due to dead-end flow, and due to the need to disassemble if necessary. A schematic diagram of the redesigned manifold is indicated in Figure 4.1.

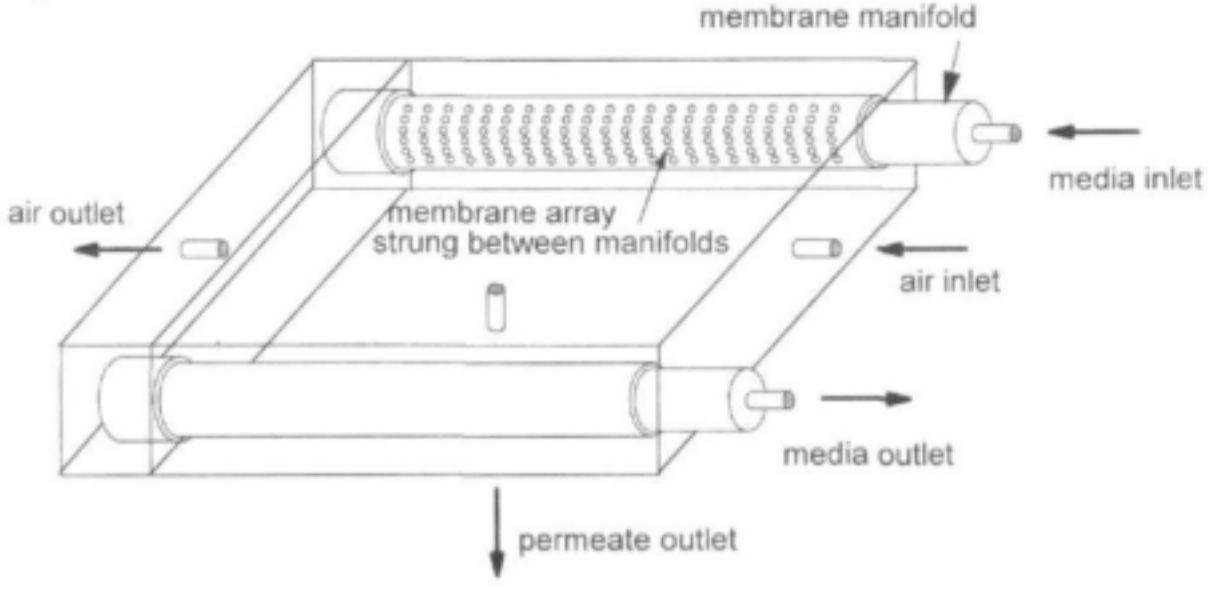


Figure 4.1: New manifold design for the* HARP *membrane reactor configuration (membranes themselves not indicated).

4.1.2 Membrane gradostat reactor

The new format of the membrane reactor was initially built for manganese peroxidase (MnP) production. This new larger membrane module was developed because large quantities of MNp were required and flask cultures were known to be unpredictable.

Operational characteristics of te new module for MnP production

Air inlet and outlet pipes were included in the chamber encasing the membranes to allow oxygen flow over the membranes during fungal growth. Air into the reactor was passed through a humidifier so as to prevent the membranes from drying. A 0.2μm filter was attached to the air outlet pipe to prevent contamination. A collection pipe was also inserted into the inner chamber so that the permeate from the membranes containing MnP could be collected. The reactor was sterilised by passage of a 4% formaldehyde solution through the reactor overnight. The formaldehyde was then drained and the reactor was allowed to stand for approximately 30min. to allow the evaporation of most of the formaldehyde without drying the membranes. The reactor was then rinsed with 10 litres of autoclaved distilled water

Inoculation of the reactor was performed by filling the inner chamber with spores suspended in distilled water and allowing the spores to adsorb onto the outside of the membranes. This was done under low pressure conditions to prevent leakage of the chamber. The spore suspension was pumped by circulatory flow through the inner chamber for a period of 24h to allow maximum adsorption of spores to the membranes. Inoculation took place at room temperature. After 24h nitrogen-limiting growth medium was passed through the membranes until the two outer chambers were full. The media was then allowed to stand in the chambers and membranes for 24h to allow the spores to settle and begin to germinate, and to prevent washing of the spores off the membranes due to permeation.

Reactor productivity

With the development of the biofilm on the outside of the membranes, the fungus began to produce MnP. The thicker the biofilm, the more MnP was produced. The MnP that was produced was washed out with the permeate from the membranes. The permeate from the reactor was collected in a 1L Erelenmeyer flask and assayed for MnP activity every 24h. Once the MnP activity was high enough, the collected permeate would be freeze dried and stored at –20°C.

Disadvantage of the capillary membrane arrangement

The majority of biofilm was present around the lower membranes of the bioreactor. This indicated that even mass transfer was not being achieved across all the membranes. Permeate from the membranes near the top of the reactor was falling on the lower membranes thus affecting the operational gradients present.

4.2 Air-lift membrane bioreactors

One embodiment in which the transverse module could be used to effect dewatering of an aerobic bioreactor, is the air-lift reactor. In this application, air is introduced into a diffuser situated at the bottom of the packed-disc reactor (Figure 4.2). The rising action of the air and density differences caused water to sweep upwards through the reactor. The circulating water sweeps the membranes, thereby reducing the deposition of foulants onto the membranes. The air also supplies oxygen to the biomass. The reactor is dewatered by applying a vacuum to the membrane lumen. The excess oxygenated water goes back into the tank.

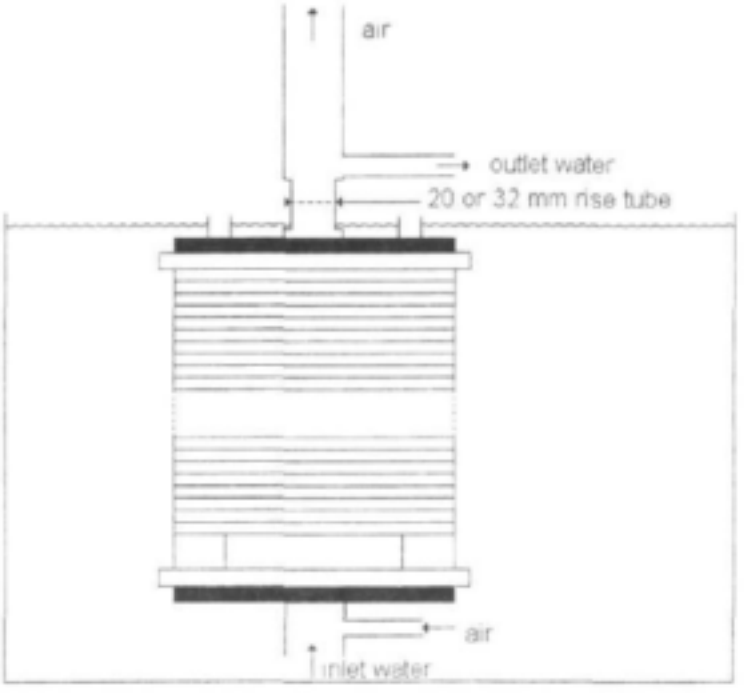
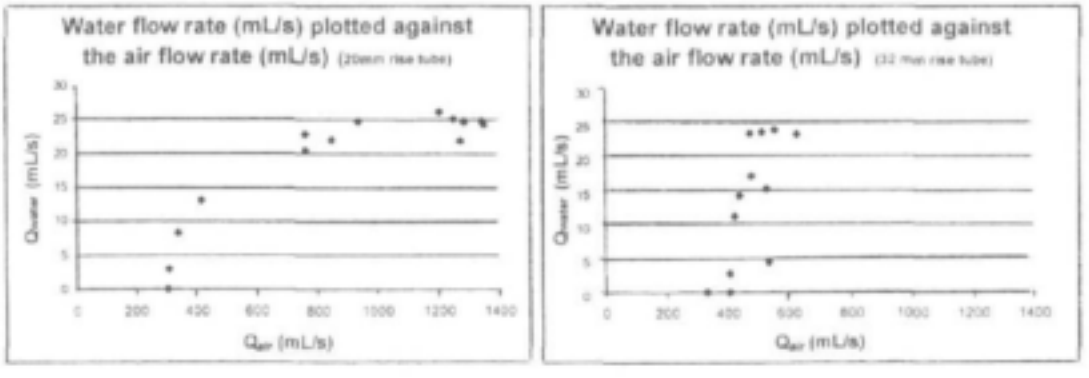


Figure 4.2: Schematic representation of one embodiment of the air-lift reactor used to determine water transport by rising air bubbles.



(a) *(b)*

Figure 4.3: Water transport rate (mL/s) as a function of air flow rate, with (a) 20mm diameter riser tube and a (b) 32mm riser tube.

The principle was never tested in a bioreactor application, as the membrane engineering group has no experience of operating such reactors. However, tests were conducted to determine the functioning air flow rate needed to obtain a certain outlet water flow rate to test the principle of air-lift reactor with Mark III discs..

This experiment was carried out within an air flow range of 300 mL/s to 1 400 mL/s and with 20 mm and 32 mm diameter riser tubes (Figure 4.3).

A schematic representation of the reactor that was constructed but never tested in a bioreactor application is shown in Figure 4.4. A coarse polyester foam filter, 10 pores per inch (PPI), was installed in the 110 mm breather tube at the top of the filter. This was to entrap aerosol

and simultaneously act as a biofilter, should low molecular mass organic fractions be carried from the reactor by small water droplets.

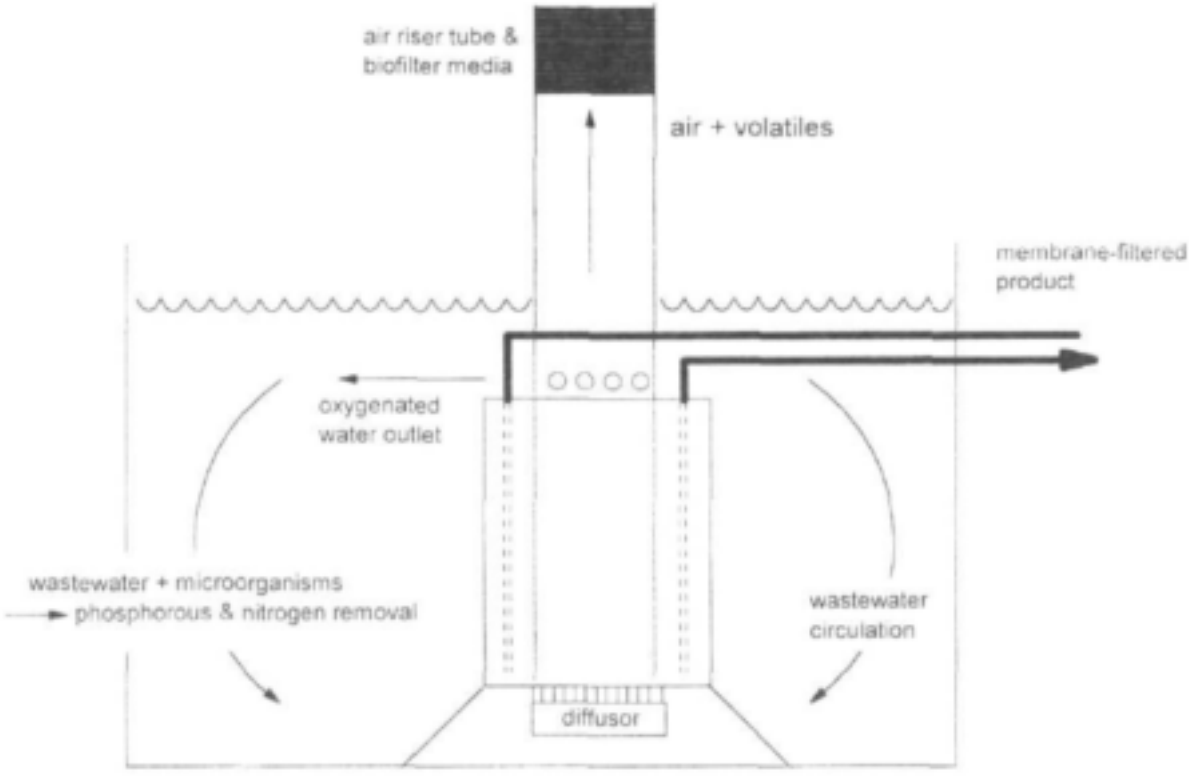


Figure 4.4: Schematic presentation of the submerged air-lift reactor principle.

5 Conclusions

- A centrifugal casting technique was developed to produce transverse flow membrane modules.
- Double skinned polysulphone capillary membranes were developed and found to yield better gas transfer than skinless membranes. By using an ethanol based drying technique, the mass transfer capability of the membranes could be improved further.
- Pebax® was found to be a more effective coating material for the membranes than silicone rubber.
- The permeability of the Pebax®-coated double skinned membranes towards O_2 and CO_2 was determined and it was found that the membrane was more permeable towards CO_2.
- The calculated liquid film resistance accounted for more than 99% of the total resistance to mass transfer and therefore, transfer of gas through the liquid boundary layer was the rate-determining step.
- The new transverse-flow module configuration was successful in enhancing mass transfer rates, compared to that obtained with the conventional axial flow configuration. Cross-packed and staggered configurations both yielded slightly higher mass transfer rates than parallel and in-line configurations.
- Mass transfer coefficients measured in a module became independent of the number of grids after about the 15^{th} row.
- Higher mass transfer rates were obtained with smaller transverse and longitudinal pitches.
- The application of larger gas pressures and TMP's can increase mass transfer rates.
- A decrease in mass transfer rates was observed when using air instead of pure oxygen to oxygenate water.
- With gas in the flowing mode, the mass transfer coefficient keeps on increasing with Re number over the range investigated. However, in the case of gas in dead-end mode, the mass transfer coefficient reaches an asymptotic value.
- These correlations can be used to design transverse flow modules for use as gas-liquid contactors.
- With increasing Re number, an increase in the pressure drop across a module, and an accompanying decrease in friction coefficients, were observed.
- A dimensionless correlation which relates the friction factor to the liquid flow velocity, and transverse and longitudinal pitches, was derived: $\xi = 47948.14 \cdot Re^{-1.999} \cdot a^{2.387} \cdot b^{3.387}$ This correlation can now be used to predict pressure drops across parallel and cross-packed, in-line and staggered transverse flow tube banks.

6 Recommendations

Many different types of membrane bioreactors have seen the light over the past few years and have found wide-spread application in the treatment of industrial and domestic wastewater and in bioconversion. Although the technology is reasonably young, strong evidence already exists that these versatile reactors outperform the more conventional aerobic and anaerobic type reactors with respect to the residual chemical oxygen demand and clarity of the final effluent.

This project was an initial attempt to provide a research tool to microbiologists to study potential applications in membrane bioreactor technology. When one considers the development of a new membrane bioreactor process and applications technology, it is clear that engineers cannot proceed without the assistance of microbiologists and *vice versa*. Such research should be approached as a team. However, the development of the system hardware (membranes, reactor configuration, operation and control) has to proceed to a point of semi-finalisation before any serious bioprocessing and the involvement of microbiologists on the process side can be considered. It is recommended that if future considerations are given to the development of membrane bioreactor technology, the work be partisioned into two stages: (a) membrane and systems development and process operation and (b) the development of the biotechnological protocol. The first stage should be conducted by engineers of different disciplines, but under the supervision of microbiologists knowledgeable of wastewater treatment. Stage two should be the responsibility of microbiologists, but be conducted with close co-operation of the engineering contingent that did the intial system's development work.

The information obtained through this study is directly applicable to immersed membrane bioreactors making use of membranes to supply oxygen in bubbless form to the biofilm immobilised on it. This class of membrane bioreactor are referred to as membrane aeration bioreactors and can be operated in anaerobic or aerobic modes of operation. Such reactors are highly efficient since the concortia of microorganisms that will develop in the reactor (free floating and immobilised) is much more diverse that that found in conventional systems.

7 References

1. RB Schaffer, FJ Ludzack, MB Ettinger, *Journal of the Water Pollution Control Federation*, 32(9) (1960), 939-941
2. Z Qi, EL Cussler, *Journal of Membrane Science*, 23 (1985), 321-332
3. LF Mockros, R Leonard, *ASAIO Journal*, 31 (1985), 628-633
4. P Côté, J-L Bersillon, A Huyard, G Faup, *Journal of the Water Pollution Control Federation*, 60(11) (1988), 1986-1992
5. M-C Yang, EL Cussler, *AIChE Journal*, 32 (1986), 1910-1916
6. W Kang, R Shukla, GT Frank, KK Sirkar, *Applied Biochem Biotech*, 18 (1988), 35-51
7. P Côté, J-L Bersillon, A Huyard, *Journal of Membrane Science*, 47 (1989), 91-106
8. M-C Yang, EL Cussler, *Journal of Membrane Science*, 42 (1989), 273-284
9. MJ Semmens, R Qin, A Zander, *American Water Works Association Journal*, 81(4), (1989), 162-167
10. AK Zander, MJ Semmens, RM Narbaitz, *American Water Works Association Journal*, 81(11) (1989), 76-81
11. T Ahmed, MJ Semmens, *Journal of Membrane Science*, 69 (1992), 1-10
12. T Ahmed, MJ Semmens, *Journal of Membrane Science*, 69 (1992), 11-20
13. MJ Costello, AG Fane, PA Hogan, RW Schofield, *Journal of Membrane Science*, 80 (1993), 1-11
14. H Kreulen, CA Smolders, GF Versteeg, WPM van Swaaij, *Journal of Membrane Science*, 78 (1993), 197-216
15. S Karoor, KK Sirkar, *Ind. Eng. Chem. Res.*, 32 (1993), 674-684
16. H Kreulen, CA Smolders, GF Versteeg, WPM van Swaaij, *Chemical Engineering Science*, 48 (1993), 2093-2102
17. MSL Tai, I Chua, K Li, WJ Ng, WK Teo, *Journal of Membrane Science*, 87 (1994), 99-105
18. SN Vaslef, F Mockros, RW Anderson, RJ Leonard, *ASAIO Journal*, 40 (1994), 990-996
19. HB Al-Saffar, JS Oklany, B Ozturk, R Hughes, *Trans I CHEM E*, 73(B) (1975), 144-150
20. M Imai, S Furusaki, T Miyauchi, *Ind. Eng. Chem. Process Des. Develop.*, 21 (1982), 421-426
21. Z Qi, EL Cussler, *AIChE Journal*, 31 (1985), 1548-1553
22. Z Qi, EL Cussler, *Journal of Membrane Science*, 24 (1985), 43-57
23. C Lipski, P Côté, *Enviromental Progress*, 9 (1990), 254-261
24. A Ito, K Yamagiwa, M Tamura, M Furusawa, *Journal of Membrane Science*, 145 (1998), 111-117
25. NS Strand, US Patent 3342720, 1964
26. NS Strand, US Patent 3342729, 1967

27. H Futselaar, RJC Zoontjes, T Reith, IG Rácz, *Desalination*, 90 (1993), 345-361

28. H Futselaar, The transverse flow membrane module (construction, performance and applications), PhD Thesis, University of Twente, The Netherlands, 1993

29. SR Wickramasinghe, MJ Semmens, EL Cussler, *Journal of Membrane Science*, 69 (1992), 235-250

30. SR Wickramasinghe, MJ Semmens, EL Cussler, *Journal of Membrane Science*, 62 (1991), 371-388

31. A Campbell-Ritchie, G Bell, JDS Gaylor in WR Bowen, RW Field, JA Howell (eds.), *Proceedings of Euromembrane '95*, vol 2, Bath, 1995, p. 146-152

32. K Esato, B Eiseman, *Journal of Thorac. Cardiovas. Surg.*, 69(5) (1975), 690-697

33. T Tsuji, K Suma, K Tanishita, Z Fukazawa, M Kanno, H Hasegawa, A Takahashi, *ASAIO Journal*, 27 (1981), 280-284

34. MF Refojo, F-L Leong, *Journal of Membrane Science*, 4 (1979), 415-426

35. B Alexander, JS Fleming, *Journal of Biomedical Materials Research*, 16 (1982), 31-38

36. RE Loewenthal, HNS Wiechers, GvR Marais, *Softening and Stabilization of Municipal Waters*, Water Research Commission of SA, 1986

37. H Futselaar, CP Borges, AC Habert, R Nobrega in WR Bowen, RW Field, JA Howell (eds.), *Proceedings of Euromembrane '95*, vol 2, Bath, 1995, p. 106-111

38. FNM Knops, H Futselaar, IG Rácz, *Journal of Membrane Science*, 73 (1992), 153-161

39. JL Smart, DR Lloyd, VM Starov, *Pervaporative extraction of volatile organic compounds from aqueous systems with use of a tubular transverse flow module*, Poster presented at NAMS 8th Annual Meeting, Canada, 1996

40. J Baudet, M Rochet, M Salmon, B Vogt, US Patent 3993816, 1976

41. J Baudet, M Salmon, B Vogt, French Patent 2222134, 1973

42. AG Bayer, German Patent 2650341, 1978

43. PL Côté, RP Maurion, CJ Lipski, US Patent 5104535, 1992

44. CL Glassford, European Patent 0374873 A2, 1988

45. J Inacio, E Nilsson, Swedish Patent WO 87/06151, 1986

46. BP ter Meulen, European Patent 0509031, 1990

47. RW Nichols, US Patent 4959152, 1990

48. RW Nichols, JC Davis, RD Littler, US Patent 5164081, 1990

49. T Saida, Japanese Patent 56-2803(A), 1979

50. H Stam in L Cecille, JC Toussaint (eds.), *Future Industrial Prospects of Membrane Processes*, Proceedings of BRITE Symposium (Brussels, Belgium), Elsevier Applied Science, London, 1988, p.135-152

51. SE Domröse, RD Sanderson, EP Jacobs, *Development of specialized cross and transverse flow capillary membrane modules*, WRC Report No., 1996

52. SE Domröse, DA Finch, RD Sanderson, *Development of transverse flow capillary membrane modules of the block type for liquid separation and bio-reactors*, WRC Report No., 1997

53. SL Matson, J Lopez, JA Quinn, *Chemical Engineering Science*, 38 (1983), 503-

54. A Laurent, JC Charpentier, *Journal of Chemical Engineering*, 8 (1974), 85-

55. H van Landeghem, *Chemical Engineering Science*, 35 (1980), 1912-

56. RE Treybal, *Mass Transfer Operations*, 3rd edition, McGraw-Hill, New York, 1980

57. A Kiani, RR Bhave, KK Sirkar, *Journal of Membrane Science*, 20 (1984), 125-145

58. V Gnielinski, *Forsch. Ing.-Wesen*, 44(1) (1978), 15-25

59. ES Gaddis, V Gnielinski, *Verfahrenstechnik*, 17(7) (1983), 410-418

60. AL London, JW Mitchell, WA Sutherland, *Journal of Heat Transfer - Transactions of the ASME*, 91(1) (1960), 199-213

61. K Hammeke, E Heinecke, F Scholz, *International Journal of Heat and Mass Transfer*, 10 (1967), 427-446

62. R Klier, *International Journal of Heat and Mass Transfer*, 7 (1964), 783-799

63. H Brauer, *Chemie Ingenieur Technik*, 36 (1964), 247-260

64. TH Chilton, AP Colburn, *I&EC*, 26(11) (1934), 1183-1187

65. EP Jacobs, RD Sanderson, US Patent 5833896, 1998

66. EP Jacobs, SE Domröse, DJ Koen, RD Sanderson, SA Patent 94/9952, 1993

67. T Graham, *Phil. Mag.*, 32 (1866), 401

68. P Meares, *Journal of the American Chemical Society*, 76 (1954), 3415

69. EE Wilson, *Journal of Heat Transfer - Transactions of the ASME*, 37 (1915), 47-82

70. PR Brookes, AG Livingston, *Journal of Membrane Science*, 104 (1995), 119-137

71. C H Yun, R Prasad, KK Sirkar, *Ind. Eng. Chem. Res.*, 31 (1992), 1709-1717

72. G Vatai, MN Tekic, *Separation Science and Technology*, 26(7) (1991), 1005-1011

73. CB Panchal, DM France, *International Journal of Heat and Mass Transfer*, 36(3) (1993), 565-576

74. EL Cussler, *Diffusion*, Cambridge University Press, 1984

75. MJ Costello, AG Fane, PA Hogan, RW Schofield, Paper presented at symposium 'Engineering of membrane processes', Germany, 1992

76. EN Sieder, GE Tate, *Ind. Eng. Chem.*, 28 (1936), 1429

77. J Lévèque, *Ann. Mines*, 13 (1928), 201,305,381

78. R Rautenbach, R Albrecht, *Membrane Processes*, John Wiley & Sons, 1989

79. EP Jacobs, WD Leukes, *Journal of Membrane Science*, 121 (1996), 149-157

80. A van der Walt, Design and characterisation of a transverse flow membrane module for gas transfer operations, M-Ing (chemical engineering), 1999, University of Stellenbosch, Stellenbosch, RSA

81 WD Leukes, EP Jacobs, PD Rose, SG Burton and RD Sanderson, *Method of producing secondary metabolites.* Assigned: Water Research Commission, SA Patent 95/7366, 1 September 1995, European patent EPO 761 608A2, USA patent 5945002, 31 August 1999.

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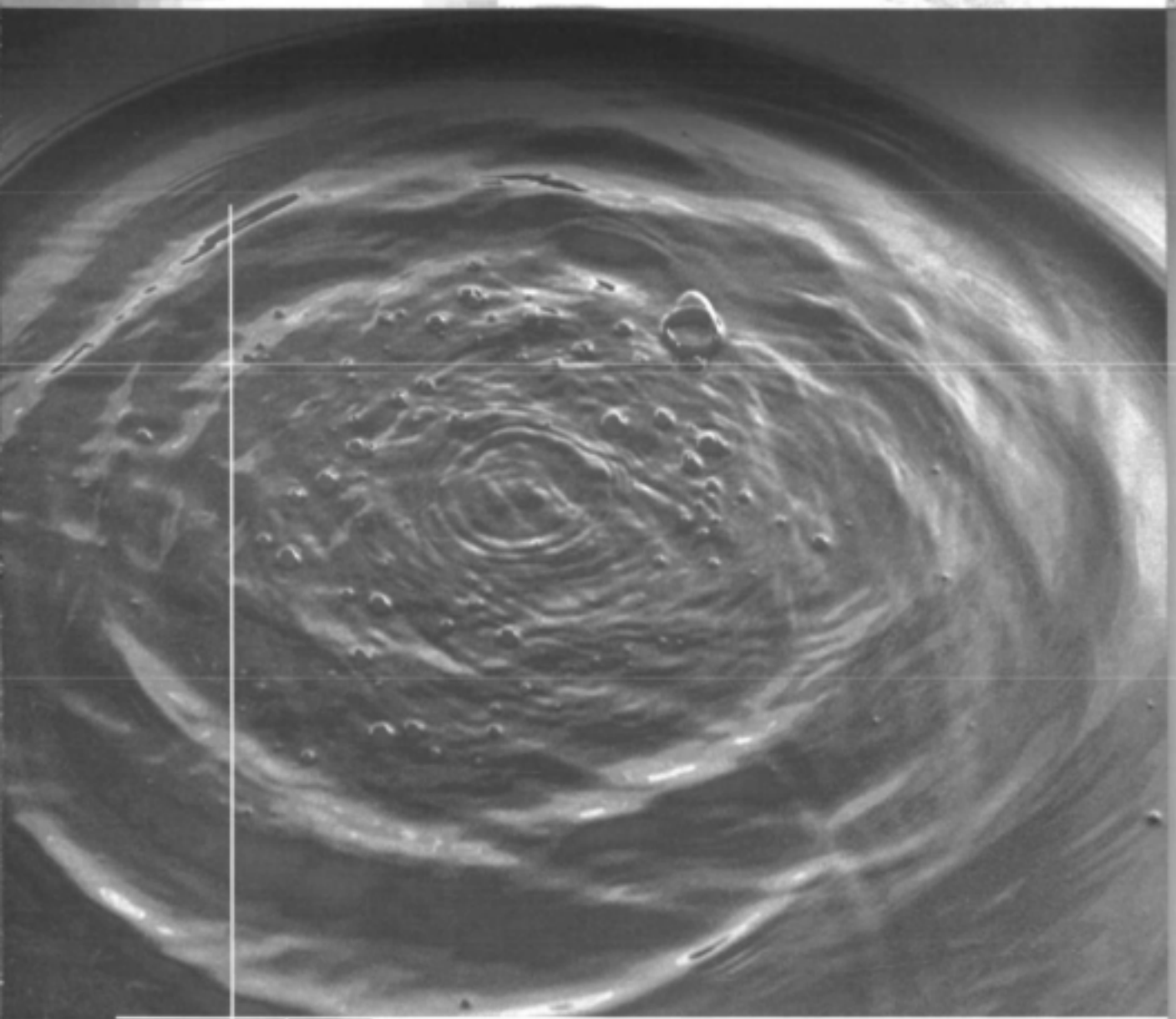

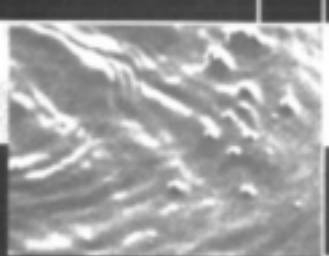

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